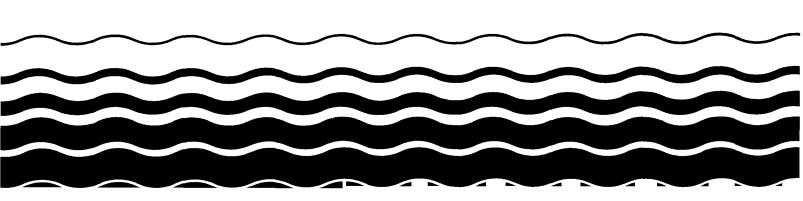
United States Environmental Protection Agency Office of Water Regulations and Standards (WH-553) Washington DC 20460 December 1982 EPA-440/4-85-015

Water

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# An Exposure and Risk Assessment for Tetrachloroethylene



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#### 16. Abstract (Limit: 200 words)

This report assesses the risk of exposure to tetrachloroethylene. This study is part of a program to identify the sources of and evaluate exposure to 129 priority pollutants. The analysis is based on available information from government, industry, and technical publications assembled in July of 1980.

The assessment includes an identification of releases to the environment during production, use, or disposal of the substance. In addition, the fate of tetrachloroethylene in the environment is considered; ambient levels to which various populations of humans and aquatic life are exposed are reported. Exposure levels are estimated and available data on toxicity are presented and interpreted. Information concerning all of these topics is combined in an assessment of the risks of exposure to tetrachloroethylene for various subpopulations.

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Tetrachloroethylene Perchlorethylene

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# AN EXPOSURE AND RISK ASSESSMENT FOR TETRACHLOROETHYLENE

bу

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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.

Michael W. Slimak, Chief Exposure Assessment Section Monitoring & Data Support Division (WH-553) Office of Water Regulations and Standards

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The Arthur D. Little, Inc., task manager for this study was Diane Gilbert. Other major contributors were Muriel Gover (human effects), Warren Lyman and Gary Magil (environmental fate), Pamela Walker and and Jack Yee (materials balance), Douglas Wallace (biotic effects and exposure), Diane Gilbert (human exposure and risk), and John Ostlund (risk analysis).

#### CHAPTER I.

#### 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 which may enter and traverse the environment thereby leading to exposure to humans and other biota. This report is the assessment for tetrachloroethylene (perchloroethylene or PCE) using available data and quantitative models where possible to evaluate overall risk. The results of this work are intended to serve as a basis for developing suitable strategies for reducing the risk, if such action is indicated.

#### A. RISK CONSIDERATIONS

#### 1. Risk Considerations for Humans

Exposure levels to individuals have been estimated for different exposure conditions. Dose/response extrapolations, based on four models, have been applied to these exposure levels using data from positive carcinogenic results in one study in B6C3F1 mice to estimate risk levels. Risk estimates of excess individual lifetime tumor incidence associated with PCE intakes due to nonoccupational inhalation range from negligible to 8 x  $10^{-2}$ , corresponding to subpopulations exposed to background PCE concentrations in air and high ambient concentrations near drycleaning facilities, respectively. Estimated excess individual lifetime cancer risk due to continuous lifetime consumption of drinking water contaminated at the average observed PCE levels is in the negligible to 6 x  $10^{-7}$  range. At the highest PCE concentrations observed in drinking water, estimated excess individual lifetime cancer risk is on the order of 6 x  $10^{-7}$ .

Considerable controversy exists regarding the most appropriate method for extrapolating human equivalent doses from animal data. Due to this uncertainty, the range of risk estimated by the various extrapolation models may under- or overestimate the actual risk to man. Overestimation appears more likely due to the conservative assumptions utilized in the calculation of human equivalent doses. In addition to the problems inherent to risk extrapolation, the results of carcinogenic studies with rats were negative, although poor survival was observed. Thus, additional uncertainty is added to these risk estimates.

Other than carcinogenic risks, the risk associated with chronic exposure to PCE cannot be quantified. The effects of chronic exposure to PCE in humans have not been well characterized, making assessment of long-term, low-level exposure to PCE difficult. Tests with laboratory animals have established lowest observed-effect levels of 386 mg/kg body weight over a 2-year period. These levels are orders of magnitude above estimated levels of human environmental exposure. No indications of teratogenic effects of PCE have been reported. Acute

human exposure to PCE is of concern at high exposure concentrations. In general, little or no effects have been observed at a concentration of  $700~\text{mg/m}^3$  PCE. Minimal effects (lightheadness, impaired coordination) become evident at  $1300~\text{mg/m}^3$  with more definite indications of CNS depression (mental confusion, lassitude) observed as the concentration increases. Kidney impairment and liver damage have been reported in humans following accidental exposure to PCE but are not well documented.

# 2. Risk Considerations for Aquatic Biota

Based upon the limited data available, aquatic biota do not appear to be generally at risk due to exposure to tetrachloroethylene. The lowest concentration at which an effect was observed on a freshwater species was 840 ug/l, a chronic value for the fathead minnow. This concentration is almost two orders of magnitude larger than typical observed ambient concentrations; the highest level observed was 147 ug/l. Effluent concentrations, however, as high as 5500 ug/l have been reported. In addition, two fish kills indicate the potential for aquatic risks in the vicinity of a discharge of effluent containing tetrachloroethylene.

#### E. MATERIALS BALANCE

#### 1. Production and Consumption

Tetrachloroethylene is a synthetic organic chemical mostly produced and used domestically. In 1978 (the most recent year for complete industry data), 329,000 MT were produced at 11 plants, mostly in the Gulf of Mexico region. After imports (17,000 MT) and exports (29,000 MT), about 317,000 MT remained in the United States for the following major industrial uses:

	MT	*** ***
Textile Cleaning	217,000	68
Metal Cleaning	55,000	17
Fluorocarbon Production	38,000	12
Other	7,000	2

PCE's properties as a solvent for fats, oils, greases, and waxes have led to its widespread use by the drycleaning industry, by textile manufacturers, in metal cleaning operations (degreasing), and a very small quantity (1.5 to 2%) as stain removers for home use. Fluorecarbon production is the only main consumptive use of PCE in which it is converted to other substances. Other minor uses include food processing, aerosol specialty products, and as a solvent in various industrial and manufacturing processes.

#### 2. Environmental Releases

The total amount of PCE released to the environment in 1978 was estimated to be about 254,000 MT, fully 80% of available domestic supply. Of this amount, about 60% was released in the form of air

emissions, about 40% was disposed of on land, and less than 1% was discharged to POTW and directly to water.

The drycleaning industry releases an estimated 121,000 MT of PCE to the atmosphere each year, or 78% of all atmospheric releases of PCE. This industry emits roughly one-half of the PCE it uses, mostly in the form of evaporative losses. Other atmospheric releases occur from metal degreasing uses and production of fluorocarbons.

Direct releases of PCE to water have only been accounted for in the metal degreasing industry and are believed to total approximately 40 MT per year. Drycleaners are believed to release about 10 MT to sewer systems. Other releases to POTW's were estimated to amount to about 400 MT of PCE each year.

Most of the processes in which PCE is used as a solvent involve in-house recycling through evaporation and condensation. Many smaller scale operations, such as machine shops, that use PCE for metal degreasing also recycle the solvent when it becomes dirty, but this work is done by independent recyclers. Recycling processes produce much of the solid waste that contains PCE in the form of greasy sludges and saturated filters; in addition, solid waste is generated by drycleaners in the form of used filter cartridges. The volume of PCE disposed of on land was estimated to be about 103,000 MT in 1978, 10% generated by the metal degreasing industry and 90% by drycleaners (recycling wastes are included in these figures). This amount, which represents one-third of the available PCE supply, is disposed of with either industrial or municipal wastes.

Transportation is not reported as a significant source of PCE loss with the exception of an occurrence of a major spill. Some evaporative losses will occur during loading and transfer. These losses, however, are negligible compared with other sources.

#### C. ENVIRONMENTAL FATE

The principal properties that control the fate of PCE in the environment are solubility, volatility, and photodegradation. PCE is quickly volatilized and then eventually photodegraded so that these are the dominant fate processes; if dispersed in water, however, it is soluble and can be transported over distances, especially when there is limited possibility for volatilization, as in groundwater.

#### 1. Air

PCE volatilizes rapidly and degrades in the atmosphere through the action of sunlight, with a half-life of about 2 days. Although this is a fairly short half-life in comparison with other chemicals, it is sufficiently long to allow dispersion of PCE from concentrated sources, such as drycleaners. Levels of PCE monitored at the vents of commercial drycleaners are typically between 6,800 and 680,000  ${\rm ig/m}^3$ . Levels at adjacent buildings have been estimated to be about 2,500  ${\rm ug/m}^3$ , and, with increasing distance, the PCE concentration drops to arbient levels of about 1 to 14  ${\rm ug/m}^3$  in urban areas. Dispersion of PCE is

also demonstrated by the identification of PCE (0.1 - 0.5  $\mu g/m^3$ ) at remote sites.

Local dispersion models were used to analyze atmospheric fate of PCE both in the immediate vicinity of and at somewhat greater distances from major sources such as drycleaners. The analysis indicated that typical industrial drygleaning sources could be responsible for levels of up to 76,300  $\mu g/m$  at a distance of 0.37 km under stable (worst case) atmospheric conditions; under unstable atmospheric conditions, the level was 21,800  $\mu g/m$  at a distance of 0.14 km from the source. Commercial drycleaning facilities were found to cause lower dispersed PCE levels in the range from 2,600  $\mu g/m^3$  (0.14 km) to 9,200  $\mu g/m^3$  (0.37 km). Modeling of PCE concentrations over a larger area and from the same sources indicated concentrations ranging from 1,100  $\mu g/m^3$  (50 m) to 4.6  $\mu g/m^3$  (5 km), for the industrial source. These numbers are comparable to levels estimated near commercial sources and to the background levels in urban areas.

The highest concentrations of PCE in air  $(6,780,000~\text{ug/m}^3)$  were detected inside drycleaning establishments. These facilities are not only the largest users of PCE, but also the largest dischargers.

#### b. Water

Only a small amount (1%) of total PCE production is discharged to water. In surface waters, PCE concentrations between undetected and 147  $\mu g/l$  have been measured. Generally, however, concentrations are below 10  $\mu g/l$ , and are detectable in less than 10 percent of the samples. The higher concentrations have been documented near several industrial discharges, which themselves may contain 0.1 to 5.5  $\mu g/l$ 

Drinking water has been found to contain up to about 5 mg/l, although less than 10% of sampled surface-water-originated supplies generally contained measurable levels. Some drinking water wells have been found to be highly contaminated-with concentrations exceeding 10,000 ug/l. In highly permeable soil from a densely populated area on Long Island, 15% of the tested wells have been contaminated with PCE and many have been closed. Piping installed in 72 Massachusetts towns was found to be the source of PCE to drinking water at levels of up to 5 mg/l. The PCE originated in a resinous liner applied to the pipes to prevent acid leaching of asbestos.

The probable pathway for groundwater (and eventually surface water) contamination originates with the land disposal of 40% of total PCE wastes on land. As it is unlikely that the typical disposal sites are protected from leachate generation and losses through percolation to the surrounding soils, a significant portion of this PCE could find its way to the water table. This is probable for two reasons: (1) PCE is soluble and if sufficient water passes through the wastes. PCE can be transported, and (2) large volumes of PCE are often disposed of at once, so that if the waste is buried too deeply for the PCE to volatilize immediately, the liquid migrates downward. This leachate can enter groundwater supplies used for irrigation or drinking water

or the groundwater can enter surface water supplies as a contaminated recharge.

Wastewaters contain PCE at concentrations up to about 2.400 ug/1; typically, concentrations are below 100 ug/1. Treatment of wastewater appears to be successful at most POTWs, with better than 90% removal usually observed. The removal process is predominately volatilization with some biodegradation by acclimated microorganisms. The stoichiometry of chlorination of wastewaters does not favor PCE formation from available substances. This is borne out by existing data concerning levels in POTW influent and effluent.

The fate of PCE in water was modeled using EPA's EXAMS for five aquatic systems. Two loading rates were applied—one at 0.004 kg/hr, simulating POTW and industrial scale discharges; the other was 160 kg/hr, corresponding to a groundwater contribution that was heavily contaminated with disposal site leachate. Volatilization, sediment content, and transport were found to be the controlling parameters. In the river environments, transport dominated the other fate processes.

#### 3. Land

Comparatively little is known about PCE's behavior in soils: however, modeling of partitioning indicates that PCE is not tightly bound to soils and can thus be expected to be relatively mobile, either volatilizing to the atmosphere or percolating to groundwater, where it is resistant to hydrolysis. Further investigations are warranted, especially to study the situation of leachate migration and attenuation from landfills containing PCE wastes.

#### D. EXPOSURE

#### 1. Human Populations

The critical exposure route for the general population is inhalation, due to the volume and large number of emission sources spread throughout population centers and the tendency of PCE to partition the atmosphere.

The ranges of exposure to PCE have been estimated for several different environmental scenarios. Total exposure by inhalation is primarily determined by an individual's proximity to key sources. Typical nonoccupational inhalation exposures were estimated to range between 0.001 mg/day (remote area, background level) to a maximum of 137 mg/day near drycleaning facilities. The use of coin-operated laundry facilities one-half hour per day could result in an estimated intake of 41 mg/day PCE. Occupational exposure may account for between 165 mg and 1150 mg per 8-hour workday, assuming a 50% retention.

Exposure via ingestion of PCE is generally low compared with inhalation. Most water supplies and foods that have been sampled

contain less than 5  $\mu g/l$  of PCE; typical estimated intakes are on the order of less than 1.0  $\mu g/l$  for water and 1.2  $\mu g/l$  for food. A highly contaminated water source (5.0  $\mu g/l$ ), such as a distribution system with a resinous liner, could result in an intake of  $\mu g/l$  mg/day.

Dermal absorption cannot be estimated at this time due to lack of data on absorption rates. This exposure route is not expected to be significant as the frequency and duration of exposure would be low.

#### 2. Aquatic Populations

Measured surface water concentrations are generally below 10  $\lg/1$ . Aquatic fate models suggest that typical effluent discharges (modeled by EXAMS) may cause localized PCE concentrations in rivers of 0.004  $\lg/1$  and in lakes and ponds of 0.52-10  $\lg/1$ . Higher input loads, occurring in the case of leachate contamination, could cause water concentrations of 0.16-7.6  $\lg/1$ . These data are not inconsistent with available monitoring data.

#### E. EFFECTS

#### 1. Humans

PCE exposure has been linked to an increased incidence of hepatic carcinoma in B6C3Fl mice at a dose of 386 mg/kg body weight by gavage, but the effect may reflect a secondary response to PCE-induced chemical hepatectomy in this species. Carcinogenicity tests with rats were inconclusive. Mutagenic findings are varied but positive results in mammalian cell transformation studies and host-mediated assays implicate PCE as a mutagen. There are no indications of teratogenic effects associated with PCE exposure.

Pronounced toxic nephropathy was seen in mice and rats chronically exposed to 386~mg/kg body weight and 471~mg/kg body weight PCE, respectively, by gavage for 78~weeks.

PCE is readily absorbed through the lungs. Approximately 57% of inhaled PCE is retained but most of this amount (80-100%) is subsequently exhaled, unchanged in expired air. A respiratory half-life of 65 hours has been estimated for man; urinary clearance of approximately 2% of retained PCE as trichloracetic acid has an approximate half-life of 1-4 hours. These values suggest accumulation of PCE may occur with repeated exposure.

In laboratory animals, acute oral LD values range from 3,980 mg/kg in the rat to 8,850 mg/kg in the mouse. Acute exposure to PCE is characterized by depression of the central nervous system, and by liver and kidney damage.

In man, the predominant effect of PCE exposure by inhalation (less than or equal to  $30~\text{mg/m}^3$ ) is depression of the central nervous system, characterized by vertigo, confusion, inebriation-like

symptoms, tremors and numbness. Accidental exposure to PCE has also been linked to kidney impairment and hepatotoxic effects. The lack of long-term exposure data makes assessment of long-term, low-level exposure to PCE difficult. However, the pronounced nephrotoxicity in rodents and increased incidence of hepatocellular carcinoma in mice raise concerns for the human health aspects of prolonged exposure to PCE.

The OSHA standard for occupational exposure is an 8-hour time-weighted average of 15 mg/m $^3$ , with an acceptable ceiling (i.e., very short-term levels) of 30 mg/m $^3$ . The  $10^{-6}$  risk level for human cancer resulting from PCE exposure from drinking water is estimated as 0.2 mg/l by the U.S. EPA.

#### 2. Aquatic Biota

Acute toxicity to freshwater species occurs in the range of 4.8 to  $21.4~\rm mg/l$  in flow-through studies, with rainbow trout being the most sensitive species tested. A chronic value for fathead minnow of  $0.84~\rm mg/l$  was reported.

Saltwater species tested include the mysid shrimp and barnacle naupii, with respective  $LC_{50}$  values of 10.2 mg/l (96 hr) and 3.5 mg/l (48 hr). The sheepshead minnow and the algae tested were less sensitive. A chronic value for mysid shrimp was found to be 0.450 mg/l, the lowest reported effect level.

No criteria have been established by EPA for the protection of either freshwater or saltwater aquatic life.

#### CHAPTER II

#### INTRODUCTION

The Office of Mater Regulations 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 the risk based on receptor exposure to these substances. The results are intended to serve as a basis for developing suitable regulatory strategy, especially for sources to the nation's waters, for reducing the risk, if such action is indicated.

This document is an assessment of the risks associated with tetra-chloroethylene in the natural and human environments. It includes summaries of comprehensive reviews of the production, use, distribution, fate, effects and exposure to tetrachloroethylene and the integration of this material into an analysis of risk. In this report the terms "tetrachloroethylene" and "PCE" are used interchangeably. Tetrachloroethylene is also sometimes called "perchloroethylene" or "tetrachloroethene."

Tetrachloroethylene is a heavy, volatile, ordorless liquid, with excellent properties as a solvent. These properties have led to PCE's widespread use (Chapter III, Materials Balance) in cleaning, manufacture and repair operations of all types and sizes. Such facilities are practically ubiquitous in the populated areas of the U.S., and face and exposure analyses have attempted to cover the extremes, as well as typical concentration levels in these situations.

Chapter IV presents the results of media specific fate models used to predict concentration levels of PCE in the air within close proximity of significant sources of PCE, equilibrium concentrations resulting from free exchange of PCE between air, soil, water and sediment; and are presented. The most current research on effects of PCE upon human and non-human receptors, a description of the populations exposed to PCE, and a statement of the risk of this exposure comprise Chapters V, VI, and VII. The Appendix describes occupational environments in which PCE is used.

Throughout the report, data have been given in metric units (mg/l, mg/kg,  $\mu g/m^3$ , etc.). In the case of data for atmospheric concentrations, which are commonly given as ppb or ppt, the conversion factor is 1 ppb = 6.78  $\mu g/m^3$  at 1 atm. and 25°C. Because few researchers include this level of detail (atm and °C) in their data; the above conversion factor has been used consistently in this work. No further mention will be made of this artifact in converting data to the metric unit system.

#### CHAPTER III.

#### MATERIALS BALANCE

#### A. INTRODUCTION AND METHODOLOGY

In this section, a materials balance is developed for tetrachloroethylene (or PCE). The materials balance considers PCE as it is released from the cultural environment to its first point of entry into the natural environment. Potential sources of PCE releases were identified by a review of activities in which the material participates from its production and use in various forms to its ultimate disposal.

For each major source of pollutant release, the amount of material released was estimated, and the environmental compartments (air, land, and water) initially receiving and transporting the material were identified, as were the locations at which the pollutant loadings take place. There are many uncertainties inherent in this type of analysis: not all current releases have been identified, past releases were not well documented, and future releases are difficult to predict. Nevertheless, sufficient information is available to indicate in general terms the nature, magnitude, location, and time dependence of pollutant loading of the environment with PCE.

In developing the materials balance for PCE, data and information were obtained from a recently completed study on tetrachloroethylene sponsored by the U.S. Environmental Protection Agency (Versar, Inc., 1980) and from other readily available literature, supplemented as necessary by contacts with industry experts.

#### B. OVERVIEW

Tetrachloroethylene is a synthetic organic chemical. In 1978, 329,100 metric tons (MT) of the compound were produced (U.S. International Trade Commission, 1979), 17,200 MT were imported, and 29,000 MT were exported (U.S. Bureau of Census, 1978). The supply available for domestic consumption totalled 317,300 MT.

Approximately 58% of the supply is used for drycleaning and textile processing. About 17% is used for metal degreasing, and about 12% is used for the production of fluorocarbons (MRI, 1977). The remainder is used in various miscellaneous applications. A summary of the production, use, and environmental releases is presented in Tables 1 and 2 and Figure 1.

Growth in production and consumption of PCE has declined in recent years; in 1978 the annual growth rate was about 3%; restrictions on the use of other solvents may create expanded markets for PCE (Versar, Inc., 1979a; U.S. EPA, 1979). This is evident in the vapor degreasing application, in which the use of the preferred solvent, trichloroethylene, is being curtailed and replaced by tetrachloroethylene.

TABLE 1. SUMMARY OF PRODUCTION AND CONSUMPTION OF TETRACHLOROETHYLENE, 1978

Supply/Consumer	Production Capacity (MT)	Supply (MT)	Consumption (MT)
Domestic Capacity (1976)	(548,900 <sup>-</sup> )		
Domestic Production (estimated 1978, at 60% of Capacity)		329,100 <sup>2</sup>	
Imports		17,200 <sup>3</sup>	
Exports			29,0004
Textile Cleaning			216,9002,5
Metal Degreasing			<b>55,400</b> 2,5
Fluorocarbons			38,1002,5
Other			6,900 <sup>2</sup> , <sup>5</sup>
Total		346,300	346,300

<sup>&</sup>lt;sup>1</sup>Versar, Inc., 1979a, for trade year 1976. <sup>2</sup>U.S. International Trade Commission, 1979.

<sup>&</sup>lt;sup>3</sup>U.S. Bureau of Census, 1978b. <sup>4</sup>U.S. Bureau of Census, 1978a. <sup>5</sup>MRI, 1977.

TABLE 2. SUMMARY OF ENVIRONMENTAL RELEASES
OF TETRACHLOROETHYLENE (ESTIMATED 1978)

Source	Air	Direct Aquatic	POTW	Land
Production	3,0001,2,3	<b>*</b> 3	*3	<b>*</b> 3
Textile Cleaning	120,600 <sup>2</sup>	*2	10+2	92,9002
Metal Degreasing	19,800 <sup>2</sup>	104	40 <sup>6</sup>	10,700 <sup>2</sup> ,5
Fluorocarbons	60 <sup>2</sup>	<b>*</b> 2	<b>*</b> 2	<b>*</b> 2
Misc. Other Uses	6,530	*	370 <sup>7</sup>	*
Total <sup>8</sup>	149,990	10+	420 <sup>9</sup>	103,600+

<sup>&</sup>lt;sup>1</sup>JRB Associates, 1979.

<sup>&</sup>lt;sup>2</sup>Versar, 1979a

<sup>&</sup>lt;sup>3</sup>U.S. EPA, 1976.

<sup>4</sup>GCA Corp., 1980

<sup>&</sup>lt;sup>5</sup>Versar 1979b.

<sup>&</sup>lt;sup>6</sup>Versar 1981. These data are preliminary and reflect indirect, i.e., untreated discharges.

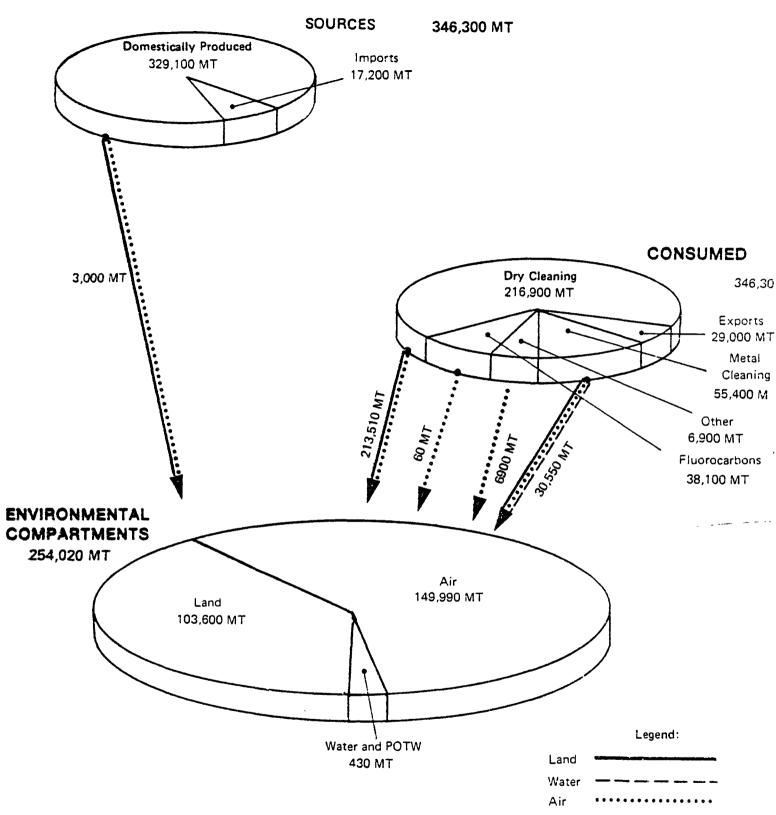
This number was determined by the difference between the total releases to POTWs and the estimated releases for Textile Cleaning and Metal Degreasing.

<sup>&</sup>lt;sup>8</sup>Total releases = 256,770 MT.

<sup>9</sup>Arthur D. Little, Inc., based on data from Feiler, 1980.

<sup>\*</sup>Insufficient data available at the present time to quantify these releases; some are believed to be negligible, and others are unknown.

Indicates these releases may be larger than indicated but cannot be quantified.



**Note:** Boundaries between receiving medium are often undefined and/or change; releases to water or land often result in atmospheric concentrations.

FIGURE 1 MATERIALS BALANCE FOR TETRACHLOROETHYLENE

About 89 percent of the PCE supply is consumed in distributed use as a drycleaner or solvent and is discharged to the environment as a consequence of its use. Virtually all of the releases are atmospheric or are in the form of solid wastes. Although some aquatic discharges from drycleaning and organic chemical manufacture have been reported, they are insigificant compared with the atmospheric emissions and are likely to be volatilized quickly to the atmosphere. An estimated 150,000 MT of airborne emissions and 100,000 MT of solid waste occur each year as the result of the production and use of PCE.

Although much of the PCE discharged to water and sewer is volatilized almost immediately, this occurrence is a fate process (see Chapter 4) and these discharges are reported as releases to the water compartment in the materials balance (Arthur D. Little, Inc. Estimate).

#### C. PRODUCTION

Tetrachloroethylene is manufactured domestically in eleven plants operated by eight companies. Table 3 lists these plants and their locations, nameplate capacities, and disposal practices; the locations of the production sites are shown in Figure 2. PCE is produced in conjunction with other halogenated organics, and the reported plant capacities are quite variable from year to year since the same process can be tuned to produce other products. Total U.S. production in 1978 was 329,100 MT (U.S. International Trade Commission, 1978).

Tetrachloroethylene is manufactured by three processes: thermal chlorination of one to three carbon alkanes, catalytic chlorination of ethylene dichloride, and chlorination of acetylene (Versar, Inc., 1979a). Because of the flexibility of the processes involved, reported applications of the three techniques used in producing tetrachloroethylene vary. Versar indicates that about one-half of the total U.S. production is via the thermal chlorination of alkanes. About 46% of the total production is via the chlorination or oxychlorination of ethylene dichloride. Approximately 3% of the production is via the chlorination of acetylene (Versar, Inc. 1980).

Feedstock and thus operating parameters vary among the producers, usually depending on what types of other products are produced at the site. The thermal chlorination process uses a variable feedstock at high temperatures. The catalytic chlorination of ethylene dichloride operates at lower temperatures, and process parameters can be adjusted to produce trichloroethene rather than tetrachloroethylene. The chlorination of acetylene, uses an aqueous catalytic mechanism at much lower temperatures than either of the other two routes.

Manufacturer/Location	Production Capacity (MT)	Reported Disposal <sup>2</sup> Practices
Diamond Shamrock, Deer Park, TX	90,700	Packaged, sealed; transported for incineration
Dow Chemical, Freeport, TX	54,400	NI*
Pittsburg, CA	9,100	N1*
Plaquemine, LA	68,000	NI*
E.I. Du Pont de Nemours, Corpus Christie, TX	72,700	NI
Ethyl Corporation, Baton Rouge, LA	22,700	Deep Well Injection
Occidental Petroleum Corp. (Hooker), Taft	, LA 18,100	NI
PPG Industries, Lake Charles, LA	90,700	Waste gas/Still residue liquids incinerated
Stauffer Chemicals, Louisville, KY	31,800	Gravity fed into land fill areas
Vulcan Chemicals, Geismar, LA	68,000	Landf111*
Wichita, TX	22,700	Landfill*
TOTAL DOMESTIC CAPACITY	548,900	

NI - Not Identified

Ló

<sup>\*</sup>Facility has potential for incineration Versar,1979a
2 MRI,1977

Source: Arthur D. Little, Inc.

FIGURE 2 LOCATION OF TETRACHLOROETHYLENE PRODUCERS WITH RESPECT TO EPA DESIGNATED RIVER BASINS

The annual releases of PCE from production facilities are difficult to assess, and widely divergent values have been reported, ranging from a low of 291 MT (JRB Associates, 1979) to a high of 4,550 MT (Versar, 1979a). There is general agreement that virtually all releases during production are airborne emissions, primarily from process vents, distillation vents, and fugitive emissions (U.S. EPA, 1977).

The wide range of estimated air emissions—291 to 4,550 MT per year—is probably due to the assumptions made in deriving these values. The low figure is probably unrealistic, as is the high value, which represents a loss of 1.5% of product from the process (U.S. EPA, 1976). In summary, environmental releases from production facilities are virtually all airborne and are estimated to total around 3,000 MT per year.

Disposal practices for solid and liquid production wastes vary. One plant reports deep well injection of tetrachloroethylene-bearing sludges. Several place the material in containers and deposit it in landfills or dump it directly in such locations. Incineration of solid waste and residual liquids is currently practiced and is mentioned in the future plans of several manufacturers (MRI, 1977). However, the high boiling point of PCE and increasing energy costs may decrease the attractiveness of disposal via incineration (MRI, 1977). At present, insufficient data exist to reliably estimate this category of discharge.

#### D. DRYCLEANING AND TEXTILE PROCESSING

PCE is miscible with most organic liquids and is a superior solvent for greases, fats, waxes, and oils. Because of these characteristics and the compound's stability and non-agressiveness towards dyes and pigments, it has been used for many years in the textile industry for drycleaning. The compound is also used in textile manufacturing for scouring, sizing, and desizing operations and as a carrier for finishes and dyes.

About 68% (216,900 MT) of annual domestic PCE consumption is for drycleaning and textile processing (MRI, 1977). The facilities are widely distributed and range in size from coin-operated laundromats, often found in shopping centers, to commercial drycleaning establishments, to large textile manufacturing plants where the crude fabric material is processed to a finished fabric product. There are currently about 25,000 commercial drycleaners in the U.S., 75% of which use tetrachloroethene as a drycleaning solvent. About 500 industrial facilities utilize both tetrachloroethene and other petroleum-based solvents (W. Fisher, International Fabricare Institute, personal communication, January, 1979).

The atmosphere is the primary environmental receptor of releases during textile cleaning. In the textile industry (as well as the metal cleaning industry), some solvent recovery is practiced; however, it is estimated that about 121,000 MT of tetrachloroethene is lost directly to the atmosphere each year from this application. Although it is clear that much of the PCE consumed for these purposes is eventually discharged to the environment, the amount of solid or liquid waste that is disposed of in landfills is dependent upon the modes of disposal employed by the waste generators. An estimated 92,900 MT are present in spent solvent solutions or sludges that result from solvent recovery processes. Emission estimates are derived from consideration of parameters discussed in several sources [(Radian Corporation, 1979; U.S. EPA, 1975, 1976, 1978, 1979; and U.S. EPA, (personal communication)].

Filter cartridges for drycleaning solvents are replaced weekly at smaller commercial cleaning establishments. Solvents in industrial and larger commercial operations are not filtered but are distilled to remove contaminants. Resulting solvent wastes can be as high as 95% oil and grease. When practical, these wastes are placed and sealed in 55-gallon drums and sold to contracting recyclers. During separation of the solvent from the oil and grease, a small amount of tetrachloroethylene is released to the air (W. Fisher, International Fabricare Institute, personal communication, 1980).

Carbon adsorption systems are being used increasingly in drycleaning operations to treat waste materials (MRI, 1977). In the process, solvents are routed through "chillers" to reduce relative temperature and then adsorbed onto carbon. Approximately 95% of the material is regulated with steam and the resulting condensate contains tetrachloroethylene as still bottoms. Current knowledge on the application of this process is limited and, therefore, the pollutant loading of the environment with tetrachloroethylene from these systems is difficult to quantify. (Arthur D. Little, Inc. Estimate).

Finally, there are some limited discharges of PCE to POTWs and water as a result of its use in the drycleaning industry. Available data indicate that 10 MT is discharged to POTWs annually, although actual releases may be larger (Versar, 1974).

#### E. METAL DEGREASING

Because tetrachloroethylene is nonflammable (i.e., no flash point) and has good degreasing characteristics, it is used in vapor degreasing applications in the metal cleaning industries as a replacement for trichloroethane (U.S. EPA, 1979). The principal disadvantage in using PCE in vapor degreasing is its relatively high boiling point, with associated high energy costs and long cooling cycles (Versar, Inc., 1979). PCE is also used in cold cleaning metal operations.

Approximately 17% (55,400 MT) of domestic tetrachloroethylene consumption is used for metal cleaning (MRI, 1977; Radian Corporation, 1979)

(See Appendix A). Metal cleaning operations represent a very distributed use of tetrachloroethylene. There are approximately 24,000 vapor degreasing and about 900,000 cold cleaning facilities at which this solvent may be used, including gas stations, machinery manufacturers, and other metal working activities (U.S. EPA, 1979). A nationwide survey conducted in 1976 by the Dow Chemical Company for the U.S. EPA, indicated that 2188 metal working plants reported using tetrachloroethylene for vapor degreasing and cold cleaning (MRI, 1977). At the present time, metal degreasing is estimated to release nearly 20,000 MT per year into the atmosphere, 10 MT to water, 40 MT to POTW, and about 11,000 MT to land.

The U.S. EPA reports that all organic solvent cleaning operations are to be subject to regulations of the Resource Conservation and Recovery Act (RCRA). Within the framework of RCRA, waste solvents and still bottoms may be disposed of by distillation and incineration, landfilling, or storage in surface impoundments (GCA Corporation, 1979). As mentioned previously, incineration is becoming less attractive because of rising energy prices.

RCRA allows organic solvent cleaners generating less than 100 Kg of waste per month of discharge into any state-authorized landfill area without using containment methods (GCA Corporation, 1979).

Approximately 37% of the metal cleaning plants recover waste solvents at their own locations and 70% of these dispose of these sludges in sanitary landfills. The remaining 63% of metal cleaning operations sell their wastes to solvent reclaimers and 20% of these discharge the materials to landfills (U.S. EPA, unpublished). The U.S. EPA estimates that 15-62.5% of the solvent consumed results in waste. If 50% of tetrachloroethylene consumption is assumed to result in sludge and with the breakdowns given above, on-site recovery appears to result in discharges of 7,200 MT to landfills, while contract recyclers dispose of 3,500 MT similarly (Versar, 1979b).

The largest release from cold metal cleaning operations is thought to be from waste solvent evaporation. The volume of evaporative emissions from a vapor degreaser is significantly less than that from a cold cleaner of similar capacity because vapor degreasing wastes have a higher boiling point, volatilizing less rapidly, and because vapor degreasing solvents contain expensive halogens, which are recycled (Bollinger and Schumaker, 1977). The U.S. EPA indicates that distillation is used to recover colvent wastes in approximately one-half of all open-top vapor degreasers (GCA Corporation, 1979).

#### F. OTHER USES

The production of fluorocarbons is the only consumptive use of tetrachloroethene and comprises about 12% (38,100 MT) of the industrial demand (MRI, 1977, Radian Corporation, 1979). The fluorocarbons derived from tetrachloroethene are used as solvents, grain fumigants, or as an anthelmintic in veterinary medicine (Versar, Inc., 1979a). The manufacture of fluorocarbons is estimated to contribute about 60 MT of atmospheric tetrachloroethene emissions (JRB, 1979).

The remainder of the PCE supply, about 6,900 MT, is used in various miscellaneous applications (Radian Corporation, 1979), such as use as a specialty solvent in food processing and in aerosol specialty products. All of the tetrachloroethylene consumed for miscellaneous uses is assumed to be dissipated in the atmosphere. Tetrachloroethylene itself is also used in very small quantities as an anthelmintic (Radian Corpoation, 1979; Versar, 1979a). In sludge form, it is occasionally applied to road surfaces as a dust preventative.

#### G. TRANSPORT

Because of its chemical characteristics, tetrachloroethylene is shipped in stainless steel, aluminum, or carbon steel tanks, usually (if not always) at full strength concentration. It is then removed by pump or air pressure. Corrosion does not pose a problem because all commercial tetrachloroethylene is reported to contain stabilizers (MRI, 1977). Following completion of transport, the tanks are flushed with water, steamed, rinsed and dried. The cleaning waters contain residual tetrachloroethylene in unidentified concentrations and are most probably discharged to local sewers (MRI, 1977). Because of the limitations on data regarding transport of the material, it was not possible to estimate associated environmental releases, although it is expected to be small with the exception of spills.

#### H. SUMMARY

Tetrachloroethylene is released to all environmental compartments, as illustrated in Figure 1 and Table 2. About 88% of the total domestic consumption is distributed (versus captive) use, and much of the material is discharged to the environment as a consequence of its use. The environmental compartment receiving the largest pollutant load of PCE is the air, which receives nearly 150,000 MT of the substance directly and indirectly each year. The sources are frequently point sources (e.g., drycleaners, production). Area sources contribute significantly to the atmospheric sources due to tetrachloroethylene's highly volatile nature resulting in indirect releases. The land compartment receives over 100,000 MT of PCE annually. Aquatic discharges of tetrachloroethylene are reported in negligible amounts.

Although tetrachloroethylene consumption in the United States grew at an average annual rate of approximately 5.3% during the 1971-1974 period, there has been a steady decline in production since 1972 ( $\simeq 4.3\%$ ), and sales declined by 7.8% for the 1973 to 1977 period. Since that time production and use have been stabilized somewhat. Further regulation of the drycleaning industry could alter the demand for PCE.

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#### CHAPTER IV

#### DISTRIBUTION OF TETRACHLOROETHYLENE

#### IN THE ENVIRONMENT

#### A. INTRODUCTION

This chapter describes the important physicochemical properties of tetrachloroethylene (Section B), provides detailed information on observed ambient levels of the chemical in all environmental compartments (Section C), describes the important pathways and degradation routes in the environment (Section D), and gives the results of three different modeling efforts that were designed to assist in the assessment of the major transport pathways (Section E). A summary statement covering all aspects is provided in Section F.

Modeling of the fate of PCE in environmental media was undertaken in order to illustrate important aspects of the chemical's fate and transport in selected environmental scenarios. One model predicts the expected concentrations (and amounts) of tetrachloroethylene in each environmental compartment (air, water, soil, sediments, biota) under the assumption that all phases are in equilibrium. By comparing the predicted concentrations (preferably the ratio of concentrations between two compartments) with measured concentrations (ratios), it is possible to determine qualitatively how close to equilibrium the various phases are, and in which direction interphase transfers of PCE are occurring. A second model examines the expected atmospheric dispersion of tetrachloroethylene downwind from a major point source such as a drycleaning or solvent degreasing establishment. The results of this analysis provide insight into the levels of exposure to PCE that may result from these major sources of PCE emissions. The third model used is EPA's EXAMS, which analyzes aquatic fate in various environmental scenarios.

#### B. PHYSICAL AND CHEMICAL PROPERTIES

At room temperature, tetrachloroethylene is a colorless, volatile, heavy liquid with a pleasant ethereal odor. It is nonflammable and incombustible, is fairly stable (the most stable of all chlorinated ethanes and ethylenes), is fairly insoluble in water, but is an excellent solvent for a variety of organic substances (e.g., fats, oils, tars, rubber, and gum). It is these characteristics that have made the chemical very useful as a drycleaning and metal degreasing solvent. The important physiochemical properties are given in Table 4.

Cleaning grades of the chemical contain from 0.01% to 0.1% by weight of stabilizers; industrial grades contain up to about 0.35 weight %.

#### TABLE 4. IMPORTANT PHYSICAL AND CHEMICAL PROPERTIES OF TETRACHLOROETHYLENE

#### General Properties

Molecular Weight 165.83 Boiling Point 121.2°C (at 760 mm Hg)

Melting Point -22.4°C

#### Vapor Phase

Autoignition Temperature none Flash Point none Flammable (explosive) Limits none Decomposition Temperature 700°C

Vapor Specific Gravity 5.76 (air = 1)- 1.12 (air = 1) - 2.43% --Saturated Air Specific Gravity

Concentration in Saturated Air 2.43% by volume (25°C)

Vapor Pressure:

-20.6°C 1 mm Hg +2.4°C 5 mm Hg 13.8°C 10 mm Hg 26.3°C 20 mm Hg 40.0°C 41 mm Hg

0.0099 centipoise (60°C) 5 ppm<sup>3</sup>, 10, 50 ppm<sup>3</sup> 1 ppm = 6.78 mg/m<sup>3</sup> (25°C, Vapor Viscosity

Odor Threshold

Atmospheric Conversion Factor

760 mm Hg)

#### Liquid Phase

Specific Gravity 1.623 (20/4°C)

Viscosity 0.84 centipoise (25°C)

Surface Tension 31.3 dynes/cm (20°C) 1.5055 (20°C) Refractive Index Dielectric Constant 2.353 (15°C)

Dipole Moment

Heat of Vaporization 50.1 cal/g (at boiling point)

Heat of Fusion 2.525 kcal/g-mole Specific Heat 0.205 cal/g-°C (20°C)

### TABLE 4 (Continued)

### Binary and Tertiary Systems

Solubility in Water	-	150 mg/l (25°C) <sup>1</sup> 400 mg/l (25°C) <sup>2</sup> 140 mg/l (25°C) <sup>3</sup> 165 mg/l (25°C) <sup>4</sup> 91 mg/l (25°C) <sup>5</sup>
	-	63 mg/1 (10°C) <sup>5</sup>
Solubility of Water in Solvent		0.008 g/100 g solvent
Solubility in Octanol	-	Infinite
Also Soluble in	-	Ethyl ether, Ethyl alcohol,
*****		benzene, chloroform, others
Will Dissolve	-	Oils, fats, tars, rubber, gum, sulfur, iodine, mer-curic chloride, aluminum chloride, ammonia (0.4% by weight at room temperature), benzoic acid, and other organic acids
Will not Dissolve (to an Appreciable Extent)	-	Sugar, glycerol, protein
Octanol/Water Partition Coefficient	-	724 <sup>6</sup> 759 <sup>7</sup> (calculated) 400 <sup>8</sup>
Henry's Law Constant Air/Water	-	0.82 <u>µg/1 (air)</u> (20°C) <sup>9</sup> µg/1 (water)

Several values are listed because of significant differences in some reported values. Value from Dilling (1977) is an average of four values from the literature (at 25°C or corrected to 25°C). The variation of solubility with temperature is given by Antropov et al. (1972) over the range of about 5°C-80°C.

General Sources: Except where noted, the following references were used: U.S. Environmental Protection Agency (1977); Franklin Institute (1975); Fuller (1976); Lapp et al. (1977); NIOSH (1976); Walter et al. (1976).

# Specific Sources:

- (1) U.S. Environmental Protection Agency (1977); Franklin Institute (1975); Fuller (1976); Lapp et al. (1977); NIOSH (1976).
- (2) Chiou et al. (1978); U.S. Coast Guard (1974).
- (3) Neely (1976).
- (4) Dilling (1977).
- (5) Antropov (1972).
- (6) Environmental Protection Agency (1977); Fuller (1976).
- (7) Neely <u>et al.</u> (1974).
- (8) Chiou et al. (1978).
- (9) Fuller (1976); Neely (1976).

The following chemicals may be used (in various combinations) as stabilizers:

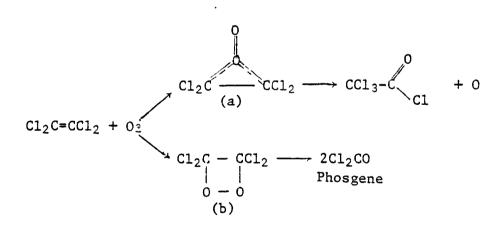
Amines (e.g., allyl amines) Epibromohydrin

Methylmorpholine N-methylpyrrole

Epichlorohydrin Allyl glycidyl ether

Stabilized tetrachloroethylene is inert to air, water, light, and common construction metals at temperatures up to  $140^{\circ}$ C. In the absence of moisture, oxygen, and catalysts, the compound is stable to a temperature of about  $500^{\circ}$ C. At  $700^{\circ}$ C, PCE decomposes upon contact with active carbon to yield hexachloroethane and hexachlorobenzene (Lapp et al., 1977).

In the absence of stabilizers, tetrachloroethylene will react with a variety of chemicals under various conditions. A summary of the available information is shown in Table 5. Oxidation (under ambient conditions) is seen to take place only slowly, unless light or some other catalyst or reaction initiator is present. Ultraviolet light can lead to fairly rapid decomposition in air (half life,  $t_{1/2}$ , is about 1/2 day); an intermediate stage in this reaction is thought to be the synthesis of peroxy compounds as shown below. Compound (a) undergoes rearrangement to form trichloroacetyl chloride and oxygen. Compound (b) decomposes to give two molecules of phosgene, a highly poisonous gas (Lapp et al., 1977; Fuller, 1976).



Tetrachloroethylene is decomposed by contact with hot metals, certain inorganic acids, hot carbon, and certain alkaline metals or compounds of them. Unstabilized tetrachloroethylene can be corrosive to metals; this has obvious implications for the "terminal" disposal of waste solutions and sludges (containing the chemical) in unlined metal drums.

TABLE 5. DEGRADATION OF TETRACHLOROETHYLENE UNDER VARIOUS CONDITIONS

CONDITIONS	RATE OF REACTION	REACTION PRODUCTS
Air, sunlight	t <sub>½</sub> ~ 2 days	Chlorine, hydrogen chlo- ride, trichloroacetic acid
Oxygen, UV light	NA <sup>2</sup>	Trichloroacetyl chloride, phosgene
Oxygen, <u>no</u> light	No reaction	
Ultra zero air, 1 50% relative humidity, light	100% decomposition in 1.5-2 hours	Phosgene and others
As above, plus added NO <sub>2</sub>	100% decomposi- tion in ~ 8 hours	Phosgene, carbon tetra- chloride
As above (no NO <sub>2</sub> ), plus hydrocarbons	100% decomposi- tion in 21-31 hours	Phosgene
Air, added NO (5 ppm), UV light	t <sub>1</sub> ~ 14.2 hours	NA
Air, added NO <sub>2</sub> (16.8 ppm), U <sup>r</sup> light	t <sub>1/2</sub> · 8.3 hours	Phosgene, formic acid, tri- chloroacetyl chloride, carbo monoxide, hydrogen chloride
High oxygen pressure, chlorine	NA	Trichloroacetyl chloride, phosgene
Ozone	Slow, t <sub>1</sub> - 11 years	Phosgene, trichloroacetyl chloride
Hydroxyl ions (in atmosphere)	Rapid, t <sub>1</sub> ~ 8 days	NA
Alkyl peroxy radicals	Slow, $t_{1/2} \sim 0.6$ years	NA
NO <sub>2</sub>	Rapid	Tetrachlorodinitroethane
SO <sub>3</sub> , 150°C	NA	Trichloroacetyl chloride

l "Ultra zero air" is a term used by some commercial suppliers of bottled air to describe a high level of purity. Unfortunately there is no standard and the meaning varies considerably.

<sup>&</sup>lt;sup>2</sup> Not available.

TABLE 5 (Continued)

CONDITIONS	RATE OF REACTION	REACTION PRODUCTS
Excess hydrogen, 220°C, reduced Ni catalyst	na <sup>2</sup>	Hydrogen chloride, ele- mental carbon
Ammonia, high pressure	NA	Ammonium chloride, ele- mental carbon
700°C, contact with active carbon	NA	Hexachloroethane, hexa-chlorobenzene
In water, 150°C	Slow	Trichloroacetic acid, hydrogen chloride
In aerated water, 25°C, dark	t <sub>12</sub> ~ 8.8 months	NA
In aerated water, ambient temperatures (- 20°C to + 40°C), natural sunlight	t <sub>1,5</sub> ≤ 6 months	NA
Strong inorganic acids; e.g., H <sub>2</sub> \$0 <sub>4</sub> + HNO <sub>3</sub> , fuming HNO <sub>3</sub>	NA	Trichloroacetyl chloride, some tetrachlorodinitro-ethane
Butyl lithium in petro- leum ether	Explosive	NA .
Molten potassium	Explosive	NA
In presence of dibenzoyl peroxide	NA	Will yield copolymers with styrene, vinyl acetate, methyl acrylate, acrylonitrile
Contact with iron at 450°C, zinc at 400°C, aluminum at 400°C	NA	Phosgene: 37, 17, and 3 mg/g of tetrachloroethylene, respectively
Human metabolism 3(anal- ysis of urine)		Trichloroacetic acid, tri-chloroethanol

From NIOSH (1976)

Sources: Lapp et al. (1977), except where otherwise noted.

# C. MEASURED CONCENTRATIONS IN THE ENVIRONMENT

# 1. Introduction

Long-term usage of tetrachloroethlyene in the U.S. — primarily for drycleaning and metal cleaning — has led to continuous losses of the chemical to the environment in all parts of the country. Losses to the environment in the U.S. were estimated to amount to 256,750 MT in 1979; about 60% of the losses are released directly to the air from point sources (Versar, Inc., 1980), and 40% to land. (Losses to water and POTWs are less than 1% of the total pollutant release.)

A relatively large amount of data exists concerning the concentrations of tetrachloroethylene in various environmental compartments. Data from U.S. sites are presented in the following figures and tables, with the exception of the data on marine waters, sediments, and biota, which are from Great Britain because data for the U.S. are lacking.

### 2. Data from Selected Surveys

In order to obtain a better understanding of the ambient concentrations of tetrachloroethylene and the variability associated with the measurements, data have been selected from a number of surveys.

The data should be viewed as examples only; to generalize from these data could result in specious results. The principal cautions are associated with the following:

- The data are usually from a small number of samples, sampling dates, and/or locations, and do not, therefore, adequately represent averaged temporal or spatial distributions.
- The concentrations measured are frequently near or below the detection limit of the analytic method used. Furthermore, the detection limit may vary, not only from study to study but also within a study for different samples.

#### a. Water

## 1. Drinking Water

The data base for PCE concentrations in drinking water includes three studies by the U.S. EPA: The Ten Cities study (U.S. EPA 1975), the National Organics Monitoring Survey (NOMS) (U.S. EPA 1978), and the Community Water Supply Survey (CWSS) (Brass 1981). The results of these

studies are presented in Table 6. In both NOMS and the CWSS, reported frequencies of detection for PCE were less than 10%. The means for the positive values ranged from 0.8  $\mu g/1$  to 3.4  $\mu g/1$ , although the medians were less than 0.5  $\mu g/1$ .

PCE has been found in well water all over the U.S. Of 36 finished drinking water supplies pumped from the ground, 22% contained PCE at detectable levels (>0.2  $\mu$ g/l). The mean of the positive values was 2.1  $\mu$ g/l and the high was 3.1  $\mu$ g/l (U.S. EPA 1980a). In a collation of State data on the ground water quality as sampled from 2940 existing wells in 17 states, the percentage occurrence of PCE in the ten states where it was detected ranged from 1% to 48%. It must be kept in mind that this sampling is biased towards contaminated supplies. As an example of the data, 372 wells tested in Nassau County, N.Y. were found to contain PCE in 57 (15%) (many of these wells were closed by the County Board of Health). The maximum concentration determined in Nassau County was 375  $\mu$ g/l (U.S. EPA 1980a).

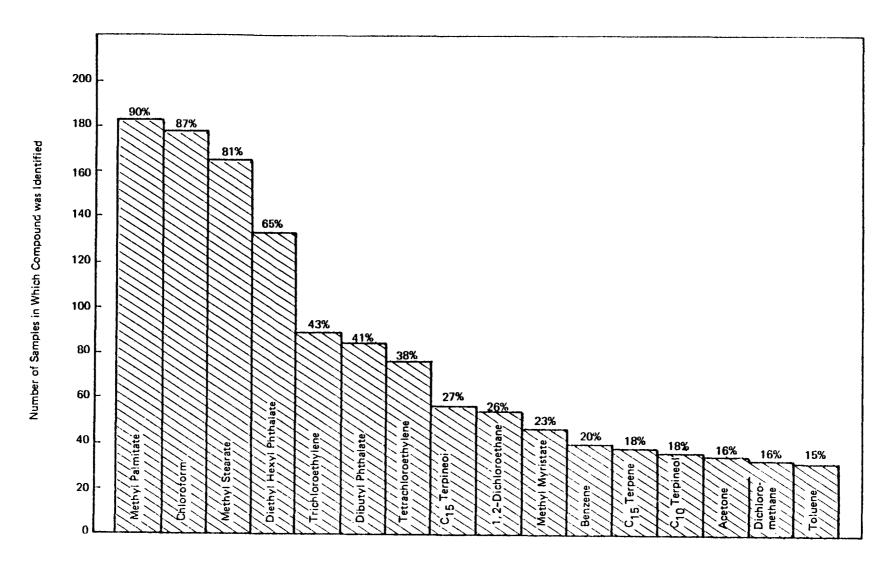
In March 1980, levels of PCE in the drinking water of 72 Massachusetts communities were found to reach 5 mg/l and averaged between 1.5 mg/l and 2.5 mg/l. These levels were caused by PCE leaching from a resinous liner of concrete pipes in public water systems. The resin has been applied to prevent leaching of asbestos fibers from the pipes by acidic wastes (Massachusetts DEQE 1980). Since then, even higher levels of PCE have been documented. Wakeham et al., (1980) found a peak of 18 mg/l in a water pipe in Falmouth, MA, but the line did not serve any households, and thus was not used for drinking water. In this study, households receiving contaminated water could have been exposed to PCE levels as high as 2.2 mg/l.

### 2. Surface Water

Reported concentrations of PCE in surface water from various surveys are depicted in Figures 3-6 and Table 7.

In a 1977 national survey of U.S. surface water in 14 industrialized river basins, Ewing et al. (1977) detected tetrachloroethylene in 38% of a total of 204 samples. Ninety-six percent of positive samples contained PCE at concentrations less than 5  $\pm$ g/l. Only two percent of the samples exceeded 10  $\pm$ g/l. Figures 3 and 4 depict the results of the survey.

Ambient surface water data were retrieved from the U.S. EPA's STORET system for the period preceeding and through 1981. Out of a total of 870 samples, only 9% were unremarked data. Ambient concentrations are summarized in Table 7 by major river basin for unremarked and remarked measurements. The mean and maximum unremarked levels for all major river basins were 8.5  $\mu$ g/l and 142.0  $\mu$ g/l, respectively. Remarked levels averaged around 10  $\mu$ g/l, an apparently commonly used detection limit.



Source: Ewing et al., 1977.

FIGURE 3 FREQUENCY OF IDENTIFICATION OF ORGANICS IN U.S. SURFACE WATERS

Note: Data are from 204 sites from 14 river basins in industrialized areas. The % figures shown = (number of positive samples/204)  $\times$  100.

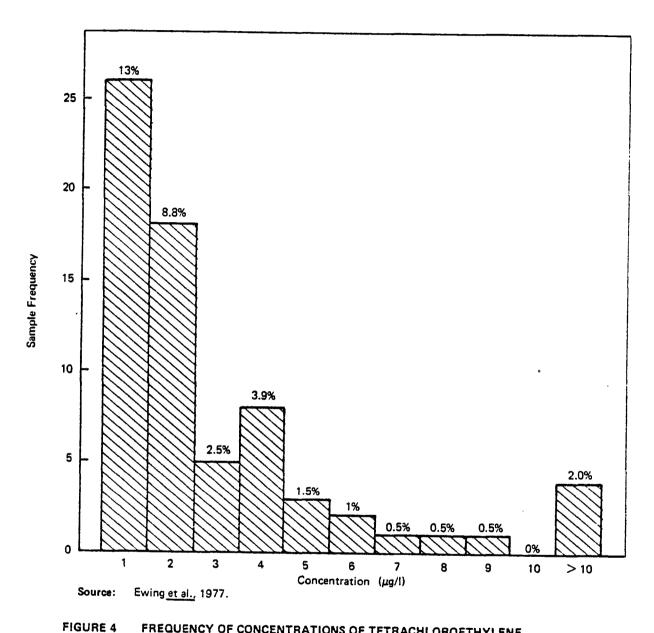
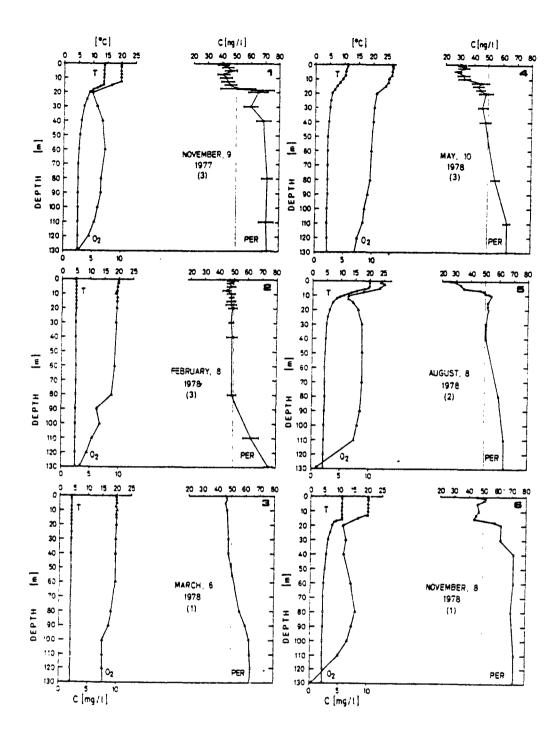


FIGURE 4 FREQUENCY OF CONCENTRATIONS OF TETRACHLOROETHYLENE FOUND IN 204 SAMPLES OF U.S. SURFACE WATERS

Note: Source cited states that tetrachloroethylene was identified in 77 of 204 samples taken at various locations in 14 industrialized river basins. Only 69 data points were reported however, and these are represented in the chart above. The number of samples in which tetrachloroethylene was not detected is not shown. The percent figures shown = (Sample Frequency/204) x 100.



Source: Schwarzenbach et al., 1979.

FIGURE 5 VERTICAL PROFILES OF TETRACHLOROETHYLENE (PCE), TEMPERATURE, AND DISSOLVED OXYGEN AT THE DEEPEST POINT OF LAKE ZURICH, SWITZERLAND

Note: Presence, in diagrams 1, 4, 5 and 6, of thermal stratification and higher concentrations of tetrachloroethylene in the lower depths.

Number in parentheses below date in each diagram indicates number of replicate samples collected at each depth.

The European abbreviation for PCE is PER and appears in this figure.

TABLE 6. CONCENTRATIONS OF TETRACHLOROETHYLENE IN U.S. DRINKING WATERS

		Concentration (μg/1)				
Study	Frequency of Detection	Means of Positives	Median of All Data	Observed Range		
NOMS Phase II <sup>2</sup> ,3 NOMS Phase III	48/111 (43%)	not quantified				
Quenched Terminal	8/106 (8%) 9/105 (9%)	1.1 0.81	<0.2 <0.2			
cwss <sup>4</sup>						
Surface Supplies Cround Supplies	3/106 (3%) 18/330 (5%)	2.8 3.4	<0.5 <0.5	<0.5-3.0 <0.5-30.0		
Ten Cities <sup>5,6</sup>	`					
Miami, FL Ottumwa, IA Philadelphia, PA Cincinnati, OH Tucson, AZ New York, NY Lawrence, MA Grand Forks, ND Seattle, WA Terrebonne Parish, LA	0.1; 0.1; D 0.2; D 0.4; D 0.1; 0.3; D <0.01 0.05; 0.46 0.07; D 0.2 ND	0.18 <sup>7</sup>	0.07	ND-0.5		

D = Detected; ND = Not Detected.

3U.S. EPA (1978).

4Detection limits for Phase II--unreported; Phase III, 0.2 μg/1.

5Brass (1981).

6U.S. EPA (1975).

7Values are actual data from ten cities.

TABLE 7. SUMMARY OF STORET DATA FOR TETRACHLOROETHYLENE AMBIENT CONCENTRATIONS IN U.S. SURFACE WATERS (AS OF END OF YEAR 1981).

B	asin	Ur	remarke	d Data			Remarke	d Data	
#	Name	No, of Samples	Mean	S.D.	Max.	No. of Samples	Mean <sup>1</sup>	s.b. <sup>2</sup>	Max
01	Northeast	0				4	1.5	0.6	2.0
02	North Atlantic	26	1.4	2.5	9.2	78	2.7	3.8	10.0
03	Southeast	3	19.6	11.2	27.0	39	6.5	2.3	10.0
04	Tennessee River	2	67.5	54.4	106.0	31	9.7	1.7	10.0
05	Ohio River	26	0.05	0.2	0.7	48	3.9	3	10.0
06	Lake Erie	5	3.8	1.3	5.0	22	55,4	50	100.0
17	Upper Mississippi River	1	63	p	63	31	14.4	21.9	50.0
)8	Lake Michigan	2	2.0	-	2.0	46	24.3	40.8	100.0
)9	Missouri River	4	32.0	45.8	100.0	198	10.8		50.0
10	Lower Mississippi River	2	5.4	6.5	10.0	107	4.8		50.0
11	Colorado River	0		• "		25	9.3	_	
12	Western Culf	2	99	60.8	142.0	46	1.2	-	10.0
13	Pacific Northwest	5	1.7	2.4	5.9	84	8.1		10.0
4	California	0			3.,	8	10.0	0	10.0
5	Great Basin	0 .				12	10.0	0	10.0
7	Hawaii	0				1	10.0		
2	Lake Superior	0				13	30.0	0	10.0
	Summary	78	8.5	24.4	142.0	792	10.0	0	30.0

Weighted average (by number of samples) for all remarked codes (K, U, and L).  $^{\circ}$ 

Source: U.S. EPA (1980b).

Standard deviation not determined when more than one remarked code reported for a basin.

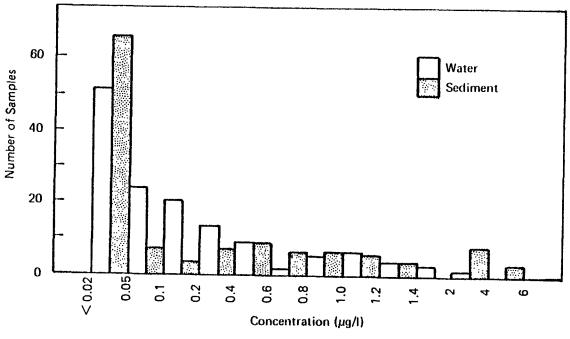
Data were examined further for those basins containing the 11 manufacturers of PCE: the Ohio River, the Lower Mississippi River, and the Western Gulf Basins. (There is a manufacturing plant in the California Basin, but no data have been listed for PCE in this region.) Concentrations were determined close to or at five of the ten facilities in these basins. In the vicinity of the E.I. DuPont plant, Corpus Christi, TX, PCE was not detected; downstream of the PPG Industries facility, Lake Charles, LA, PCE was also not detected. By the Dow Chemical plant, Freeport, TX, in waters affected by tidal action, concentrations were 10  $\mu\text{g}/1$  at two separate sites. The intake for the Vulcan Chemical, Geismar, LA, facility was found on one occasion to contain 5  $\mu\text{g}/1$ , while the Stauffer Chemical, Louisville, KY, effluent had levels between 300  $\mu\text{g}/1$  and 5500  $\mu\text{g}/1$  in four separate samples.

Figure 5 shows data on PCE concentrations in a Swiss lake. The data show correlations between increasing depth, increasing PCE levels, and decreasing temperature. It is known, however, that PCE solubility is directly related to temperature. Thus, these data are indicative that an alternative process is dominating system behavior. While replicate samples were uncommon in this program, the data for all 6 sampling days are consistent in demonstrating this relationship. It is postulated that the increase in PCE concentrations with depth is a function of increasing suspended sediments at greater depths, due to thorough mixing below the thermocline (Schwarzenbach et al. 1979).

The British data for sediment and water concentrations shown in Figure 6 are not conclusive, but do show the presence of PCE in sediments at concentrations in the same general range as the overlying marine waters (Pearson and McConnell, 1975).

Figure 7 shows data for surface waters that were suspected of PCE contamination due to their proximity to hazardous waste disposal sites. PCE levels were found in the range 0.02-60 mg/l (Touhill, Suckrow and Associates, 1979). Because these sampling programs were not comprehensive, it is impossible to say whether these numbers are extreme values or if they are typical.

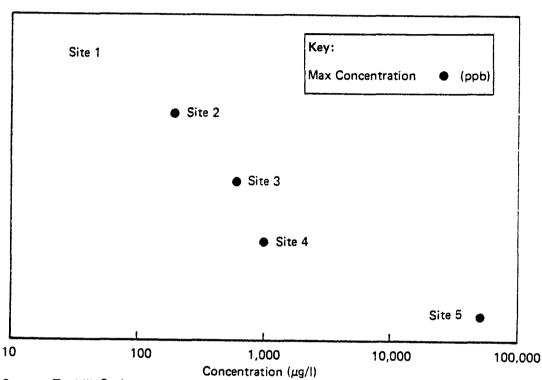
Data for PCE concentrations in wastewaters before and after teratment are shown in Table 8. Combined sewage may contain up to 2412  $\mu g/1$ , although influent levels were typically below 100  $\mu g/1$ . Effluents were much lower, usually below 5  $\mu g/1$ , indicating removal efficiencies usually above 90%. Wastewater sources in these studies were domestic, industrial, and commercial.



Source: Pearson and McConnell, 1975.

FIGURE 6 CONCENTRATION OF TETRACHLOROETHYLENE IN MARINE WATERS AND SEDIMENTS (LIVERPOOL BAY, GREAT BRITAIN)

Note: These data show no direct correlation between the concentrations in sediments and in the overlying waters at the time of sampling. One would expect, assuming a sediment adsorption coefficient (K<sub>oc</sub>) of ~ 300 and a sediment organic-carbon content of 10%, that the concentration in the sediments would be about 30 times that in water (expressing both concentrations in ppb) if the two phases were in equilibrium.



Source: Touhill, Suckrow and Associates, Inc., 1979.

FIGURE 7 MAXIMUM CONCENTRATIONS OF TETRACHLOROETHYLENE DETECTED IN THE LEACHATE FROM, OR GROUNDWATERS NEAR, FIVE WASTE DISPOSAL SITES

Note: The researchers evaluated composition data (from a variety of published and unpublished sources) on leachates, and contaminated ground and surface waters in the proximity of 27 sites known to contain hazardous wastes. Tetrachloroethylene was listed as a contaminant for five of these sites; it may have been present — but not analyzed for — at additional sites. Sites 1, 2 and 5 involved the collection of groundwater samples while "leachate" was collected at sites 3 and 4. Thus one can probably assume, as a rough approximation, that about one quarter of the unsecure hazardous waste disposal sites in the U.S. may involve some surface or groundwater contamination by tetrachloroethylene. Such sites (with tetrachloroethylene) probably number in the thousands.

TABLE 8. TETRACHLOROETHYLENE IN WASTEWATER TREATMENT SYSTEMS

	Concentration (μg/1)						
	Tap Water	Various Sewer Sites <sup>3</sup>	Influent	Primary Sludge	Digested Sludge	Effluent	Percent Removal
Cincinnati, OH	$ND^2$	2.8 + 2.4(6)	1	_	_		
St. Louis, MOl	2	20 + 10(8)	45			_	-
Hartford, CT <sup>1</sup>	ND	8.0 + 9.6(7)	26	_	_	_	-
Atlanta, GΛ <sup>l</sup>	2	$53 \pm 70(9)$	239	_	-	<del></del>	<u>-</u>
Rye Meads, UK <sup>4</sup>	_	_	5	5	_	0.5	96
Davyhulme, ŲK <sup>4</sup>	_	_	6	5	_	ND	100
Saltford, UK <sup>4</sup>	graph.	-	30	66	_	9 2	93
Countess Wear, UK <sup>4</sup>		_	2412	38	_	144	93 94
Minworth, UK <sup>4</sup>	-	-	46	17		0.5	99
Indianapolis, 1N <sup>5</sup>	_		51	293	_	ς	00
Cincinnati, OH <sup>5</sup>		<u></u>	5	61	_	3	90 40
Lewiston, PA <sup>5</sup>	_	_	45	1601		3	93
Atlanta, GA <sup>5</sup> _	-	-	305	958	10	1.34	65
St. Louis, MO <sup>5</sup>	_	_	115	14	ND	26	77
Pottstown, PA <sup>D</sup>		_	9	1642	423	0	100
Frand Rapids, M1 <sup>5</sup>		-	15	32	ND	3	80
Mint, MI <sup>5</sup>	-		26	-	-		96
lartford, CT <sup>5</sup>	-	_	4		_	0	100

<sup>1</sup> Levins et al. (1979 a-d) all data are averages from several sample analyses over 3-6 day sampling periods.

<sup>&</sup>lt;sup>2</sup> ND: None Detected

 $<sup>^3</sup>$  Simple average of average values at each site given along with standard deviation. Number in parenthesis indicates number of sites sampled. Sites were at varying distances (upstream) from POTW. Sewer sites sampled did not cover all sections of POTW collection area and thus area with significant Atetrachloroethylene discharges may have been missed.

<sup>5</sup>Burns and Roe, unpublished data, 1979.

## b. Air

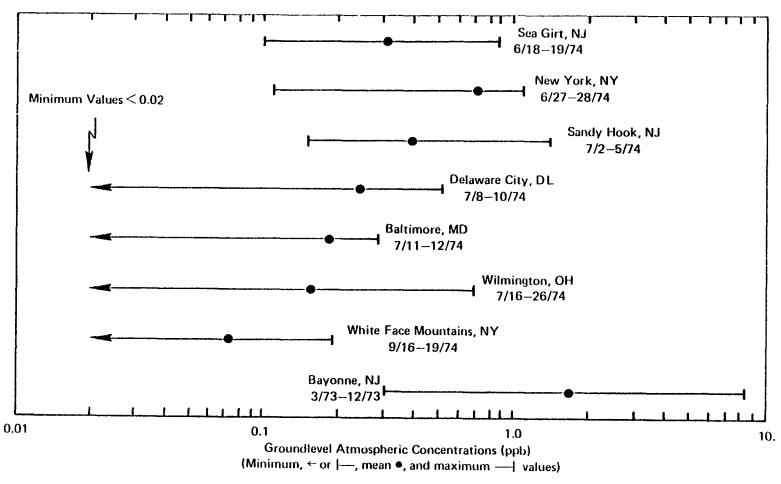
The most recent data on levels of PCE in urban air were developed by Singh et al. (1979, 1980). These researchers sampled seven cities in the western half of the U.S. and determined mean concentrations between  $2~\mu\text{g/m}^3$  and  $10~\mu\text{g/m}^3$ . The average of these mean values was 4.3  $\mu\text{g/m}^3$  and the overall range of observations was 0.23-51.56  $\mu\text{g/m}^3$ .

Concentrations of PCE that have been measured in the atmosphere are shown in Figures 8-10. Ground-level sampling (Lillian et al. 1975) in the Eastern U.S. (Figure 8) included an average value from a remote mountain site of 0.50  $\mu g/m^3$  (0.07 ppb) and average concentrations at urban sampling sites between 1.02  $\mu g/m^3$  (0.15 ppb) in Wilmington, OH, and 1.15  $\mu g/m^3$  (1.7 ppb) in Bayonne, N.J. The highest value reported was 68  $\mu g/m^3$  in the New York City sampling.

In a Los Angeles sampling program (Figure 9), PCE concentrations at ground level were generally (50% of the time) less than  $13.6~\mu g/m^3$  (2 ppb). The recorded high in this study was  $30.5~\mu g/m^3$  (4.5 ppb) (Simmonds, et al. 1974). These values do not differ greatly from those values measured in eastern cities, nor from the data of Singh et al. (1979, 1980).

Pellizari et al. (1979) investigated levels of PCE in four highly industrialized areas: Niagara Falls, NY; New Jersey; Baton Rouge, LA; and Houston, TX. They found average values for these areas ranging from 0.12-210  $\mu g/m^3$ , with the high found in the New Jersey area. These authors also investigated levels near a chemical waste disposal site and found trace levels to 395  $\mu g/m^3$ , with a median of 1.2  $\mu g/m^3$  for 23 measurements in various locations around the site.

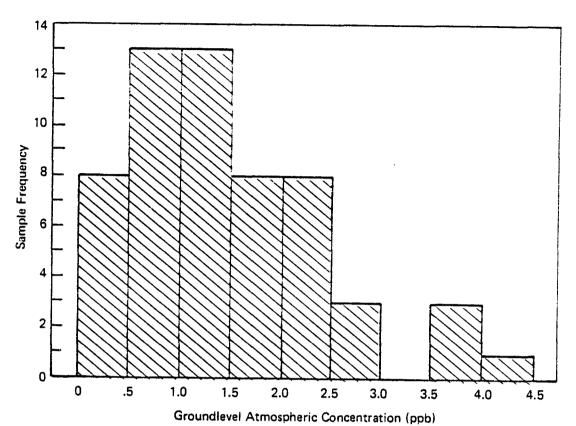
Measured variations in PCE concentrations over the course of a day are presented in Figure 10, which shows the results of three sampling programs at an urban site, suburban site in the Los Angeles Basin, and a remote (mountain) site (Lillian et al. 1975). In each case, the level changes dramatically near evening. In central New York City, two distinct concentration peaks were observed, reaching 68  $\mu g/m^3$  (10 ppb) and 64  $\mu g/m^3$  (9.5 ppb) at 9:30 a.m. and 6:30 p.m., respectively. The PCE levels were less than 1.4  $\mu g/m^3$  (0.2 ppb) at night and about 2.2  $\mu g/m^3$  (0.34) during the day. At both the suburban and the remote sites, only one unique peak was documented during the sampling day. These values were 68 and 47  $\mu g/m^3$  for the suburban and remote sites, respectively. Of significance is the observed drop in air levels to below detectable limits for the 10 hours 12:00-10:00 a.m. at the remote site. This is a clear indication that PCE is found at increasing levels during the day due to importation from upwind sources. The suburban site shows a late night and early morning drop, and may be reflecting changes in a nearby urban area (Los Angeles).



Source: Lillian et al., 1975

FIGURE 8 ATMOSPHERIC CONCENTRATIONS OF TETRACHLOROETHYLENE AT SELECTED SITES IN THE EASTERN U.S.

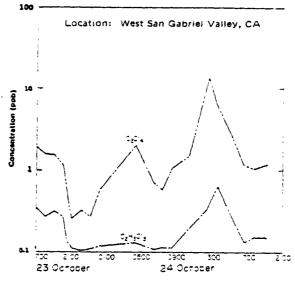
Note: Samples were collected at only one site in each city or location. The number of samples collected during the indicated sampling period was not specified. The means reported are of determinations where detectable levels were measured. In a short-term monitoring effort in New York city, levels as high as 9.8ppb were observed. A large clean oceanic air mass had moved into the Baltimore area during the sampling period and this, the authors suggest, probably accounts for the generally low levels of all halocarbons measured at this site.



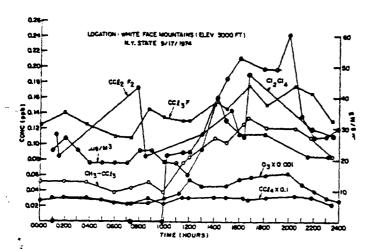
Source: Simmonds et al., 1974

FIGURE 9 ATMOSPHERIC CONCENTRATIONS OF TETRACHLOROETHYLENE IN THE LOS ANGELES BASIN

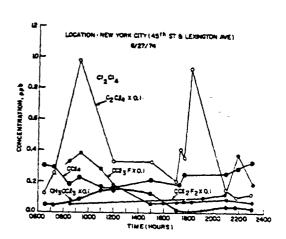
Note: Samples (total of 58) were collected at about 41 sites in the Los Angeles Basin during September 22 and 28, and October 4, 1972. In general, different sites were selected for each sampling day although some sites were used more than once on a sampling day. All measurements have been lumped together in the chart above. Winds headings were near 225° for most of the sampling periods with wind speeds in the range of 5–10 knots. The average of all measurements was 1.25 ppb. The highest daily average (2.2 ppb) was obtained on a day with visible smog and generally stable inversion conditions.



Source: Simmonds et al., 1974.



Source: Lillian et al., 1975.



Source: Lillian et al., 1975.

FIGURE 10 DIURNAL VARIATIONS IN THE GROUND LEVEL ATMOSPHERIC CONCENTRATIONS OF TETRACHLOROETHYLENE ( ${\rm C_2Cl_4}$ ) AND OTHER HALOCARBONS

Note: The large diurnal fluctuations seen at ground level for tetrachloroethylene are presumably due to shifting wind patterns in combination with the influence of major emission sources. Photochemical degradation could result in a diurnal fluctuation of 1-15% (i.e., a decrease of this amount at the end of a sunlit day).

Areas with high population densities in Amsterdam were studied for PCE levels in exhaled air of residents near drycleaning establishments. Using the relationship that ambient air levels are 2.5 x exhaled levels as discussed by these authors, ambient air levels were calculated from the data of Verberk and Scheffers (1980). It was estimated that workers in 12 shops were breathing, on the average, 182,500  $\mu g/m^3$ , while residents living above the shops breathed 12,250  $\mu g/m^3$ . One home away, estimated PCE levels were 2500, two houses away - 550 and across the street, estimated levels were less than 250  $\mu g/m^3$  (Verberk and Scheffers, 1980).

Figure 11 shows that as altitude is increased, the levels of most halocarbons drop significantly. In particular, PCE concentrations change from about 2.7  $\mu g/m^3$  (0.4 ppb) at 500 m to 0.07  $\mu g/m^3$  (0.01 ppb) at 3000 m. It follows the same general shape as the temperature curve, showing an abrupt change at about 1700 m and 8°C, the location of a distinct inversion layer. The declining concentrations above the inversion are interpreted to mean that local emissions are the only source of atmospheric PCE at this site (Simmonds et al. 1974). Whether this is true as one moves East has yet to be determined.

## c. Biota

The only data for PCE levels in biota are British and for fish in salt or briny water. In Table 9, the observed levels in flesh range from 0.3  $\mu g/kg$  to 11  $\mu g/kg$ , while for liver the range is from 1.0  $\mu g/kg$  to 41  $\mu g/kg$ . The slightly higher range for the latter may be attributed t the higher fat content of liver. Average water concentrations were found to be about 0.5  $\mu g/l$  (Pearson and McConnell, 1975). Thus, it plausible to assume that some degree of bioaccumulation is taking p However, the lower levels of the local food chain were not sampled plankton, filter feeders, nekton.

# d. Foodstuffs

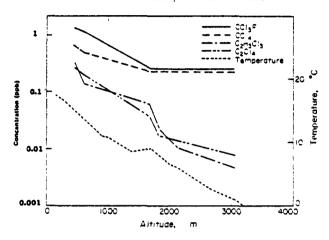
The only data for PCE levels in foodstuffs are from Gr (McConnell, et al. 1975). The highest levels are observed high fat contents, i.e., butter, margarine, eggs, oils, (5-13  $\mu g/kg$ ). Levels in tea and coffee were also high vegetables, and meats are in a lower range of values. given in Table 10.

# 3. Summary

Table 11 summarizes ranges of PCE concentmental media, foodstuffs, and biota abstracte above. Monitoring of PCE in the environment levels are found in close proximity to sour as opposed to degradative processes may be fate of PCE. The fact that, despite lar intensive users of PCE, monitored lever 20 cg/m³ (except in industrial location indicates that degradative processes may PCE's fate. The behavior of PCE in water nealthough volatilization may dominate the loss.

Δ;

### Distribution of atmospheric halocarbons



Source: Simmonds et al., 1974.

FIGURE 11 TYPICAL CONCENTRATIONS OF HALOCARBONS, INCLUDING TETRACHLOROETHYLENE (C<sub>2</sub>Cl<sub>4</sub>), AND AMBIENT TEMPERATURE VS ALTITUDE

Note: Data are for the Inglewood, CA area. The concentration of each compound is seen to decrease with altitude up to the 1700 meter level where a significant inversion layer was observed. The concentration of tetrachloroethylene continues to decline with increasing altitude above this point. Simmonds et al. believe that the C<sub>2</sub>Cl<sub>4</sub> measured represents emissions only from stationary sources in the Los Angeles Basin.

SPECIES	ORGAN	SOURCE 1	CONCENTRATION <sup>2</sup>
Raja clavata (ray)	Flesh	Liverpool Bay	(µg/kg) 0.3 - 8
The state of the s	Liver	Liverpool Bay	14 - 41
Pleuronectes platessa (plaice)	Flesh	Liverpool Bay	4 - 8
	Liver	Liverpool Bay	11 - 28
Platycthys flesus (flounder)	Flesh	Liverpool Bay	2
	Liver	Liverpool Bay	1
Limanda limanda (dab)	Flesh	Liverpool Bay	1.5 - 11
	Liver	Liverpool Bay	15 - 30
Scomber scombrus (mackerel)	Flesh .	Liverpool Bay	1
	Liver	Liverpool Bay	$ND_3$
Limanda limanda (dab)	Flesh	Redcar, Yorks	5.1
	Flesh	Thames Estuary	3
Pleuronectes platessa (plaice)	Flesh	Thames Estuary	3
Solca solea (sole)	Flesh	Thames Estuary	4
	Guts	Thames Estuary	1
Aspitrigia cuculus (red gurnarch)	Flesh	Thames Estuary	1
	Guts	Thames Estuary	2
Trachurus trachurus (sead)	Flesh	Thames Estuary	4
Trisopterus luscus (pout)	Flesh	Thames Estuary	2
Squalus acanthias (spurdog)	Flesh	Thames Estuary	1

SPECIES	organ	Source <sup>1</sup>	CONCENTRATION <sup>2</sup>
Scomber scrombrus (mackerel)	Flesh	Torbay, Devon	(μg/kg) ND
Clupea sprattus	Flesh	Torbay, Devon	1.6
Cadus morrhua (cod)	Flesh	Torbay, Devon	< 0.1
	Air Bladder	Torbay, Devon	3.6

Source: Pearson and McConnell (1975).

 $<sup>^{1}\</sup>mathrm{The}$  average concentrations found in water were 0.5  $\mu g/1$ .

 $<sup>^2\</sup>mathrm{Wet}$  tissue.

<sup>3&</sup>lt;sub>Not detectable.</sub>

TABLE 10. CONCENTRATION OF TETRACHLOROETHYLENE IN FOODSTUFFS

FOODSTUFF	TETRACHLOROETHYLENE CONCENTRATION (µg/kg)
Dairy Products	
Fresh Milk Cheshire Cheese English Butter Eggs	0.3 2 1.3 ND
Meat	
English Beef (steak) English Beef (fat) Pig's Liver	0.9 1.0 5
Oils and Fats .	
Margarine Olive Oil (Spanish) Cod Liver Oil Vegetable Cooking Oil Castor Oil	7 7 2 0.01 3
Beverages	<b>~~</b> .
Canned Fruit Drink Light Ale Canned Orange Juice Instant Coffee Tea (packet) Wine (Yugoslav)	2 ND ND 3 3 ND
Fruits and Vegetables	
Potatoes (South Wales) Potatoes (Northwest England) Apples Pears Tomatoes* Black Grapes (imported) Fresh Bread	ND 0.7 2 2 1.2 ND 1

ND - Not detected

Source: McConnell et al. (1975).

<sup>\*</sup>Tomato plants were grown on a reclaimed lagoon at Runcorn Works of ICI.

TABLE 11. RANGES IN CONCENTRATION OF TETRACHLOROETHYLENE IN THE ENVIRONMENT

	Number of	Concentr	ation 1
	Sites 2	Typical Range	High Value
AIR		$\mu g/m^3$	ug/m <sup>3</sup>
Background (remote sites, groun level) Urban Locations (ground level)	15-25 ~ 20	<0.1 - 0.5 1.0 -14.0	0.61 68.0
Troposphere (0-20,000 ft.) Stratosphere (20,000-30,000 ft. Near Manufacturing and User Sit Near Chemical Dump Site		0.07-0.14 0-0.07 0.12-2.10 1.2	0.15 0.12 394
Work Areas inside Drycleaning Establishments (DCE) Above Drycleaning Establishment Adjacent to DCE Two Buildings Away from DCE Across the Street from DCE	>100 12 12 12 12	47,500-237,000 12,250 2,500 550 250	>6,780,000    
WATER		(µg/1)	)
Drinking Water (surface) Drinking Water (ground) Marine Waters Rain Water Sewer Waters (4 cities) Municipal Waste Waters (treated Waste Water from Drycleaning Establishments Contaminated Wells, Leachate	>100 <400 > 2  30 7 3 several	<0.2-3 <0.5-4 0.18 (.04) <sup>3</sup> 2-50 4-5  5,000-110,000	3 5000 2.6 0.15 <sup>4</sup> 200 10 1,000,000 >10,000
SEDIMENTS, SLUDGES		(µg/kg	<u>g)</u>
Marine Sediments (Liverpool Bay POTW Sewage Sludge <sup>5</sup>	1 2	0.02-1 290, 7, 61	4.8 <del></del>
BIOTA 7	Number of Species <sup>2</sup>	(µg/kg	(3)
Marine Fish (flesh) Marine Fish (liver) Marine Algae Marine Invertebrates Birds (various parts, eggs) Mammals Humans (various parts)	15 15 6 13 8 2 (8 subjects)	1-5 5-20 13-20 1-9 1-25 0.6-3 <.5-6	11 56 22 15 39 19 29
FOODSTUFFS	Number of Foods <sup>2</sup>	(ug/kg	;)
Various Foods	25	ND-3	13

## Notes to Table 11

- <sup>1</sup> The concentrations given in this table are generally representative of the available data resulting from actual measurements. Whenever possible, data from measurements in the U.S. were used.
- Approximate number of sites (species, goods) for which data were available. Exact number not always specified in original reports.
- <sup>3</sup> Estimated using a water/air partition coefficient of 1.22 (see Table 4) and an assumed average air concentration of 0.03 ppb.
- Datum is from one site in England near an organochlorine manufacturing plant.
- <sup>5</sup> Wells and leachate are presumably contaminated by nearby industrial waste disposal sites.
- $^6$  Three values given are for: (1) primary sludge at plant A (290  $\mu g/kg$ ), (2) secondary sludge at plant A (<7  $\mu g/kg$ ) and (3) combined sludge at plant B (61  $\mu g/kg$ ).
- <sup>7</sup> The concentration of tetrachloroethylene in the waters from which these species (excluding humans) were taken averaged 0.5 ppb.

# D. ENVIRONMENTAL PATHWAYS AND FATE

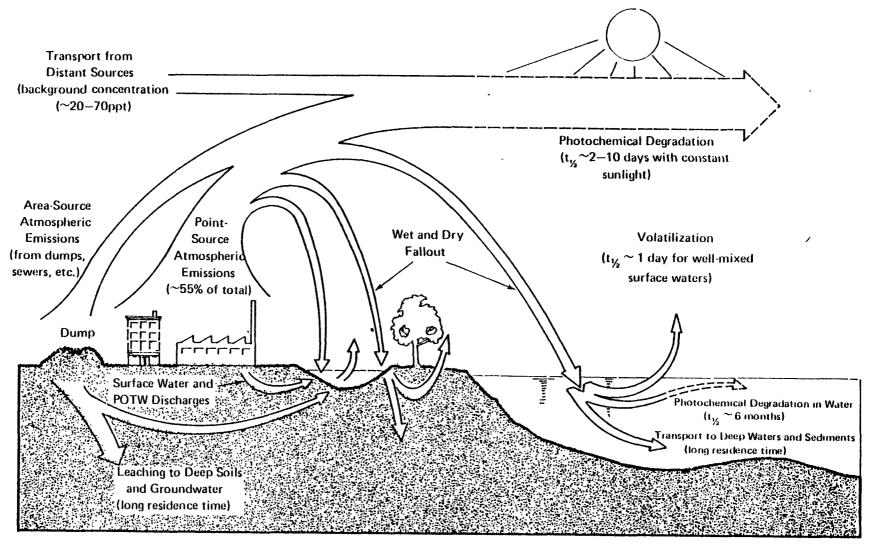
### 1. Overview

Figure 12 provides a schematic overview of the potential environmental pathways (transport and degradation) of tetrachloroethylene. The major sources may be grouped as follows:

- Point-source atmospheric emissions
   (e.g., manufacturing sites, drycleaning and solvent degreasing establishments, solvent reclaimers).
- Area-source atmospheric emissions
   (e.g., chemical dump sites, sewer system manholes, waste
   water treatment impoundments [lagoons, aeration basins,
   etc.]).
- Area-source discharges to land (sites used for disposal of waste solvent and solvent sludges from reclaiming operations).
- Point-source discharges to sewers and surface waters
   (waste solvent or condensate from carbon control
   systems discharged from user facilities, e.g., dry cleaners and metal degreasing establishments).

The direct releases of PCE waste streams to air or surface waters appear not to contain any other chemicals that materially affect transport and fate. The one exception is for the waste sludges from manufacturer, user, and solvent reclaimer facilities. These wastes will differ significantly in their tetrachloroethylene content, in the nature of the other wastes present, and in the actual manner of disposal. All of these factors may alter the rate of escape (via volatilization or leaching) from the sludge into other environmental compartments (air, soil, ground water), and they may alter the relative amounts that are transported to other compartments, but there will be no influence on the major degradation pathways.

When finally released to the environment, tetrachloroethylene follows a few important transport and degradation pathways (see Figure 12). Because the atmospheric lifetime is on the order of a few days, long-distance aerial transport (hundreds to thousands of kilometers) is possible; photochemical degradation during sunlight periods is the only significant degradation pathway. Minor amounts may be removed from the atmosphere by wet and dry fallout. Tetrachloroethylene in well-mixed surface waters will volatilize fairly rapidly (half-life ~1 day) into the atmosphere; photochemical degradation provides a minor loss pathway. The chemical can easily be transported to deep soils and ground waters, and to deep surface waters and sediments, and in these compartments the chemical will have a relatively long residence time, perhaps on the order



Note: Surface water discharges to large water body not shown for clarity, but should be considered an important pathway.

Source: Arthur D. Little, Inc.

of several years or decades unless the turnover or mixing time in the compartments is shorter. While photochemical degradation plays no part in these deep compartments, biochemical and chemical degradation may cause gradual reduction of PCE levels.

The soil-to-groundwater pathway mentioned above is a key link in a potentially significant pathway leading to drinking water contamination. The complete pathway is:

Several factors combine to make this pathway one of concern: (1) over 100,000 MT /yr of PCE are disposed on land in the U.S. (Chapter III) (2) numerous land disposal sites are presumably involved; (3) the mobility of PCE in soils is relatively high; (4) PCE is not readily degraded while in the soil/groundwater compartment; and (5) conventional treatment at water supply treatment plants will generally be ineffective in removing PCE from the water supply.

The following subsections provide a more detailed discussion of the transport and fate in each major environmental compartment.

### 2. Behavior in Air

Once PCE is in the atmosphere, aerial transport plays a major role in the chemicals distribution throughout the environment, at least on a regional basis. The compound is, however, subject to relatively rapid chemical or photochemical degradation so that it does not continually accumulate in the atmosphere and does not, itself, reach the upper stratosphere\* (ozone layer) in sufficient concentrations to affect the ozone concentration (Lapp et al., 1977; Ross et al., 1977).

Tropospheric attack on tetrachloroethylene may be by oxygen atoms, hydroxyl free radicals, or ozone molecules; principal reaction products from tropospheric degradation (Table 5) would include trichloroacetic acid, phosgene, chlorine, hydrogen chloride, and other chemical species. Rates of reaction, or associated half-lives, for a number of these reactions (under laboratory conditions) were shown in Table 5. These data indicate that a relatively short tropospheric half-life, perhaps 1-10 days, is possible. Other estimates, based both on laboratory work and on an atmospheric budget model, indicate longer tropospheric half-lives (see Table 12).

<sup>\*</sup>This may not hold true for some of the degradation products.

TABLE 12. TROPOSPHERIC HALF-LIFE OF TETRACHLOROETHYLENE

Half Life	Method	Reference
0.9 days 1	Experiment with simulated atmosphere containing initially 3.9 mg/m <sup>3</sup>	Dilling <u>et al.</u> (1976)
1.5 days <sup>1</sup>	Experiment with simulated atmosphere containing initially 13 mg/m <sup>3</sup>	Dilling <u>et al.</u> (1976)
l day	Estimate	Lapp <u>et al.</u> (1977)
4 days	Atmospheric budget	Lapp <u>et al.</u> (1977)
10 days	OH concentration and rate constant	Lapp <u>et al.</u> (1977)
12 weeks	Laboratory rate	Pearson and McConnell (19
21 weeks	Atmospheric budget model	Lapp et al. (1977)

 $<sup>^{1}</sup>$ Under conditions of bright sunlight.

Various studies have been conducted on the atmospheric reactions of tetrachloroethylene. One study showed that oxidation of the chemical may be initiated by a chlorine atom with a long-chain free radical process resulting; the major products of reaction at high oxygen pressure were found to be trichloroacetyl chloride (75%) and phosgene (25%). The quantum yield for oxidation was 300; oxygen was found to have an inhibiting effect on the photochlorination reaction (Lapp et al., 1977).

The photooxidation may also be initiated directly by sunlight, in which case a  $C_2Cl_3$  radical is formed along with a chlorine radical:

$$C1_2C = CC1_2 \frac{light}{} C1_2C = CC1 + C1$$

The latter may then initiate the chain-reaction process mentioned above. A study of this light-initiated reaction found a linear relation-ship between the rates of trichloroacetyl chloride formation, phosgene formation, and absorbed light. Yields were found to be independent of the tetrachloroethylene pressure (Lapp et al., 1977).

Both hydrocarbons and nitrogen oxides (at least NO<sub>2</sub>) have an inhibiting effect on the photooxidation of tetrachloroethylene. (See Table 5 for some data.) In one study—not necessarily contradictory—tetrachloroethylene decomposition rates increased as the concentration of tetrachloroethylene and NO were (simultaneously) increased; a tenfold increase in the concentration of both species resulted in a 3.0-fold increase in the decomposition rate (Dilling et al., 1976).

A significant fraction of tetrachloroethylene in the atmosphere may be associated with water droplets and dust particles, especially organic particles. (Table 4 has data on distribution coefficients.) From the atmosphere, tetrachloroethylene could enter the hydrosphere by direct transfer (dry impact), washout by rain, or dry fallout of particles with adsorbed tetrachloroethylene.

## 3. Behavior in Water

Tetrachloroethylene undergoes hydrolysis very slowly in the presence of water. The reaction products from hydrolysis

$$C1_2C = CC1_2 + H_2O \frac{150^{\circ}C}{C1_3COOH} + HC1$$

are trichloroacetic acid and hydrochloric acid.

The half-life for chemical degradation to be expected in natural water bodies has been reported from two different studies. In one (see data in Table 13), a half-life of 8.8 months was associated with a test system containing aerated water at  $25^{\circ}$ C with no light. With natural sunlight and ambient temperatures (which ranged from  $20^{\circ}$ C to  $+40^{\circ}$ C),

TABLE 13. DECOMPOSITION RATES OF TETRACHLOROETHYLENE IN AERATED WATER IN THE DARK AND IN NATURAL SUNLIGHT 1

	Concentration (mg/l)						eaction
Initial		Six 1	ix Months Twelve Months <sup>2</sup>			W-16 T#6-	
Dark	Light	Dark	Light	Dark	Light	$k^3$ , mo <sup>-1</sup>	Half Life, Months
1.00	1.00	0.63	0.52	0.35	0.24	0.079 <u>+</u> .002	8.8
				0.41	0.25		

<sup>&</sup>lt;sup>1</sup>Dark reaction is at 25°C; natural sunlight reaction carried out at ambient temperatures (-20°C + 40°C).

<sup>2</sup>Duplicate test results.

<sup>3</sup>Decomposition constant calculated on the assumption of a first order

reaction.

the chemical degradation half-life was about 6 months (Dilling  $\underline{et}$   $\underline{al.}$ , 1975). The second study resulted in an estimate of 72 months for the chemical degradation half-life in water (Pearson and McConnell, 1975). The difference in the two estimates may be due to the fact that in the latter case the researchers corrected for the loss of tetrachloroethylene into the air space over the liquid samples (Lapp et al., 1977).

The main process for the removal of tetrachloroethylene from shallow surface waters is volatilization (Dilling et al., 1975). Laboratory experiments have measured the rates of evaporation from a stirred beaker (250 ml beaker, 1 mg/l of chemical in 200 ml water, solution depth 6.5 cm, still air, 25°C, stirred at 200 rpm) yielding half-lives for evaporation of  $26 \pm 3$  minutes (Dilling et al., 1975) and  $24 \pm 3$  minutes (Neely, 1976). The results have been found to agree well with theoretical predictions derived from interphase transfer processes (Chiou et al., 1978; Neely, 1976). The calculated half-life corresponding to the experimental situation described above is 26.5 minutes (Neely, 1976).

The theoretical model referred to above allows a rough estimate of the half-life for evaporation  $(t_{1/2})$  into still air from any well-agitated surface water of depth (d) by the following equations:

at 25°C  

$$t_{1/2}$$
 (min.) = 4.08 d (d in cm)  
at 1.5°C  
 $t_{1/2}$  (min.) = 4.15 d (d in cm)

The good agreement between the experimental and theoretical half-lives (at 25°C) is considered somewhat fortuitous. The second equation (for use at 1.5°C) underestimated the measured half-life under the laboratory conditions described: 27.0 minutes predicted, 37.5 minutes measured (Neely, 1976).

The evaporation rates for tetrachloroethylene were also measured under conditions more nearly like those found in the environment. Addition of various contaminants (clay, limestone, sand, salt, peat moss, and kerosene) to the water had relatively little effect on the evaporation rate. However, an increase in the wind speed across the top of the beaker from  $0 \pm 0.2$  mph to  $2.2 \pm 0.1$  mph caused a significant increase in the evaporation rate; after  $\overline{20}$  minutes, the solute evaporation was about 17% greater with the higher wind (Dilling et al., 1975).

A somewhat different study -- involving laboratory aquaria -- also showed the significance of evaporation in the loss of tetrachloroethylene and other chlorinated hydrocarbons from aquatic systems (Jensen and Rosenberg, 1975). Natural seawater was used in this study, which was

carried out to investigate the degradability of the chemicals. In experiments with both open and closed systems, the researchers found that evaporative losses (from the aquarium) were greater than losses by degradation. No significant differences in degradation were noted between a closed system kept lighted and one kept in darkness. Losses of tetrachloroethylene from the "open" system (a partially covered aquarium, 40-1 capacity, filled with 20-1 of seawater, held at 11°C to 12°C) amounted to just over 50% after eight days.

In addition to the predictive equations discussed above, one other approach to predicting the rate of volatilization from surface waters has been described by Smith et al. (1980). Using this approach we estimate approximate half-lives for volatilization from a "typical" river, lake, and pond as 1.3, 5.0, and 6.4 days, respectively. By comparison, when a well mixed depth (d) of 5 m is inserted in the Neely equation above, the half-life  $(\mathbf{t_{1/2}}) = 4.08$  (500) min = 1.4 days. The predictions for rivers could probably be taken as an upper limit for POTWs with aeration basins or other well mixed impoundments. If, for example, one assumed a volatilization half-life of 0.5 days for such POTWs and a residence time in the aeration basin of 1-2 days, a volatilization loss of 75% to 94% would be expected. This is in line with a 81-96% volatilization loss that may be inferred from the measurements of tetrachloroethylene in the influent, aqueous effluent and sludge from one POTW (Feiler, 1979).

# 4. Behavior in Soils and Sediments

The movement of tetrachloroethylene through soils or sediments has not been studied, although movement would clearly be possible as a result of leaching (transport in solution) and/or volatilization (transport in the vapor phase in unsaturated soils). It may be presumed that, when water is present, a partitioning exists between the two phases, which may or may not be at equilibrium. Chemical and biological degradation play a very minor role, if any, and the chemical would be expected to persist in deep soils and groundwaters. There are data on the concentration in sediments from one area, Liverpool Bay (see Figure 6), but there there is no direct evidence of any transformations that may be taking place. The Liverpool Bay data showed no direct correlation between concentrations in sediment and that of the overlying water at the time of sampling (Pearson and McConnell, 1975).

The persistence of tetrachloroethylene in soils is not well documented. It is possible, however, that certain reactions, presumably biochemical, could occur in cultivated soils that could assist in the loss of PCE from the soil compartment. Such reactions have been seen for chemically similar compounds, including ethylene dibromide, 1,2-dibromo-3-chloropropane, and 1,3-dichloropropane. None of these compounds was detected in food crops grown in soil pretreated with the chemicals; no noticeable tendency for bioaccumulation was observed; and the chemicals were found to disappear fairly rapidly from the soil. An increase in the amounts of inorganic bromide and chloride ion was, however, found in the plants (National Academy of Sciences, 1975).

Tetrachloroethylene has the potential to move from land disposal sites, through the soil, to underground aquifers. Two case histories, involving the contamination of water-supply wells for two towns and an industrial park, have been reported (Jarema, 1977). In one case, the water drawn from a 250-ft deep well was thought to have been contaminated by inadvertent spillages (during loading and unloading operations) at an adjacent industrial site; concentrations of tetrachloroethylene up to 50  $\mu g/1$  were found in the raw water from the contaminated well. In the second case, discharge of waste solvents into a dry well resulted in the contamination of one town well located approximately 200 yards away; the concentration of tetrachloroethylene in the (raw) well water was 4  $\mu g/1$ . Wells from a nearby industrial park were found to have a PCE concentration of 0-600  $\mu g/1$  (Jarema, 1977).

For tetrachloroethylene in topsoils or in landfills that have not been sealed, volatilization may be a significant loss mechanism. Atmospheric concentrations near one dump site in Edison, NJ, showed significantly elevated levels of the chemical; the highest concentration, from a sample collected on the dump site, was nearly  $400,000 \text{ ng/m}^3$  ( $\sim 58 \text{ ppb}$ ) (Pellizzari, 1978). This value was three to four orders of magnitude higher than atmospheric concentrations at more distant or remote sites.

There appear to be little or no data on the composition and disposal practices of solvent sludges that are disposed of on land. The solvent content can apparently vary from just a few percent to nearly 100 percent, depending in large part on the extent and efficiency of solvent recovery operations at the user sites. The initial solvent sludge will obviously contain the oils, greases, dirt, etc., that the solvent was used to remove. It appears likely, however, that such wastes are comingled with other wastes (e.g., lubricating oils in the case of automotive repair shops) before final disposal, so that the final wastes have a variety of characteristics. The extent to which such wastes have been disposed of in corrosion-resistant drums and/or in secure landfills is unknown, but is thought to be very small. Current RCRA regulations prohibit durmmed disposal of PCE except for small generators (<100 kg/mo).

Wastes from drycleaning establishments are also sludges containing a large amount of PCE. However they are generally collected in disposable filter cartridges which are disposed of along with other municipal wastes.

The fate of the PCE depends upon the ultimate disposal of the nunicipal wastes. If they are buried deeply beneath other wastes or covered with soil, the potential exists for groundwater contamination through leachate migration. PCE contained in wastes left on the surface would tend to be volatilized.

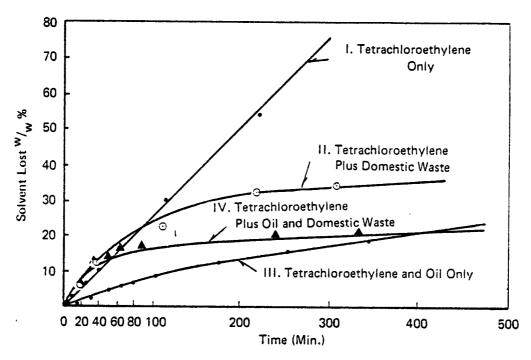
Jones and McGugan (1977/78) have documented that a significant amount of the tetrachloroethlyene in land-disposed solvent sludges can escape to the atmosphere. In one set of experiments conducted by these authors, the rate of evaporation of the chemical from a pulverized domestic waste was compared with the rate of evaporation from a liquid pool (of the chemical) under the same environmental conditions. In a second set of experiments with the pool and pulverized waste, the rates of evaporation of the chemical were measured after a tetrachloroethylene-oil mixture was added. The data from these tests, shown in Figure 13, indicate that as much as 20-30% of the tetrachloroethylene that is land-disposed may be volatilized within 4-5 hours after disposal. Over a period of several days, the amount lost by this mechanism could clearly be much higher.

Further tests were conducted by the same research group on the potential for the leaching of tetrachloroethylene through domestic waste to groundwaters (Jones et al., 1977/78). When the solvent, in the form of filtration residues from drycleaning processes, was added to domestic wastes\* at a loading of about 200 mg/l, leachate did not contain concentrations of the chemical above the detection limit of 2 mg/l. This held true even for one experiment in which the possibility for volatilization was eliminated by a cap placed over the waste container. After the leach tests with this capped container, about 15% of the tetrachloroethylene initially added was recovered from the waste by extraction with 68 1 of petroleum spirit. In contrast, petroleum extract of a column that had been left open to the air did not contain detectable levels of tetrachloroethylene. It appears from these tests that the combination of volatilization and adsorption of tetrachloroethylene (in waste sludges) applied to domestic refuse can significantly reduce the potential for groundwater contamination.

### 5. Biodegradation

One biodegradability test on PCE has been carried out with a static culture flask screening procedure (Tabak  $\underline{\text{et}}$   $\underline{\text{al.}}$ , 1980). This test utilizes BOD dilution water containing 5 mg/l of yeast extract as the synthetic medium, a 7-day static incubation at 25°C followed by 3 weekly subcultures (totaling 28 days of incubation), and incorporating settled domestic wastewater as a microbial inoculum. Tests were carried out in glass stoppered reagent bottles (to minimize volatilization losses) and in darkness (to minimize photodegradation losses). Volatility controls,

<sup>\*</sup>Fifty kg of fresh, untreated domestic wastes placed in steel columns about 56 cm in diameter and 90 cm deep.



Source: Jones and McGugan, 1977/78.

FIGURE 13 VOLATILIZATION OF TETRACHLOROETHYLENE
AND TETRACHLOROETHYLENE—OIL MIXTURES
FROM LIQUID POOLS AND DOMESTIC REFUSE

Note: An open square tray 1m x 1m x 3cm (deep) was used to measure volatilization from liquid pools. An open square tray 1m x 1m x 0.5m (deep) was used for the experiments with domestic waste. Weight loss was the parameter monitored in all experiments. The domestic waste, when placed in the tray, had a density of ~ 350 kg/m³. The weights of material used for each test were

Test	Weight (kg)			
(See Figure)	Tetra.	Waste	Oil	
ı	20.2	_		
11	29.0	155	_	
111	16.3	_	7.75	
IV	16.3	167	7.2	

The conditions under which the two sets of tests were run were as follows:

	i and ii	iii and iv
Mean wind speed(m/sec)	~ 10	~ 2.5
Ambient Air Temperature(C)	~ 12	~ 22
Solvent Pool Temperature(OC)	~ 15	~ 19-35
Waste Surface Temperature (OC)	~ 12-20	~ 18

utilizing a non-biological system (medium-test compound without inoculum), were held for a period of 10 days and then analyzed to determine volatilization losses. The concentration of PCE used in both the inoculated and volatility-control tests was 5 mg/l. The volatility-control showed a 23% loss of PCE (at 25°C, 10-day period) from the flask, due (presumably) to volatilization. The original culture, and first, second, and third subcultures showed PCE losses of 45%, 54%, 69%, and 87%, respectively. These percentages are uncorrected for volatilization losses. Tabak et al. (1980) conclude from these tests that PCE under went "significant degradation with gradual adaptation."

Two analytical studies have considered the fate of PCE during wastewater treatment, a process which may involve biodegradation as a mechanism for pollutant removal.

Burns and Roe, Inc. (unpublished, 1979) sampled influents, final effluents and at intermediate treatment stages of nine publicly owned treatment works (POTW's) throughout the U.S. (see Table 8). Percent removals of PCE at these 9 POTW's were between 40 and 100%, and averaged 69%. In almost every case, PCE concentrations in primary sludges were much higher (by factors of 2 to 182) than influent levels, while levels in digested sludge were either "not detected" or much lower than primary sludges. Because primary sludge does not involve biological activity while digested sludge does, these data indicate that PCE may be biodegraded by aquatic micro-organisms. Acclimation was not studied in these analyses. An alternative explanation involves volatilization during secondary treatment.

A study of five treatment works in the United Kingdom (Brown and Phil, 1978) also gives evidence for biodegradation of PCE. The researchers did not sample biologically produced sludges. However, the high percent removals and the fact that PCE levels in effluents and primary sludges were of the same order of magnitude are indicative of an active removal mechanism for PCE following the physical settling process which produces primary sludge. Brown and Phil state that both biodegradation and volatilization were important processes for PCE removal and felt, without hard data however, that the latter process might remove more PCE from wastewater during treatment than the former.

Although not shown in Table 8, Burns and Roe, Inc. data included pre- and post-chlorination effluent concentrations. In no case was the chlorinated effluent higher in PCE, which indicates that as the "per" chlorinated form of ethylene, it is least likely to be produced by treatment.

## E. CONCENTRATION ESTIMATES BASED ON ANALYTIC MODELS

### 1. Overview

Analytic models are used to increase understanding of complex systems in which many interacting physical processes and chemical reactions determine the fate of given substances. The major path-

ways describing environmental fate of PCE are shown schematically in Figure 14. The pollutant releases from the six sources are weighted in order to indicate which compartments receive the largest inputs. The pathways through which PCE moves are shown in broken lines to indicate that, despite our knowledge of both the input amounts and the dominant fate processes, the proportion of the PCE input that follows each pathway is unknown. Three major pathways are shown in the figure:

- (1) Landfills ——groundwater ——surface water ——air
- (2) Landfills —— air
- (3) POTW ——surface water ——air

Three models have been selected to consider these pathways and the source emissions/discharges.

The first is a general environmental partioning model, which demonstrates the tendency of a chemical to accumulate, disperse or degrade in all compartments and which compartments will be most affected. The second model performs an atmospheric dispersion analysis of the emissions from two types of drycleaning operations; the large commercial and the point source industrial facility. These sources were selected because they contribute the largest air emissions of PCE. While nearly comparable amounts of PCE are conveyed to landfills, about 30% volatilized in simulation experiments. In addition, the levels of PCE in air monitored near a chemical dump were more than three orders of magnitude less than levels measured near commerical Thus due to the lack of information on exact volatilization rates of PCE from waste disposal sites, it was not possible to model releases from this source. The three pathways in Figure 14 that lead to the surface water compartment are analyzed by use of the U.S. EPA's EXAMS model.

## 2. Equilibrium Partitioning

As an initial step in hazard or risk assessments for toxic chemicals, in the planning of laboratory and field tests, and in the interpretation of data on ambient concentrations, it is important to understand the likely transport and fate of the chemical. Which environmental compartment (air, water, soils, sediments, biota) will be most affected? Which degradation pathways (photolysis, hydrolysis, biodegradation, etc.) will be most important? Rough guesses can often be made by simple inspection of the chemical's properties and reaction rate data (if such are available) or by the use of mathematical models that seek to yield defensible and quantitative estimates for dynamic situations. Unfortunately, realistic chemical fate models usually require extensive input information on both the chemical and environmental compartments of concern (such are not always available), and a

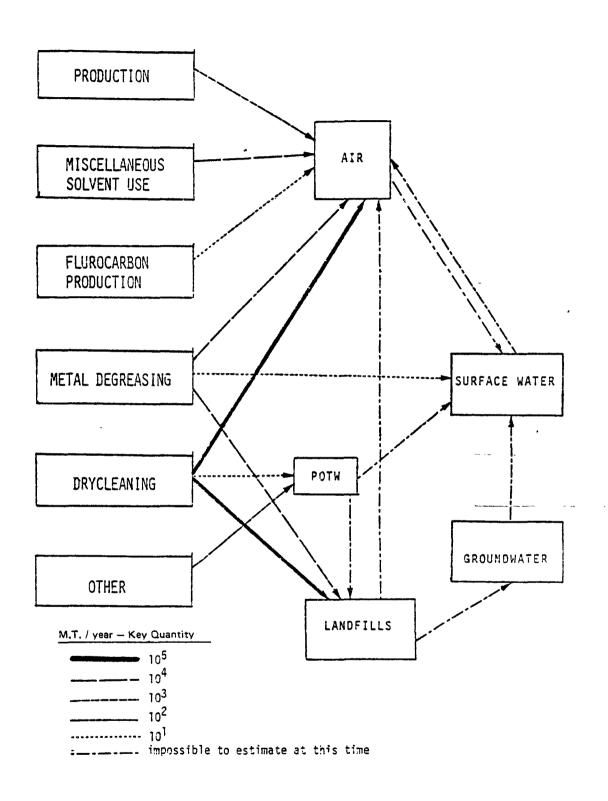


FIGURE 14 SUMMARY OF ENVIRONMENTAL FATE OF TETRACHLOROETHYLENE

computer for solving the lengthy calculations. A simple, initial estimate of environmental partitioning is thus desired; one involving an approach with minimal data requirements and capable of solution with a hand calculator. Such an approach has recently been proposed by Mackay (1979) in a treatment based upon the fact that in a system at equilibrium, the fugacity of the pollutant must be the same in all phases.

A three-tiered approach has been proposed by Mackay (1979). In Level 1 (the approach used here) all environmental compartments (phases) are assumed to be directly or indirectly connected, and at equilibrium. The compartments considered are air, surface water, suspended sediments, bottom sediments, soil, and aquatic biota. The Level I calculations require that these compartments be roughly described (volumes, temperature, sediment and biota "concentrations," etc.) and the model output will clearly depend on the nature of the "environment" selected. The compartment-specific parameters chosen here (somewhat arbitrarily) are listed in Table 14. A schematic diagram of the selected "environment" is shown in Figure 15.

The Level I calculations do not consider degradation, or transport into or out of the selected environment. A relatively small number of chemical-specific parameters (also listed in Table 14) are required for the equilibrium partitioning. If one desires an absolute estimate of the equilibrium concentrations in each phase, it is necessary to estimate the total amount of the chemical that is likely to be in the selected environment.\* We have taken this amount to be 11 moles/km  $^2$  (1.82 kg/km²), or just 11 moles in our compartment whose surface is 1 km². This amount is equivalent to the pollutant releases in the U.S. over a 12-day period, divided by the area of the 48 contiguous states. Implicit in the selection of this quantity is an assumed atmospheric half-life (due to photochemical degradation) of about 4 days in constant sunlight or 8 days when diurnal light cycles are considered.

Details of the calculational methods are provided by Mackay (1979) and are not repeated here. The calculations were carried out for three different temperatures (0°C, 10°C and 20°C) in order to assess the importance of this parameter of equilibrium partitioning. The results of the calculations are given in Table 15. Not indicated by the numbers in this table is the prediction that 99.8% of the chemical resides in the atmosphere (at equilibrium) in the selected environment.

It is interesting to compare the numbers in Table 15 with measured ambient concentrations (Table 11). The atmospheric concentration is estimated with some degree of accuracy but it appears, not surprisingly, that measured concentrations in other phases (especially surface waters and biota) are higher than would be expected under equilibrium conditions. Air/water partitioning varied from 0.0072 (mg/kg:ug/kg) at 20°C to 0.0133 at 0°C.

<sup>\*</sup>Note that predicted ratios of concentrations between two phases will not be affected by the number selected.

TABLE 14. VALUES OF THE PARAMETERS USED FOR LEVEL I CALCULATION OF EQUILIBRIUM CONCENTRATIONS OF TETRACHLOROETHYLENE USING MACKAY'S FUGACITY METHOD

Chemical-Specific Parameters

onemater opecation ranameters		Parameters Values At:				
			<u>20°C</u>	<u> 10°C</u>	0°C	
•	Sol	ubility (mg/L):	140	104	82.7	
•	Vap	or pressure (mm Hg)	14.4	8.04	4.32	
•	Ads	orption coefficient $(K_p)$ for:				
	a)	suspended sediments	29	34	38	
	b)	sediments	29	34	38	g/Mg g/m <sup>3</sup>
	c)	soils	5.8	6.8	7.7	√ g/m <sup>3</sup>

- Octanol/water partition coefficient (all temperatures): 724 (Used for estimating a bioconcentration factor for aquatic biota.)
- Total amount of chemical in compartment: 11 moles/km<sup>2</sup> (1.82 kg/km<sup>2</sup>) (Equivalent to total U.S. environmental losses over 12 day period, divided by area of 48 contiguous states.)

# Compartment-Specific Parameters 1

- Temperature: 20°C, 10°C and 0°C
- Concentration(S) of suspended sediments: 10g/m<sup>3</sup>
- Concentration(S) of soils and sediments:  $2 \times 10^6 \text{ g/m}^3$
- Volume fraction (B) of aquatic biota:  $50 \times 10^{-6} \text{ m}^3/\text{m}^3$
- Fraction (y) of aquatic biota equivalent to octanol: 0.2
- Accessible volume for each subcompartment:
  - 1. Air:  $1 \text{ km} \times 1 \text{ km} \times 3 \text{ km} \text{ (high)} = 3 \times 10^9 \text{ m}^3$
  - 2. Surface water:  $1 \text{ km} \times 0.05 \text{ km} \times 3 \text{ m} \text{ (deep)} = 1.5 \times 10^5 \text{ m}^3$
  - 4. Sediments:  $1 \text{ km} \times 0.05 \text{ km} \times 10 \text{ cm} \text{ (deep)} = 5 \times 10^3 \text{ m}^3$
  - 6. Soils:  $1 \text{ km} \times 0.95 \text{ km} \times 14 \text{ cm} \text{ (deep)} = 1.3 \times 10^5 \text{ m}^3$

(Note: in the preliminary calculations, the suspended sediments and aquatic biota are assumed to have the same "accessible volume" as the surface water subcompartment.)

<sup>1.</sup> Parameters for specific compartments may be selected to reflect the nature and size of any area of concern. The values used here are considered to be reasonable rather than typical.

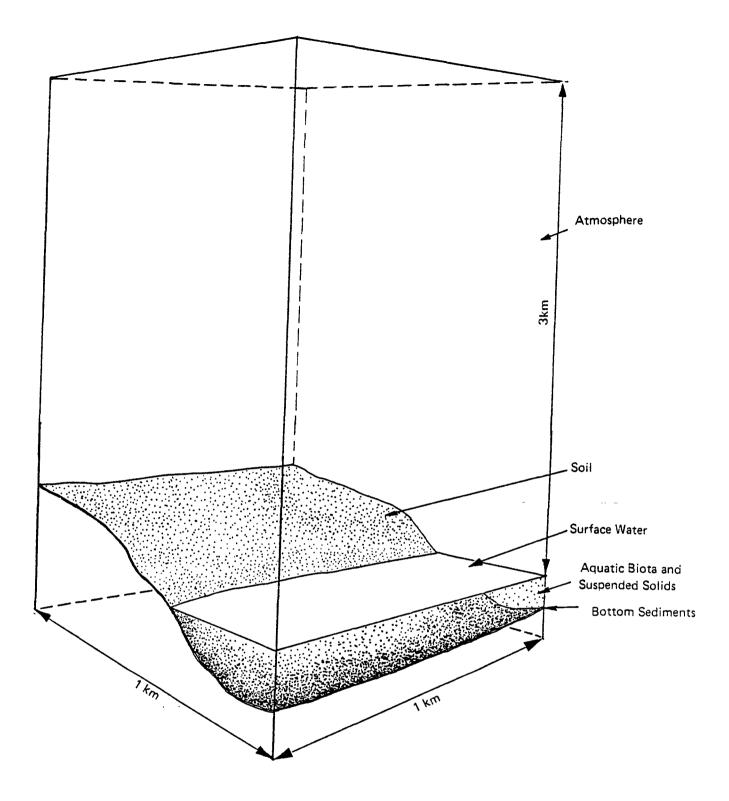


FIGURE 15 SCHEMATIC OF ENVIRONMENTAL COMPARTMENT SELECTED FOR ESTIMATION OF EQUILIBRIUM PARTITIONING OF TETRACHLOROETHYLENE

**Note:** Diagram is not to scale. Dimensions and accessible volumes of each subcompartment given in Table 15.

TABLE 15. LEVEL I CALCULATIONS OF EQUILIBRIUM CONCENTRATIONS OF TETRACHLOROETHLYENE USING MACKAY'S FUGACITY METHOD

	Concentration (ng/kg) <sup>1</sup> at:				
Compartment	20°C	10°C	0°C		
Air	90	90	90		
Surface waters	0.65	0.84	1.2		
Suspended solids	19.	28.	46.		
Sediments	37.	57.	92.		
Aquatic biota	94.	120.	170.		
Soils	7.5	11.	19.		

<sup>&</sup>lt;sup>1</sup>Two significant figures are reported for the sole purpose of allowing a better assessment of the effect of temperature on the calculations. The estimates should not, however be considered significant to this extent in an absolute sense. One significant figure or only an order of magnitude will be reasonable for most chemicals.

It is more likely that soils (in remote sites) would be in equilibrium with the air, and here the model predicts a soil concentration on the order of 10 mg/kg. Unfortunately, there are no data from soil analyses with which to test this prediction. Similarly, it is likely that surface waters and suspended sediments in the real world would be near equilibrium, and here the model predicts the ratio of concentrations (sediment/water) to be about 30. Again there are no data with which to check the prediction.

The numbers in Table 15 indicate that, for a system at equilibrium, seasonal cycles involving temperature changes of about 20°C will change the concentrations in all compartments, except air, by a factor of two. The highest concentrations are associated with the colder temperatures.

## 3. Atmospheric Dispersion of Releases from Drycleaning Operations

As previously presented, the overwhelming source of atmospheric emissions of PCE is the textile drycleaning industry. Within this industry, however, there are three identifiable categories of drycleaning operations, and the quantity of atmospheric emissions, and the specific nature of the emission and dispersion characteristics of each of these categories vary significantly. Commonly used analytic and algorithmic methods for estimating ambient levels of an air contaminant were adapted and applied to model the fate of pollutant releases from drycleaning plants in two of the industrial categories. Estimates have been made of both short-term (i.e., a few hours) concentrations in the very near vicinity of a plant and long-term (i.e., annual average) concentrations over a larger geographical area. In order to carry out these calculations, several assumptions and estimations have been necessary and these are discussed in the following paragraphs.

## a. Development of Emission Source Parameters

In order to fulfill the input data requirements of the computer program used to calculate long-term concentrations with respect to emission source parameters, several information resources were reviewed. The estimation of PCE emission rates was considered to be the most important single factor in the use of the model. For the other parameters (exist gas temperature and volume in particular) reasonable or conservative assumptions were made in conjunction with available industry data or U.S. EPA reports from actual operating conditions at specific drycleaning operations. To the extent possible, PCE emission rates were calculated and compared for more than one set of throughput estimates.

The method used to estimate PCE emission rates from the three generic types of drycleaning establishments was based on national statistics concerning PCE consumption as was presented previously. An average emission rate of PCE for each type of establishment was computed by dividing the total number of pounds of PCE released to the atmosphere per year for each type of plant in the U.S. by the

number of plants of that type reported to be in operation. The values for this calculation were provided by an industry organization (W. Fischer, IFI, 1980, private communication). Additional information from this source made it possible to make assumptions about the normal operating schedule of typical drycleaning plants of the various types. For the large commercial type of facility, 18,750 plants had a total atmospheric emission of  $106.4 \times 10^6$  pounds/year. Large industrial plants (270 plants) had a total emission of  $28.67 \times 10^6$  pounds/year. Performing the calculation using the data and the assumed operating schedule data given in Table 16 yielded the emission rates given in the table (in units appropriate to the air quality models). Note that the emission rate of PCE for the industrial area source and industrial point source are the same; these two categories were defined to evaluate the effect of differences in the other emission characteristics. Note also that different assumptions about the operating schedule result in calculated emission rates ranging between 1.5 g/second to 5.4 g/second. The value of 3.6 g/second in the model for the industrial source was a reasonable comprise.

A calculated value of the PCE emission rate for large commercial drycleaning operations of 3.44 g/second was based on the industry survey data given in Table 16. This was compared with the computed results for PCE emission rates based on an EPA estimate of PCE loss of 4.1 kg PCE/100 kg of laundry, and a daily throughput and operating schedule of 455 kg per facility per 12-hour day (Kleeberg and Wright, 1978; McCoy 1976; U.S. EPA, 1979a). This estimated value was 0.432 g/sec. or about 20% greater. The higher value was chosen as model input because it is based on the results of a well-controlled, EPA-sponsored, comprehensive source test and materials balance conducted at a large commercial drycleaning establishment (McCoy, U.S. EPA 1979b). These specific test results have been used and cited by EPA in policy-making support documents (EPA, 1970; Kleeberg and Wright, 1978; McCoy, 1976). Furthermore, the lower emission rate calculated from the industry statistics includes a wide range of individual source characteristics, such as operator competence, machine capacity, level of maintenance control/vapor recovery systems, etc. This is not as likely to be true with respect to the large industrial sources, since there are fewer sources and therefore less variation among the sources is probable. Economic incentives for efficient operation of an industrial source may be larger than for a commercial operation as well.

## b. Assessment Methodology and Values for Short-Term Concentration Estimates

Algorithmic treatment of short-term atmospheric dispersion is usually structured by determining the elevation of the plume above the ground surface and the horizontal and vertical dimensions of the plume of emitted gases downwind of an idealized "point source" of emissions (e.g., a chimney stack, or a roof-top vent). The plume dimensions are determined by a variety of meteorological parameters,

TABLE 16. ATMOSPHERIC EMISSION PARAMETERS FOR THREE CATEGORIES OF DRYCLEANING OPERATIONS USED IN ATMOPSHERIC DISPERSION MODEL

	Source Description				
Parameter	Industrial Area Source	Large Commercial Point Source	Industrial Point Source		
Emission Rate (g/sec) <sup>1</sup>	3.577	0.432	3.577		
Stack Height (m)	10	10	15		
Side Width (m)	100	-	-		
Exit Temperature (°C)	28	28	28		
Exit Gas Velocity $(m/sec)^2$	_	1.2	2.0		
Stack Diameter (m)	· <del>-</del>	0.5	0.5		

for 270 industrial plants, we used a 52 wk/yr 6 days/wk 12 hr./day operating schedule, and a loss rate of  $28.67 \times 10^6 \ \text{lb/vr}$ 

for 18,750 commercial plants, we used a 52 wk./yr., 5 day/wk. 8 hr/day schedule and a loss rate of  $106.4 \times 10^6$  lb/yr

The latter figures were adjusted (see text) to accommodate EPA data.

<sup>1</sup> Emission rates were computed in general on the basis of the nation-wide materials balance, as follows:

<sup>&</sup>lt;sup>2</sup>Exit gas velocities determined from typical values. Industrial source: 825 ft.<sup>3</sup>/min. through a 1.5-ft diameter vent or duct. Large commercial source: 500 ft<sup>3</sup>/min through same size duct.

<sup>&</sup>lt;sup>3</sup>Emission temperature of 85°F.

the emission characteristics of the source, and the relative geometries of the emission source, and the specific locations at which concentrations are to be estimated.

The most widely used technique for estimating the dimensions of the plume of emissions is to assume that the concentration distributions in the horizontal and vertical dimensions are each Gaussian in nature, and then to apply dispersion equations given by Turner (1970). The principal dispersion equation given by Turner is:

$$\begin{split} \texttt{X}(\texttt{x},\texttt{y},\texttt{z};\texttt{H}) &= \frac{\texttt{Q}}{2\pi \texttt{u}\sigma_{\texttt{y}}\sigma_{\texttt{z}}} \quad \exp\left[-\frac{\texttt{y}^2}{\sigma_{\texttt{y}}^2}\right] \left\{ \exp\left[-\frac{1}{2} \frac{(\texttt{z}-\texttt{H})^2}{\sigma_{\texttt{z}}^2}\right] + \\ &\exp\left[-\frac{1}{2} \frac{(\texttt{z}+\texttt{H})^2}{\sigma_{\texttt{z}}^2}\right] \right\} \end{split}$$

where X = ambient air concentration in  $\mu g/m^3$  x,y,z = downwind, crosswind, and elevation coordinators respectively for a given source - receptor geometry

= horizontal plume dimension  $\sigma_{\mathbf{y}}$ 

= vertical plume dimension

= elevation of plume centerline above ground surface (effective stack height)

= wind speed

= emission rate (source strength) of air pollutant in g/sec.

The equation yields estimated short-term (i.e., about 1-hour) concentration levels, due principally to the level of resolution in the meteorological data upon which the semiempirical parts of the dispersion equation were founded. Average concentrations for multiple. consecutive hours can be determined by summation of individual hourly estimates (which vary according to meteorological conditions), and division by the number of estimates.

Several tools such as graphs and interpolation tables have been developed to aid in the determination of individual hourly concentration estimates. For this particular study, graphs provided by Turner (1970) were used to estimate ambient concentration for a specific emission source strength (mass of pollutant emitted per unit time) and ambient wind speed.

Applying this methodology to the "model" drycleaning plants described in Table 16 at representative urban wind speed produced the results shown in Table 17. This table shows some extremely high values, particularly for stable atmospheric conditions: note, however, that these estimates are for extreme, "worst-case" conditions for very brief averaging times. Thus, Table 17 suggests a qualitative

picture of potential worst-case ambient concentrations for very short time periods. More significantly, it indicates the relative "spread" of estimated maximum concentrations and the downwind distance of these for different meteorological conditions. In terms of observed frequency, the atmospheric conditions specified at the top and bottom of Table 17 are much less common than the ones indicated in the middle.

Examination of figures provided by Turner (1970) showed that under all atmospheric stability classes for emission sources such as a typical commercial drycleaning plant, a relative concentration isopleth of  $10^{-3}$  m<sup>-2</sup> extends at least 50m downwind. Applying the commercial emission rate given in Table 16 gives, as a rough estimate, a short-term concentration at this distance of about  $150 \pm 50~\mu\text{g/m}^3$ . Similarly, in the immediate vicinity of an industrial drycleaner emitting PCE at the rate given in the table, short-term concentrations would be in the range of 900 to 1800  $\mu\text{g/m}^3$ .

It is important to note that these concentration estimates are representative of estimated levels for very short time periods. If estimates for slightly longer time periods (such as 8, 12, or 24 hours) were to be extrapolated from these values, PCE's persistence in air and the dynamic fluctuations in wind direction and wind speed would have to be considered. Also, variation in the operation of the emission source would need to be considered, because, for example, an industrial plant is likely to emit no PCE at all during certain periods of the day and/or at night because of batch operation. In this context, it is important to note that the emission rate given for the industrial plant in Table 17 was based on a noncontinuous operation, specifically, 12 operating hours per day and 6 operating days per week. If the industrial plant were assumed to operate continuously (24 hours/day, 7 days/week), the emission rate and the resulting "worst-case" ambient concentration estimates would be reduced by a factor of 6x12 or 0.43.

# c. Methodology and Values for Long-Term Concentration Estimates

Rather than make 87600 hourly calculations of estimated concentrations at each one of a field of locations and determine annual average concentrations for each, a computer program is used incorporating a meteorological joint frequency function. This tabulation represents the normalized frequency of specific wind direction class, wind speed class, and stability class joint occurrences. This is also known as a "stability wind rose."

For this project a slightly modified version of the standard CDM dispersion model program was used (Busse and Zimmerman, 1973). This model has been developed by EPA, and is frequently used for estimating long-term (seasonal or annual) quasi-stable pollutants concentrations at ground-level receptors using average emission rates point and area sources. A stability wind rose appropriate for input to CDM was readily available (due to other ongoing projects), and this tabulation was for a major urban area in the Northeastern United States. The wind rose aggregated over all stability classes is shown in Figure 16.

TABLE 17. DISPERSION MODEL PARAMETERS AND ESTIMATED PCE CONCENTRATIONS IN AIR NEAR INDUSTRIAL AND COMMERCIAL SOURCES

Meteorological Conditions			Maximu Concentrati		
Atmospheric Stability Class	Wind Speed (m/sec.)	Effective Stack Height (m)	Industrial Sources	Large Commercial Source	Downwind Distance of Maximum Concen- trations (km)
Highly Unstable	1.5	20	720	86.4	~0.1
Unstable	2.5	20	475	57.0	0.14
Slightly Unstable	3.0	17	600	72.0	0.16
	3.5	15	648	77.8	0.145
Neutral	3.5	17	411	49.4	0.30
	4.5	15	432	51.8	0.26
	7.0	10	668	80.2	0.21
Slightly Stable	2.5	17	576	69.1	0.43
	3.0	15	624	74.9	0.37
	4.0	10	1125	135.0	0.22
Stable	1.5	15	1128	135.4	0.62
	2.5	10	1656	198.7	0.37



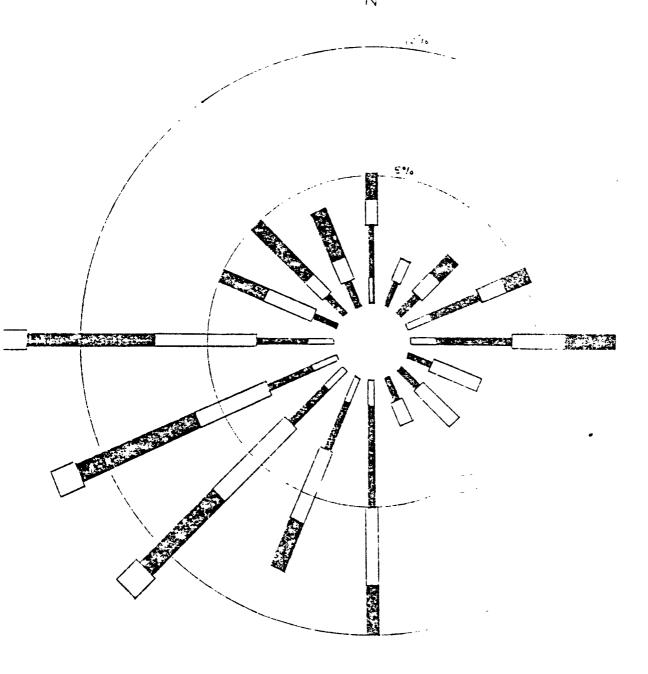




FIGURE 16 STABILITY WIND ROSE FOR NIAGARA FALLS USED IN LONG-TERM PCE CONCENTRATION ESTIMATES FOR COMMERCIAL AND INDUSTRIAL DRYCLEANING OPERATIONS

The emission source data used in this modeling was that given in Table 16. The network of receptor locations was chosen to give adequate spatial coverage and satisfactory resolution of concentration values. As an aid to interpretation of the model results, a computerized graphics system made possible the preparation of contour or isopleth maps shown as Figures 17 and 18. These figures show the concentration pattern determined by the CDM model for the industrial drycleaning plant. Figure 18 is an enlarged view in the immediate vicinity of the plant location.

The CDM program permits the estimation of ambient impacts from emission sources which do not conform to the usual parameterization of point sources. These types of sources are known as area sources and an example of one would be a low one or two story building with roof to vents or a horizontal duct venting to the atmosphere. In addition, area sources typically have relatively cool low gas volume emissions to the atmosphere, so that their emissions have relatively little plume rise due to buoyancy forces (which are caused by the temperature gradient between the atmosphere and the exhaust gases) and momentum forces (which are caused by the mass flux and exit velocity of the exhaust gases). The model run described below analyzed point and area source characterizations of the model drycleaning plants, as described in Table 16.

The results of the initial model runs provide an indication of annual average ambient levels of PCE that could be expected in the vicinity of a drycleaning plant. The ambient impact from the "average" sized plant appeared to have a negligible effect over the long-term. In other words such sources do not appear to have an effect on the average observed background level, as indicated by monitoring programs. Similarly, a large commercial operation was responsible for a maximum concentration of less than  $6.8\mu\text{g/m}^3$  at a downwind distance of 500m. This level too is lower than annual averaged background levels. The maximum long-term concentrations of PCE near an industrial plant were about the same, whether it was treated as a point source or as an area source. The maximum value was about 27  $\mu\text{g/m}^3$ , and was predicted at a distance of 500 m from the source also.

On the initial grid of receptor locations, the maximum concentration estimates for all three model source types, were found for receptors close to the source. Thus it was suspected that still higher concentrations might be determined by the model if receptors were placed closer to the sources than 500 m. Therefore, a second set of model runs as obtained for a receptor grid having a finer spatial resolution around the emission source and including receptor locations as close as 60 m from sources.

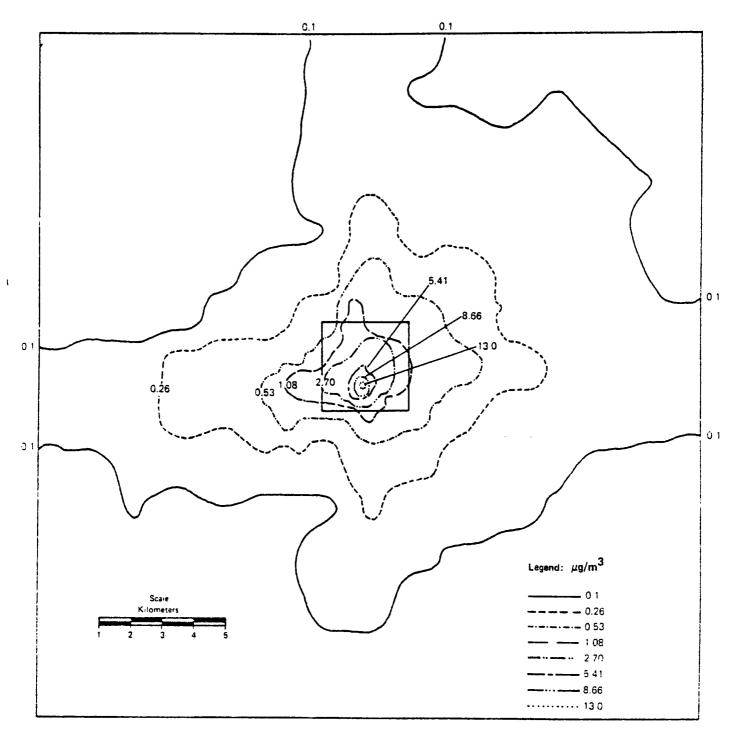


FIGURE 17 SIMULATED PCE CONCENTRATION ISOPLETHS FOR AN INDUSTRIAL POINT SOURCE

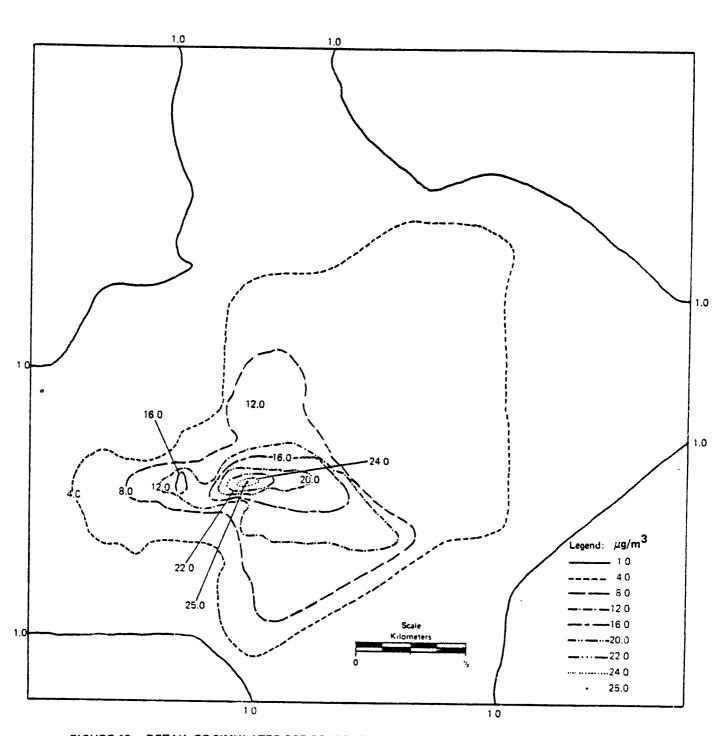


FIGURE 18 DETAIL OF SIMULATED PCE CONCENTRATION ISOPLETHS FOR AN INDUSTRIAL SOURCE

As expected, significantly higher concentrations were estimated for the receptors close to the emission source. The highest concentration in the immediate vicinity of the commercial plant (modeled as a point source) was estimated at about 20  $\rm ug/m^3$  at a distance of 100 m. Maximum average concentrations due to the industrial plant, modeled both as an area source and as a point source, were also estimated to occur at approximately the same distance. For the industrial plant treated as a point source, the maximum concentration was determined to be  $136~\mu \rm g/m^3$ , while the area source model indicated maximum concentrations of over  $920~\mu \rm g/m^3$ . The validity of the area source dispersion algorithm at such close distances is questionable, however, because of computational instabilities in the coding and execution of the algorithm. In reality, the ambient impact of the source, if more properly characterized as an area source, would probably be lower at this distance than as estimated by the point source algorithm.

## 4. EXAMS Concentration Estimates

### a. Introduction

The EXAMS model has been developed by EPA Athens Environmental Research Laboratory in order to help assess the behavior of a pollutant in various characteristic aquatic systems. The output of the model includes:

- simulations of steady-state concentrations and pollutant mass distribution among water, sediment and biota in different compartments (e.g. water column, bed sediment),
- (2) percentage of system loading removed by each chemical and biological kinetic process, and
- (3) concentration die-away time following cessation of discharge.

As input, the model requires the pollutant's physicochemical properties, environmental reaction rate constants, and loading rate to the system. The assumptions of the model include a continuously discharging source at a constant level, a box of water made up of a system-defined number of well-mixed compartments, and first-order rate kinetics in all processes. A more thorough discussion of the model is given in Lassiter, et al. (1978) and Baughman and Burns (1980).

Three pathways are modeled using the EXAMS.

- 1. Metal Degreasing Effluents——Surface Water (——Air)
- 2. Landfill Leachate Groundwater ——Surface Water (——Air)
- 3. Drycleaning and other Discharges——POTW's——Surface Water (——Air)

The model does not give air concentrations resulting from the introduction of a given amount of PCE to the water column, but because the model accounts for volatilization, the air compartment is shown in parentheses as it completes the pathway.

The four scenarios modeled by EXAMS were as follows:

- 1. Metal Degreasing: 10,000 kg/yr direct aquatic discharge from 2,188 plants. Lacking data on effluent PCE concentrations and effluent flow rates, the loading rate was estimated by apportioning the discharge equally between the plants and assuming a 6 hour/day period over which the discharge would occur.
  - Loading rate = 0.004 kg/hr as discharge
  - Type of receiving water bodies: rivers clear and turbid
- Levels measured in contaminated wells range between 0.4 mg/l and 10 mg/l; thus these values are assumed to be indicative of those in some leachate plumes from landfills. Based on a study of leachate plumes in Long Island (Kimmel and Braids, 1980), the plume width varied from 0.6 km (the width of the landfill) to 0.2 km, at which point the plume intersected a stream. To develop a worst case scenario we postulated a highly permeable 3.85 x 10<sup>4</sup> liter/day/m² (10<sup>5</sup> gal/day/ft²) sand aquifers which intersects a water body fairly close to the landfill. The cross section at intersection is 500 m x 2 m and the metric daily discharge is 4.075 x 10<sup>9</sup> liters. A concentration of PCE in the leachate of 1.0 mg/l yields the following load:
  - Loading rate = 160 kg/hour as groundwater interflow
  - Water bodies: river and turbid river, pond, lake
- 3. Landfill Leachate II: a less drastic case of leachate contamination of surface water would involve a less permeable aquifer  $(10^2 \text{ gal/day/ft}^2)$ , a lower concentration of PCE (0.2 mg/l) and an intersection with the water body further from the source, which reduces the cross sectional area of the plume  $(120 \times 1 \text{ m})$ .
  - Loading rate = 0.004 kg/hour, as interflow
  - Water bodies: same as scenario 2, above.
- 4. Drycleaning and Other Discharges to POTW's: while the amount of PCE which is treated by POTW's has been approximated, the exact input to a POTW is unknown. This scenario is

based on a POTW of average size (3 MGD) with effluent PCE concentrations on the high side (10  $\mu g/1$ ) of monitored values, thus a loading rate can be estimated.

- Loading rate = 0.004 kg/hr, as discharge
- Water bodies: river and turbid river
- Results correspond to those of scenario 1

The modeling results were based on use of the measured value for the ratio of rate of volatilization of PCE:rate of volatilization of  $0_2$ . This relationship is given as:

$$K_{\text{vol}} = K_{0_2} \frac{MW_{0_2}}{MW_{PCF}} = 0.44$$

Because the measured value (Smith, et al., 1980) of  $0.52 \pm 0.09$  agreed closely with the theoretical value, we opted to use the measured value for the input parameter.

## b. Results

Two runs were made to analyze scenarios 1 and 4, whose loading rates, quite accidentally, were about equal. The model specification for scenario 2 and 3 called for the loading to occur through ground-water flow to surface waters. However, EXAMS only accepts discharges to surface waters directly and scenarios 2 and 3 were modeled in this manner instead, to at least approximate the impact of the high loading rate on the five ecosystems.

The key results of all modeling efforts are shown in Table 18, which shows applied and actual loading rates, maximum concentrations in the water column, the percent of the load which volatilizes, and system self-purification times. There is a difference between applied (input) and actual (level accepted by EXAMS) for hydrologically closed systems — ponds and lakes. This difference arises only when the applied load is above the capacity of the system to dissipate it. Thus it shows the loading rate at which all inputs are either dispersed, degraded or otherwise transported. The excess load in this case, would "puddle" at the bottom of the water column as PCE's specific gravity is greater than that of water.

These are clear differences in the way these ecosystems respond to inputs of PCE.

- 1. Ponds and lakes require from 70 to 210  $\underline{\text{days}}$  to purify themselves while river systems needed between 61 and 132  $\underline{\text{hours}}$ . The hydraulic retention time is the controlling variable.
- 2. The amount of organic material present in the system may be an important factor as there are differences between the eutrophic

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TABLE 18. SUMMARY OF RESULTS OF EXAMS MODELING OF PCE CONCENTRATIONS IN AQUATIC ECOSYSTEMS

Ecosystem	Applied Load (kg/hr)	Actual Load (kg/hr)	Maximum Concentration in Water Column (µg/l)	Maximum Concentrations in Sediments (µg/kg)	Percent of Load which Volatilizes <sup>l</sup>	Percent in Water Column <sup>2</sup>	System Self- Purification Time
River	0.004	0.004	0.004	0.03	1.6	91.8	131.8 hours
	160	160	160	1200	1.6	91.8	129.8 hours
Turbid River	0.004	0.004	0.004	0.02	1.6	94.9	63.4 hours
	160	160	158	810	1.6	94.9	61.3 hours
Pond	0.004	0.004	10	460	93.2	40	210 days
	160	2.4 .	6200	270,000	93.2	40	210 days
Eutrophic Lake	0.004	0.004	0.52	2.0	95.8	97	74.6 days
	160	58.2	7600	29,000	95.8	97	74.6 days
Oligotrophic Lake	0.004	0.004	0.55	0.48	95.2	99.3	70.6 days
	160	58.2	8100	7100	95.2	99.3	70.6 days

<sup>1</sup> For PCE this percentage plus the percent of the load which is transported, add up to 100%.
2 The percent of PCE in the water column and the percent of PCE in bottom sediments add up to 100%.

and oligotrophic lake, and the turbid vs. the clear rivers. There are insufficient data here to analyze this further, and in any case, the lack of a complete input data base for PCE renders these results "indicative" rather than "conclusive."

- 3. Downstream advection is the critical removal mechanism in short river reaches, while volatilization is the most important factor in ponds and lakes and in long river reaches.
- 4. The maximum concentrations of PCE in water and sediment are a function of loading rates. Water concentrations ranged between 0.004 μg/l and 8.1 mg/l. These numbers are less than most positive monitoring data. Sediment concentration maxima ranged between 0.02 μg/kg and 270 mg/kg, which correspond well with the values in Table 11.
- 5. Only in the pond scenario does the percent of PCE in sediments exceed the percent in the water column (60% and 40%, respectively) while in all other scenarios the water column holds over 92% of the total accumulation.

Use of EXAMS, even with crudely estimated loading rates, has provided simulated concentrations that are believable when compared with monitoring data. Because the input data to characterize the full range of behavioral mechanisms of PCE in aquatic systems are lacking, it would be misleading to draw further conclusions from the observations made above.

#### F. SUMMARY

Physicochemical Properties - Tetrachloroethylene is a volatile liquid and a relatively stable chemical. It is readily degraded by photochemical reactions in the atmosphere (and to a much smaller extent in surface waters), but it is resistant to hydrolysis and biodegradation. Phosgene, a highly toxic chemical, is one of the degradation products from the photochemical reactions in air. Adsorption on soils and sediments, and bioconcentration in aquatic biota, will take place (concentration factors are about 30 and 100, respectively), but not to the extent that food chain contamination is of concern.

Mobility and Persistence - Tetrachloroethylene is very mobile in the environment. Atmospheric transport can carry the chemical hundreds to thousands of kilometers downwind from the original emission sources. The atmospheric residence time is estimated to be in the range of 2-10 days in sunlight. Transport through soils to deep wells has resulted in water supply contamination at a number of sites. In deep soils and groundwaters, as well as in deep surface waters and sediments, the chemical may have a residence time of 7-14 years, unless the turnover time is smaller for the compartment. Significant amounts of the chemical can be transported in water (solubility is ~100 mg/l at 20°C). In well-mixed surface waters volatilization, will be an

important loss pathway; this pathway will be important for ponds, lake surfaces, sewers and sewage treatment plants. Half-lives for volatilization will be on the order of hours to a few days for these cases. Volatilization from contaminated topsoils and dump sites will also be an important pathway.

Ambient Levels - The entire atmosphere, all surface waters, and topsoils will contain some tetrachloroethylene. Background concentrations are, however, below 1  $\mu g/l$  or  $\mu g/kg$ . Most surface waters in industrialized or heavily populated river basins will show elevated (>1  $\mu g/l$ ) levels of the chemical. Drinking water in the U.S., however, typically contains <0.2  $\mu g/l$ . Elevated levels in the atmosphere (6.8  $\mu g/m^3$ ) are found near manufacturing and user sites, near land disposal sites (where waste solvent, solvent sludges, or POTW sludges are usually sent), and are likely to be found near sewer vents in certain commercial/industrial sectors. Concentrations above 10  $\mu g/l$  have been found in the leachate from some dump sites. Aquatic biota, food, and humans contain 1-20  $\mu g/kg$  of the chemical

Equilibrium Distribution Model - A relatively simple equilibrium distribution model was used to predict concentrations in various environmental subcompartments. The results indicate that - at equilibrium - about 99.8% of PCE would reside in the atmosphere. The predicted atmospheric concentration of  $0.6~\mu g/m^3$  (v/v) is fairly close to the ranges measured: <0.1-0.5  $\mu g/m^3$  at remote sites and 1.0-14 at urban sites (cf. Table 11). The ratio of water to air concentrations is 0.007 at 20°C. Predicted concentrations for biota and surface waters appear to be somewhat lower than actual values. If the model is accurate, this implies a nonequilibrium situation and a net flux of PCE from these phases into the atmosphere. Increasing environmental temperatures are predicted (under equilibrium conditions) to have a negligible effect on atmospheric concentrations and to result in a lowering of concentrations in other subcompartments (water, sediments, soil and biota).

Atmospheric Dispersion Modeling - With standard air dispersion modeling procedures, ambient concentrations of PCE were estimated for a variety of meteorologic and emission source operating conditions. For estimates of concentrations in the proximity of PCE sources the meteorological conditions included those likely to produce high ambient concentrations near a large commercial or industrial drycleaning plant. For area concentrations a computerized model (developed by U.S. EPA) was applied to these two source types with average climatological data typical of a population center in the Northeastern U.S.

The "worst-case" estimates for the immediate vicinity of a large commercial source are  $150 \pm ~50~\mu g/m^3$  ( 15~ppb to 30~ppb, v/v), and between  $900~\mu g/m^3$  and  $1800~\mu g/m^3$  (132-265~ppb, v/v) for the industrial source, each at distances of 50~m. downwind from the source. These values are roughly consistent with concentrations of PCE measured in the air:  $0.12-210~\mu g/m^3$  and a high value of about  $394~\mu g/m^3$  near manufacturing and user sites, based on measurements at several sites.

EXAMS Water Distribution Model - The EPA's standard computerized model for the determination of chemical fate in aquatic ecosystems was used to analyze four scenarios for five ecosystems. The scenarios were: industrial discharges to rivers at a loading rate of 0.004 kg/hr, POTW discharges to rivers at the same rate, and modeling all ecosystems for input in the form of contaminated groundwater which included a leachate plume from landfills containing PCE wastes. The leachate plume contamination scenario was modeled at two loading rates, 0.004 and 160 kg/hr, the latter representing an extreme situation. The modeling results led to the following conclusions:

- 1. Ponds and lakes (systems with long hydraulic retention times) require far longer times than rivers for 99% reduction of PCE following the cessation of loading.
- 2. Volatilization is the primary mechanism for PCE reduction from the aquatic environment, provided that aqueous concentrations are sufficient to drive that process.
- 3. The maximum concentrations of PCE in the water column and in sediments are a function of the loading rate and the presence of organic matter as sediment or as suspended solids (although this latter relationship has not been quantified due to lack of data). Concentrations in water were between 0.004  $\mu$ g/l and 7.6 mg/l. Sediment levels were in the range of 0.2  $\mu$ g/kg and 270 mg/kg.
- 4. The water column generally accumulates more than 92% of the total PCE in the aqueous systems analyzed, with the exception of the pond where the sediments contained 60% of the accumulated PCE.

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#### CHAPTER V

## EFFECTS OF TETRACHLOROETHYLENE ON HUMANS AND AQUATIC BIOTA

## A. HUMAN TOXICITY

## 1. Introduction

Exposure to the chlorinated hydrocarbon tetrachloroethylene has been associated with various hepatotoxic and nephrotoxic effects; depression of the central nervous system; and eye, nose and throat irritation. A potential carcinogenic risk to man has also been suggested by the occurrence of hepatocellular carcinoma in mice given PCE by gavage. A discussion of these effects associated with PCE exposure follows.

## 2. Metabolism and Bioaccumulation

Evidence concerning absorption of PCE is predominantly limited to the inhalation route, although some investigation of dermal absorption has been conducted. Ogata and co-workers (1971) estimate that approximately 57% of inhaled PCE is retained by humans. In a series of studies, Monster (1979 a,b,c) noted total uptake of PCE was influenced more by (lean) body mass than by respiratory minute volume of adipose tissue (i.e. distribution volume is larger when body weight is higher).

Retained PCE is primarily eliminated unchanged in expired air (Stewart et al., 1961; Ideda, 1977). Monster (1979 a,b,c) noted 80-100% elimination of retained PCE in the expired air of six male volunteers by 162 hours following PCE exposure; an additional 2% of the PCE uptake was converted to trichloroacetic acid and subsequently eliminated in the urine. The time course of PCE concentration in blood and exhaled air showed that a long period was necessary to complete elimination of PCE. A respiratory half-life of 65 hours has been estimated for PCE in man; the urinary half-life for its metabolite, trichloroacetic acid, is somewhat longer (144 hours) (Ikeda, 1977). Thus, an accumulation of PCE in the body would occur with repeated exposure. McConnell et al. (1975) reported some evidence of PCE in human tissues at extremely low concentrations ( $\mu$  g/kg).

With respect to dermal exposure, Riihimaki and Pfaffli (1978) found that in ambient air, concentrations of 88.5 mg/m $^3$  PCE readily penetrated human skin; the small number of human volunteers precluded conclusive quantification of PCE absorption. In another study, Stewart and Dodd (1964) reported the presence of  $160-260~\mu \text{g/m}^3$  in the expired air of human volunteers 5 hours after immersing their thumbs in PCE for 40 minutes.

Schumann and Waţanabe (1979) recently reported that in B6C3F1 mice exposed to 1.47 mg/m³ of <sup>14</sup>C-tetrachloroethylene for 6 hours, 63% of the radioactivity was excreted in the urine as nonvolatile metabolites. An additional 12% of the radioactivity was excreted unchanged in expired air. Similar exposure of Sprague-Dawley rats, however, resulted in the elimination of only 19% of the radioactivity in urine, with an additional 68% of the dose eliminated in expired air. The mouse metabolized 7-8 times more PCE per kilogram of body weight than did the rat, with approximately 7-9 times more radioactivity irreversibly bound to hepatic macromolecules in the mouse than in the rat. No radioactivity was detected bound to purified hepatic DNA at times of peak macromolecular binding in the mouse.

## 3. Animal Studies

## a. Carcinogenicity

The carcinogenicity data indicate that PCE is an apparent liver carcinogen in the mouse; the data in rats are inconclusive. USP-grade PCE was administered by gavage to groups of 50 male and female B6C3F1 mice at predetermined maximally tolerated dose and one-half this amount 5 days per week for 78 weeks. The dose of PCE was changed during the course of the experiment in order to prevent excessive loss of animals; time-weighted average doses were 386 and 772 mg/kg\* for females and 536 and 1072 mg/kg for males. The vehicle control group consisted of 20 mice of each sex.

Hepatocellular carcinoma was found in 40% to 65% of all treated mice compared with 0-10% incidence in controls (see Table 19). Five hepatocellular carcinomas metastasized to the lung (NCI, 1977).

TABLE 19. INCIDENCE OF HEPATOCELLULAR CARCINOMA IN PCE-TREATED B6C3F1 MICE

		Male			Female		
Vehicle Controls	2/20	(10%)		0/20	( 0%)		
Low PCE Dose	32/49	(65%)	p<.001	19/48	(40%)	p<.001	
High PCE Dose	27/48	(56%)	p <.001	19/48	(40%)	p<.001	

Source: NCI (1977)

<sup>\*</sup>Note that all references to dose (given as mg/kg) are dose/kilogram body weight.

A concurrent study conducted with groups of 50 Osborne-Mendel rats given time-weighted doses of 941 mg/kg and 471 mg/kg for males and 949 and 474 mg/kg PCE for females by gavage produced no significant increase in neoplastic lesions. However, the high incidence of dose-related early deaths confound the interpretation of these results. Fifty percent of the high dose males died by week 44 and 50% of the high-dose females were dead by week 66 compared with a median survival time of 88 and 102 weeks, respectively, for male and female control rats. Toxic nephropathy was observed in 79% of the treated rats but in none of the controls. Due to poor survival and the poor response (5% hepatocellular carcinoma) of this strain to the positive control, carbon tetrachloride, the results of this carcinogenicity bioassay were considered inconclusive (NCI, 1977).

Recently, NIOSH (1973) reported no statistically significant increase in tumors in Sprague Dawley rats exposed to 44.3 or  $88.5\,\mathrm{mg/m^3}$  PCE by inhalation (the study duration was not given). A higher, but not statistically significant incidence of adrenal pheochromocytoma was noted in females at the  $44.3\,\mathrm{mg/m^3}$  level only and increased mortality occurred in the  $88.5\,\mathrm{mg/m^3}$  treated males.

Thus, a single positive finding of liver carcinoma in B6C3Fl mice has been linked to PCE exposure. The lack of a dose-response and the high effect level, however, suggest that the observed tumorigenesis may be secondary to rapid cellular proliferation and liver regeneration resulting from a partial chemical hepatectomy induced by toxic levels of PCE.

## b. Mutagenesis

Negative findings were reported in two bacterial mutagenicity assays with PCE. Bartsch <u>et al</u>. (1979) noted negative results with two strains of <u>Salmonella typhimurium</u> (TA100, TA1530) exposed to PCE vapor in the presence of mouse liver microsomal activation.

In a second study, a concentration of 149 mg/l PCE was not mutagenic when tested with Escherichia coli K12 in the presence of a liver microsomal fraction (Greim et al., 1975).

Cerna and Kypenova (1977), however, found increased mutagenic activity in Salmonella typhimurium TA100 without metabolic activation at 0.01-1 mg/ml concentrations. These investigators also reported positive results in a host-mediated assay in mice with S. typhimurium strains TA1950, TA1951, and TA1952 at 1/2 LD and LD levels. No evidence of dose-dependence was seen.

In another study, Price and co-workers (1978) reported that PCE (97  $\mu$  M) induced phenotypic transformations of F1706 rat embryo cells [(178 foci/3 dishes vs 124 foci for the positive control, 3-methylcholanthrene (0.37  $\mu$  M)]. Isogenic Fischer rats inoculated subcutaneously with transformed cells produced undifferentiated fibrosarcomas in all seven rats within 45 days of inoculation.

Although the mutagenic findings are varied, the strong positive results in mammalian cells supported by positive results in the host-mediated assay implicate PCE as a mutagen. Further investigations are needed to clarify the mixed response in bacterial systems.

## c. Teratogenesis

Administration of 44.3 mg/m<sup>3</sup> PCE by inhalation to pregnant Swiss Webster mice 7 hours per day on days 6-15 of gestation produced a significant decrease in fetal body weight (1.19 g vs. 1.3 g for controls) and significantly greater incidences of subcutaneous edema (59% vs. 27% for controls), delayed ossification of skull bones (100% vs. 69% for controls) and split sternebrae (24% vs. 0% for controls). Similarly treated Sprague Dawley rats exhibited a light but significant decrease in maternal weight gain and a significant increase in the percent of fetal resorptions (9% vs. 4% for controls) (Schwetz et al., 1975).

Nelson (1979) found that pregnant Sprague Dawley rats exposed to  $133~\text{mg/m}^3$  PCE, 7 hours per day on days 7-13 or 14-20 of gestation had a significant reduction in the proportion of pups born alive (no values given). Behavioral tests indicated poorer initial performance with respect to neuromuscular activities in PCE-exposed offspring but differences disappeared with age. Analysis of brain neurotransmitters in newborn and 21-day-old offspring of PCE-exposed dams indicated a significant reduction in acetylcholinesterase levels in offspring from both treatment regimens and a reduction in dopamine in offspring of dams initially exposed during the second week of gestation.

PCE injected into the air space of developing chick embryos at doses of 25-100  $\mu$ mol/egg influenced survival if treatment occurred on the sixth day of incubation but was more or less ineffective in comparison to olive oil controls when treatment occurred on the second day of incubation. The number of dead embryos treated on the sixth day roughly corresponded to dose: 60%, 20% and 10% mortality for the 100, 50 and 25  $\mu$ mol groups compared with 14% mortality in olive oil-treated controls. An increase in the embryonic length of dead embryos demonstrated delayed lethal toxicity due to declining dose (e.g., 1.5 cm at 100  $\mu$ mol PCE/egg, 2.3 cm at 50  $\mu$ mol/egg). Six of 61 surviving embryos (9.8%) exposed to 5-100  $\mu$ mol PCE/egg were malformed (predominantly skeletal anomalies) compared with two of 56 (3.6%) olive oil-treated controls (Elovaara et al., 1979). However, the extreme sensitivity of this assay procedure frequently results in false positive results, making experimental findings difficult to interpret with certainty.

## d. Other Toxicological Effects

In laboratory animals, the acute oral (LD $_{50}$ ) values range from 3980 mg/kg-4680 mg/kg in the rat (Withey and Hall, 1975) to 8850 mg/kg in the mouse (Stecher, 1968). In mammals, acute exposure to PCE is characterized by depression of the central nervous system, cardiac depression, decreased respiration, decreased blood pressure and excessive fluid accumulation, congestion and inflammation of the lungs (NIOSH, 1978). The liver appears to be the principal target organ of PCE toxicity (i.e., liver enlargement, fatty degeneration and abnormal

liver function tests) but damage to the proximal convoluted tubules of the kidney has also been noted in mice, rats and rabbits (NIOSH, 1978; NCI, 1977).

A significant incidence of toxic nephropathy was noted in both B6C3Fl mice and Osborne Mendel rats in the National Cancer Institute's bioassay on the carcinogenicity of PCE (NCI, 1977). Time-weighted average doses of 386 mg/kg and 772 mg/kg for female and 536 mg/kg and 1072 mg/kg for male B6C3Fl mice given by gavage 5 days per week for 78 weeks results in 82-100% incidence of toxic nephropathy (see Table 20). Similarly, 58% to 94% of Osborne Mendel rats given time-weighted oral doses of 474 mg/kg and 949 mg/kg (females) or 471 mg/kg and 941 mg/kg PCE (males) for 78 weeks also exhibited toxic nephropathy (see Table 21).

Kidney damage has also been noted after inhalation of PCE. Carpenter (1937) reported congestion and granular swelling in kidneys of rats exposed to  $1540~\rm{mg/m^3}$  PCE, 8 hours per day, 5 days per week for a period of 7 months.

Liver injury resulting from PCE exposure was noted by Kylin <u>et al.</u> (1963) who reported moderate fatty degeneration of the liver following a single 3-hour exposure to  $1340 \text{ mg/m}^3$  of PCE. Exposure to this same concentration 4 hours per day, 6 days per week for 8 weeks enhanced the severity of the lesions induced by PCE (Kylin et al., 1965)

In a series of inhalation studies, Rowe (1952) reported loss of coordination and equilibrium, weight loss, increased liver and kidney weights, and central fatty degeneration and swelling of the liver in guinea pigs exposed to  $100-370~\text{mg/m}^3$  PCE 7 hours per day for 10-236~days. Rabbits exposed 7 hours per day for 39 days to  $370~\text{mg/m}^3$  PCE exhibited central nervous system depression and slight liver toxicity but displayed no adverse effects following exposure to  $60~\text{mg/m}^3$  for 222 days. Similar results were noted in two rhesus monkeys following 179 seven hour exposures to  $60~\text{mg/m}^3$  PCE over a 250-day period.

Reports from the Russian literature (Tsulaya et al., 1977; Bonashevskaya, 1977 a,b) also indicate that daily exposure of rats to  $19~\text{mg/m}^3$  of PCE for 94 days can disrupt central nervous system function, blood enzyme activity, the normal morphology of the liver, lungs and mast cells, DNA synthesis by the liver and the biological oxidation in the liver, lungs and adrenal glands.

TABLE 20. INCIDENCE OF TOXIC NEPHROPATHY IN B6C3F1 MICE GIVEN PCE BY GAVAGE FOR 78 WEEKS

	Ma	le	Female	
Vehicle Control	0/20	(0%)	0/20	(0%)
Low PCE Dose	40/49	(82%)	46/48	(96%)
High PCE Dose	45/48	(94%)	48/48	(100%)

Source: Adapted from NCI (1977)

TABLE 21. INCIDENCE OF TOXIC NEPHROPATHY IN OSBORNE-MENDEL RATS GIVEN PCE BY GAVAGE FOR 78 WEEKS

	Ma	le	Female		
Vehicle Controls	0/20	(0%)	0/20	(0%)	
Low PCE Dose	43/49	(88%)	29/50	(58%)	
High PCE Dose	47/50	(94%)	38/50	(76%)	

Source: Adapted from NCI (1977)

## 4. Human Studies

In man, the predominant effect of PCE exposure ( $\geq 155~\text{mg/kg}$ ) is depression of the central nervous system characterized by vertigo, impaired memory, confusion, irritability, "inebriation-like" symptoms, tremors and numbness (NIOSH, 1978; U.S. EPA, 1979). PCE is a skin, eye and respiratory tract irritant (NAS, 1977; U.S. EPA, 1979) and has been linked to cases of peripheral neuritis (NIOSH, 1976). Kidney impairment, toxic chemical hepatitis, and enlargement of the liver and spleen have been reported following accidental exposure to PCE (NIOSH, 1978). The level of PCE permissible in U.S. working environments is 670 mg/m³ (100 ppm) (NIOSH, 1976).

Because of the widespread use of PCE in industry, the acute central nervous system effects of PCE have been examined in some detail (Rowe et al., 1952; Carpenter, 1937; Stewart et al., 1961, 1970, 1977; Medek and Kovarik, 1973). In general, little or no effects occur at a concentration of 700 mg/m³ PCE. Minimal effects (sensory changes, light-headedness, impaired coordination) become evident at 1300 mg/m³, with more definite indications of CNS depression (mental confusion, lassitude) observed as the concentration increases. At 10,000 mg/m³ PCE, signs of inebriation occur. Volunteers exposed to 13,400 mg/m³ PCE were forced to leave the chamber after 7.5 minutes (Rowe et al., 1952).

Essentially no data, however, are available on the long-term effects of PCE exposure: Stewart and co-workers (1977) examined 12 human volunteers exposed to  $168~\text{mg/m}^3$  and  $670~\text{mg/m}^3$  PCE for 5.5 hours per day repeated up to 53 days. No consistent neurological changes due to PCE exposure could be documented.

Kidney impairment and liver damage have been reported in humans following accidental exposure to PCE (NIOSH, 1978) but are not well documented. Supporting evidence for hepatotoxic effects were presented by Coler and Rossmiller (1953). Three of seven men occupationally exposed to PCE concentrations of 1890  $mg/m^3$  to 2600  $mg/m^3$  had evidence of impaired liver function. In view of the very high incidence of toxic nephropathy in both mice (82-100%) and rats (58-94%) chronically exposed to PCE and the induction of hepatocellular carcinoma in mice but not rats exposed to PCE, the significance of long-term, low-level exposure to PCE to human health is difficult to assess, but is, nevertheless, an area of concern. Indeed, a preliminary report on a cohort mortality study of 330 laundry and dry cleaning workers indicates an increased proportion of cancer deaths, particularly of liver cancer and leukemia. The small number of deaths, however, may have biased the findings, and cautious interpretation of the study is needed until additional members of this occupational group are examined (Blair et al., 1979).

# 5. Overview

Tetrachloroethylene, a widely used industrial solvent, is readily absorbed through the lungs. Approximately 57 percent of inhaled PCE is retained but most of this amount (80-100%) is subsequently exhaled, unchanged in expired air. A respiratory half-life of 65 hours has been estimated for man; urinary clearance of approximately 2% of retained PCE as trichloroacetic acid has an approximate half-life of 144 hours. These values suggest accumulation of PCE may occur with repeated exposure.

In laboratory animals, acute oral LD $_{50}$  values range from 3980 mg/kg in the rat to 8850 mg/kg in the mouse. Acute exposure to PCE is characterized by depression of the central nervous system, and by liver and kidney damage.

Pronounced toxic nephropathy was seen in mice and rats chronically exposed to 386 mg/kg and 471 mg/kg PCE, respectively, by gavage for 78 weeks.

PCE exposure has been linked to hepatic carcinoma in B6C3Fl mice at a dose of 386 mg/kg given by gavage. This effect may possibly reflect a secondary response to PCE-induced hepatectomy. Carcinogenicity assays in rats were inconclusive. Mutagenic findings are varied but positive results in mammalian cell transformation studies and host-mediated assays implicate PCE as a mutagen. There are not indications of teratogenic effects associated with PCE exposure.

In man, the predominant effect of PCE exposure by inhalation  $(\geq 30~\text{mg/m}^3)$  is depression of the central nervous system, characterized by vertigo, confusion, inebriation-like symptoms, tremors and numbness. Accidental exposure to PCe has also been linked to kidney impairment and hepatotoxic effects. The lack of long-term exposure data makes assessment of long-term, low-level exposure to PCE difficult. However, the pronounced nephrotoxicity in rodents and increased incidence of hepatocellular carcinoma in mice raise concerns for the human health aspects of prolonged exposure to PCE.

# B. EFFECTS ON AQUATIC ORGANISMS

Data concerning the toxicity of PCE for aquatic biota are extremely limited and have been found for only a few fresh and saltwater species (Table 22).

In a bioassay with fathead minnows (Pimephales promelas), Alexander et al. (1978) compared the results of a flowthrough test in which the concentration was measured with a static test in which the concentration was calculated. The 96-hour LC $_{50}$  (median lethal concentration) for PCE in the flowthrough experiment was 18.4 mg/l, while the static test result was 21.4 mg/l. Similarly, U.S. EPA (1980a) reported a 96-hr. LC $_{50}$  of 13.5 mg/l for fathead minnow in a flowthrough test. Because of the volatility of PCE, the flowthrough test results were

TABLE 22. THE TOXIC EFFECTS OF PCE ON AQUATIC ORGANISMS

Species	Concentration (mg/1)	Test Type and Duration	Effect	Reference
<ul> <li>Freshwater Species</li> </ul>				retelence
Rainbow trout (Salmo gairdneri)	4.8 - 5.8	96 hr flowthrough	LC <sub>50</sub>	U.S. EPA 1980a
Fathead minnow ( <u>Pimephales</u> promelas)	14.4	96 hr flowthrough	EC <sub>50</sub> , loss of	Alexander <u>et al</u> . (1978)
Fathead minnow (Pimephales promelas)	18.4 - 21.4	96 hr flowthrough	equilibrium <sup>LC</sup> 50	Alexander et al. (1978)
Fathead minnow (Pimephales promelas)	0.84	chronic embryo- larval	chronic value hatchability	U.S. EPA (1980a)
Bluegill Sunfish (Lepomis machrochirus)	12.9	96 hr static	survived growth and deformities  LC 50	
<u>Daphnia magna</u> Alga ( <u>Selenastrum</u>	17.7 >816	48 hr static	I.C <sub>50</sub>	U.S. EPA (1978) U.S. EPA (1978)
capricornutum)	7 010		EC <sub>50</sub> , reduction in cell number and	U.S. EPA (1978)
• Marine Species			chlorophyll <u>a</u>	
Dab ( <u>Limanda limanda)</u> Sheepshead minnow (Cyprinodon variegatus)	5 >29.4; <52.2	96 hr 96 hr	LC <sub>50</sub>	Pearson and McConnell (1975)
Mysid shrimp (Mysidopsis bahia)	0.450	Life cycle	Chronic value	U.S. EPA (1978) U.S. EPA (1978)
Mysid shrimp ( <u>Mysidopsis bahia</u> )	10.2	96 lır	LC <sub>50</sub>	U.S. EPA (1978)
Barnacle naupii (Elminius modestus)	3.5	48 hr	LC <sub>50</sub>	Pearson and McConnell (1975)
Alga (Phaeodectylum tricornutum)	10.5	-	EC <sub>50</sub> , uptake of CO <sub>2</sub>	Pearson and McConnell (1975)
Alga ( <u>Skeletonema</u> costatum)	504~509	96 hr	EC <sub>50</sub>	U.S. EPA (1978)

considered to be more accurate. Rainbow trout were considerably more sensitive, and the 96-hour LC $_{50}$  valves were 5.8 and 4.8 mg/l with and without the presence of the solvent dimethylformamide (U.S. EPA 1980a).

Other freshwater organisms bioassayed for sensitivity in static bioassays were the bluegill sunfish (Lepomis macrochirus), Daphnia magna, and the alga Selenastrom capricornutum (U.S. EPA, 1978). For the bluegill, the calculated 96-hour LC50 was 12.9 mg/l. The 48-hour LC50 for the daphnia was 17.7 mg/l. The median effects concentration (EC50) for a reduction in cell number and chlorophyll-a mass in the alga was greater than 816 mg/l.

The lowest effect level for a freshwater species is a chronic value established for fathead minnow of 0.840 mg/l based upon an embryo-larval test (U.S. EPA 1980a); this is the only chronic study for a freshwater species.

Among marine species, the barnacle Elminius modestus had the lowest reported 96-hour LC $_{50}$  (3.5 mg/l), as calculated by Pearson and McConnell (1975). The only saltwater finfish tested was the sheepshead minnow (Cyprinodon variegatus), for which the estimated 96-hour LC $_{50}$  was between 29.4 mg/l and 52.2 mg/l (U.S. EPA, 1978).

The lowest effects concentration for a saltwater species reported was 0.450 mg/l, a chronic value for the mysid shrimp (Mysidopsis bahia). The 96-hour LC50 for this species was found to be 10.2 mg/l (U.S. EPA, 1978). Among marine algae, Phaeodectylum tricornutum (EC50 = 10.5 mg/l) was apparently more sensitive to PCE than Skeletonoma costatum, with 96-hour EC50 values based upon effects on chloraphyll-a of 504-509 mg/l (U.S. EPA, 1978).

All available aquatic toxicity data are summarized in Table 23. It should be emphasized that with the exception of the data of Alexander et al. (1978), and U.S. EPA (1980a), the  $LC_{50}$  values presented are probably overestimated because of the rpaid evaporation of PCE. Moreover, since the effects of certain water parameters (e.g., hardness, temperature) on PCE toxicity are not known, it may not be appropriate to compare the results of unrelated studies.

Two fish kills directly attributed to PCE have been reported in the last ten years. In 1970, discharges from a textile mill into an estuary killed 500 fish in two days. A much more serious kill of 16,300 fish occurred in 1974 as the result of a spill of PCE from an overturned tanker truck into a freshwater stream. In neither case were concentrations reported; however, it is likely that the spill produced much higher PCE concentrations than the industrial discharges (U.S. EPA Files, 1980b).

The U.S. EPA (1980a) has not established water quality criteria for the protection of aquatic life at this time due to the inadequacy of the data base.

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### CHAPTER VI

# EXPOSURE TO TETRACHLOROETHYLENE

### A. HUMAN EXPOSURE

## 1. Introduction

In estimating exposure to PCE, the populations and subpopulations exposed to the chemical were identified. The duration of exposure was estimated and the total possible intake from such exposures was calculated. These estimated exposures are not definitive, but rather indicative of the range of potential exposures.

The preceding analysis of the fate of PCE in the environment has shown that measurable levels of PCE may occur in all environmental media--air, water, soil and sediment. Monitoring data substantiate this, showing a wide range of PCE levels in the human environment. Therefore three exposure routes--inhalation, ingestion and dermal--were considered, indicating, where possible, which routes are most significant.

Identifying exposed populations and estimating the duration of exposure requires knowledge concerning the sources of PCE release to each environmental medium and the types of human activities occurring in proximity to each source type. Factors considered relevant to PCE exposure are: place of residence and/or occupation, use of coin-operated laundries, and consumption of food and water containing PCE. The exposure analysis considers three settings that differ with respect to the number of PCE sources and. therefore, concentration: urban, remote, and near manufacturer and user sites.

Because PCE is used primarily in the work environment, occupational exposure is of great concern. Since the associated risks are being investigated by other federal agencies, they are not stressed in this report. The occupationally exposed subpopulation that handles PCE directly is considered briefly in order to place the estimated environmental exposures into perspective. The facilities in which PCE is used are also viewed as point sources to the environment. Exposures in the vicinity of such sources are estimated on the basis of the dispersion analyses performed in Chapter IV, monitoring data, and the work of Verberk and Scheffers (1980).

# 2. Exposure Situations

# a. Populations Exposed Through Ingestion

Humans may be exposed to PCE via ingestion of contaminated foodstuffs and drinking water. Surface water may be contaminated by direct discharge of factory effluents, sewers, transportation spills, and through

contact with contaminated ground water. Landfills are postulated as a likely source of ground water pollution, through leaching, as well as surface runoff.

The data on PCE concentrations in drinking water were detailed previously in Table 6 (Chapter IV). The range in mean values for the positive samples in surface supplies was 0.18  $\mu g/1$  (Ten Cities) to 2.8  $\mu g/1$  (CWSS), with the value for NOMS (0.81  $\mu g/1$ ) in between. Medians in all three surveys, however, were below 0.5  $\mu g/1$ .

Human exposure to PCE via drinking water in the U.S. has been estimated by making a number of assumptions as shown in Table 23. For the 117 million persons utilizing surface water supplies (Temple, Barker and Sloane, 1977), it was assumed that 8% or 9 million persons ingest detectable levels of PCE ( $\geq 0.2~\mu g/1$ ) in their drinking water. This assumption is based on the data from NOMS, which showed that 8% of the cities sampled contained detectable levels. Although there is no direct correlation between the frequency of detection and the population served, such an assumption provides a rough method for estimating nationwide exposure. It is apparent that most persons (an estimated 108 million) are exposed to levels less than 0.2  $\mu g/1$  PCE in drinking water from surface supplies and thus ingest less than 0.4  $\mu g$  per day.

Estimating exposure of persons utilizing ground water supplies is more difficult since the sampling is more limited and is generally biased toward the sampling of contaminated supplies. A very rough approximation can be made from the CWSS data (see Chapter IV), in which about 5% of the samples contained detectable levels of PCE ( $\geq 0.5~\mu g/1$ ). On this basis, about 4 million persons could be exposed to detectable levels (with a mean 3-4  $\mu g/1$ ) of PCE in ground water supplies.

There is evidence, however, of some highly contaminated supplies as a result of a local contamination incident (disposal site, spill, etc.) or leaching in the distribution system. These occurrences are umpredictable and the size of the population exposed cannot be estimated. Judging from the ground water data discussed in Chapter IV, such incidents appear to be fairly common. Worst case exposures of this type are estimated in Table 23.

Ingestion of PCE may also occur in foodstuffs. Unfortunately, the data on PCE levels in food are sparse as was shown in Chapter IV. The only available data, a British study, were used to estimate a potential ingestion exposure via food of 1.2  $\mu g/day$  (see Table 24). Due to the limited data base, however, it is unknown if this estimate is representative of typical U.S. exposure.

### b. Populations Exposed Through Inhalation

Exposures are estimated from a concentration, an exposure duration and an intake rate. For inhalation exposures to PCE, the concentrations will vary with proximity to a source or sources, and will also vary

TABLE 23. ESTIMATED HUMAN

EXPOSURE TO TETRACHLOROETHYLENE IN DRINKING WATER

Population	Size	Estimated Exposure (µg/day)	Assumptions
General population	108 million	<0.4	<0.2 µg/l in surface water; 2 l/day
	9 million	2-6	1-3 µg/l mean of positive samples; 8% of population receiving detectable levels; 2 l/day
General population	71 million	<1	<0.5 µg/l in ground water; 2 l/day
	4 million	6-8	3-4 µg/l mean of positive samples; 5% of population receiving detectable levels; 2 l/day
Isolated Exposures:			
Contaminated wells		750	worst case - 375 $\mu$ g/l in well water; 2 1/day
Contamination from distribution system		10,000	worst case - 5000 µg/1 in tap water; 2 1/day

temporally with weather conditions and source operations. Thus, when analyzing a particular exposure scenario, such as an activity taking place in an urban area, the exposure concentration could vary considerably depending upon the locations of source and receptor (see Figures 17 and 18). Similarly, the duration of exposure can vary from zero to an entire day. Therefore, in the following analysis of exposure scenarios, although a PCE concentration and a characteristic exposure duration were selected for each scenario, the selected concentration generally represents a range of mean values for that type of environment as shown in Chapter IV, Table 11. The intake rate, however, remains fixed: the average adult human breathes at a rate of 1.2 m $^3$ /hour while awake and at 0.4 $^3$ m /hour when sleeping (ICRP 1975). Furthermore, it is assumed that approximately 50% of inhaled PCE is retained and absorbed (Ogata et al., 1971).

Table 25 presents the various inhalation exposure situations analyzed for PCE and the associated estimated exposures. These numbers do not represent actual exposures but suggest the possible ranges of such exposures. At this juncture, it is not possible to quantify the numbers of people who may fall into each category with the associated exposure levels and durations actually designated for each cohort. However, such cohorts would include the following:

- 1. People living far from PCE sources (i.e., in remote areas),
- 2. People living in urban areas with low PCE levels,
- 3. People living in urban areas with higher PCE levels,
- 4. People living near manufacturing or user sites,
- 5. People living near a drycleaning establishment,
- 6. People working in any of the five above situations while living in another, and
- 7. People using coin-operated laundry facilities equipped with drycleaning equipment.

Table 26 describes occupational exposures, with concentration data and workers exposed. Note that the concentrations and exposures are given in units that are three orders of magnitude higher than those for non-occupational exposure.

# c. Populations Exposed Through Dermal Absorption

Dermal exposure may occur through use of PCE and contact with contaminated air and water during various activities. Although information is available concerning quantities of water that are actually in contact with the skin in daily washing activities and during water sports activities, the rate of absorption by the skin has not been documented for PCE. The potential exposure via this route is probably very low in comparison with that of other exposure routes.

TABLE 24. ESTIMATED HUMAN EXPOSURE TO TETRACHLOROETHYLENE IN FOOD

Food or Food Group	PCE Concentration (µg/kg) <sup>1</sup>	Consumption (g/day) <sup>2</sup>	Exposure (µg/day)
Milk	0.3	266	0.08
Cheese	2	15	0.03
Butter	13	6	0.08
Meat	1	207	0.2
Oils and fats	7	8	0.06
Fruits and vegetables	2	343	0.7
Fruit drink	2	29	0.06
Fish	13	11	0.01
TOTAL			1.20

<sup>&</sup>lt;sup>1</sup>See Table 10, Chapter IV.

 $<sup>^{2}</sup>$ USDA (1980).

 $<sup>^3</sup>$ Lower end of the range of 1-5 µg/kg was taken since these samples were taken from a relatively contaminated area (Liverpool Bay and Thames Estuary).

TABLE 25. ESTIMATED EXPOSURE OF HUMANS
TO TETRACHLOROETHYLENE VIA INHALATION

Subpopulation	Concentration 1 (µg/m³)	Duration (hours/day)	Estimated Exposure <sup>2</sup> (µg/day)
Rural/remote	0.1-0.5	24	1.1-6
Urban	1-14	24	11-160
Near Manufacturing Sites & Industrial Areas	0.12-210	24	1.3-2400
Near Drycleaning Facilities	250-12,250	24	2,800-137,000
Use of Coin-Operated Laundry Facilities with Drycleaning Equipment	136,000	0.5	41,000

<sup>&</sup>lt;sup>1</sup>These levels generally represent a range of average concentrations for different locations and were taken from Chapter IV, Table 11 and Table 26 for coin-operated laundry facilities with drycleaning equipment.

 $<sup>^2</sup>$ A respiratory flow of 1.2 m³/hour during a 16-hour day and 0.4 m³ for 8 hours at night (ICRP 1975). A retention of approximately 50% is assumed (Ogata et al. 1971).

TABLE 26. ANALYSIS OF OCCUPATIONAL EXPOSURE TO TETRACHLOROETHYLENE<sup>1</sup>

Exposed Populations	DRYCLEANING			DEGREA			
and Exposure Levels	Commercial	Industrial	Coin-Op	Fabric Scouring	Vapor	Cold	
Total Employees per Plant	4	46	1	110	5	2	
Concentration in General Workplace (TWA <sup>2</sup> , mg/m <sup>3</sup> )	47.5	34	136	34	136	Brida Brida	
Directly Exposed Employees <sup>3</sup>	1.	4	_	10	4	2	
Concentration of Direct Exposure (TWA, mg/m <sup>3</sup> )	203	203	_	203	237	136	
Calculated Exposures (mg/day) <sup>1</sup>	225-970	160-970	650	160-970	650–1150	650	TOTAL
Total Employees	100,000	13,500	22,000	315,000	32,000	90,000	572,500
Number of Facilities	18,750	270	14,500	2,500	3,600	45,800	85,000

<sup>4</sup>Based upon an 8-hour workday, a respiratory flow rate of 1.2 m<sup>3</sup>/hr. and 50% retention of inhaled PCE.

<sup>&</sup>lt;sup>1</sup>Data and references in Appendix A, which profiles the industry.

<sup>2</sup>TWA - time weighted average, in this case, over the 8-hour working day.

<sup>3</sup>"fotal employees" is an industry figure and includes the entire available workforce. The number employed thus cannot be derived by multiplying the number of facilities by the total employees per model plant.

# 3. Results of Exposure Calculations

The total daily exposure ranges calculated above are summarized in Table 27. Clearly the proximity of the human receptor to the source of PCE is the critical element determining the extent of innalation exposure. In urban areas non-industrial drycleaning facilities represent highly concentrated sources of PCE. The exposure potential of these facilities falls on local residents, users, workers and maintenance staff of these establishments.

In general, drinking water does not appear to contribute greatly to overall exposure to PCE. In rural areas, however, drinking water does represent a major fraction of total estimated exposure due to the lower ambient air concentrations of PCE in these areas. However, certain incidents of contaminated water supplies have made drinking water an important route of exposure in some cases. Although information is extremely limited regarding levels of PCE in food, the preliminary estimate included in Table 27 suggests that food does not represent a significant source of PCE exposure.

# B. EXPOSURE OF AQUATIC BIOTA

A formalized exposure analysis is not possible for aquatic systems. The two fish-kill incidents described in Chapter V graphically present the exposure events of concern: an accidental spill and an industrial discharge; however, ambient concentrations associated with these spills were not reported.

The mean of unremarked ambient levels of PCE (as of 1981) in surface water according to STORET was 8.5  $\mu g/l$ . The maximum was 142  $\mu g/l$ . Ninetyone percent of all observations were at or below the detection level (usually 10  $\mu g/l$ ). In a 1977 study, PCE was detected in 38% of national samples in industrialized regions, for the most part at levels <5  $\mu g/l$ ; only 2% of the samples exceeded 10  $\mu g/l$ .

TABLE 27. SUMMARY OF ESTIMATED HUMAN EXPOSURE TO TETRACHLOROETHYLENE

Exposure Ro	oute	Estimated Exposures (µg/day)
Drinking water		
general population	on - surface water - ground water	<0.4 <1
smaller subpopula	tion - surface water - ground water	2-6 7-8
Food		1.2
Inhalation 1		
Rural/Remote		1.1-6
Urban		11-160
Near Manufact	uring Site/Industrial Are	a 1.3-2400
Near Dryclean	ing Facilities	2,800-137,000
Use of Coin-O with Dryclean	perated Laundry Facilitie ing Equipment	s 41,000
Occupational <sup>2</sup>		160,000-1,150,000
Isolated Exposures		
Drinking Water	- Contaminated Wells	750
	Contamination in Distribution System up to	10,000

 $<sup>^{1}\</sup>mathrm{Assumes}$  50% respiratory retention and various durations of exposure (see text).  $^{2}\mathrm{See}$  Table 26.

### REFERENCES

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### CHAPTER VII

#### RISK CONSIDERATIONS

The desired output of this risk assessment is the quantification of risks associated with use and production of tetrachloroethylene (PCE) to various subpopulations of humans and other classes of biota. This requires careful: (1) identification of the populations exposed, (2) evaluation of the ranges in each subpopulation's exposure, (3) consideration of the effects levels or dose response data for the species of concern and/or proxies for these species and (4) extrapolation of effect levels from dose/response data for laboratory animals to the human subpopulations at risk.

# A. RISKS ASSOCIATED WITH HUMAN EXPOSURE

## 1. Introduction

To assess the risks of PCE exposure, several human exposure situations derived in Chapter VI were compared with dose levels of PCE that have caused adverse effects in man and/or laboratory animals. The risks most clearly associated with PCE exposure in laboratory animals are carcinogenesis, CNS disturbances, kidney impairment and hepatotoxic effects (Table 28). Quantitative estimates were made of human carcinogenic risk based on animal data. The estimated margins of safety for acute effects associated with various exposure situations were approximated as well. However, there is at present no basis for quantifying the effects of chronic exposure.

One study indicated PCE is a liver carcinogen in mice; results with rats were negative but were confounded by poor survival. Malignant transformation of PCE-exposed rat-embryo cells to tumor-producing cells has been demonstrated <u>in vitro</u>.

Preliminary data in a retrospective human mortality study also suggest an increased incident of cancer-related deaths, particularly of liver cancer and leukemia in laundry and drycleaning workers. However, the small population examined makes uncertain the findings and cautious interpretation of this study is needed until additional members of this occupational group are examined. Further research is needed to clarify the carcinogenicity of PCE in man and to establish dose-response relationships.

The chief target organs of PCE toxicity in animals are the liver and kidney. Liver enlargement, fatty degeneration and abnormal liver function tests as well as kidney damage, particularly to the proximal convoluted tubules, have been linked to PCE exposure. Disruption of the central nervous system has also been reported. However, dose-response relationships for these effects are unclear.

TABLE 28. ADVERSE EFFECTS OF TETRACHLOROETHYLENE ON MAMMALS

Adverse Effect	Species	Lowest Reported Effect Level	No Apparent Effect Level	
•		(% of incidence)	<u>)</u>	
Hepatocellular carcinoma	Mouse	386 mg/kg (65%) by gavage		
Toxic nephropathy	Mouse	386 mg/kg (82%) by gavage		
	Rat	471 mg/kg (88%) by gavage		
Mutagenicity (cell transformation)	Rat (embryo cells)	97 umol in vitro		
CNS disturbances	Man	1360 mg/m $^3$ by inhalation	678 mg/m <sup>3</sup>	
Median Oral Lethal Dose	Rat	3980 mg/kg (50%)	The therman	

Inhalation appears to be the dominant PCE exposure route for humans. Ambient air levels of PCE, even in urban areas, are several orders of magnitude lower than inhalation levels associated with toxicological effects in humans. Exposure calculations (Table 29) indicate that non-occupational inhalation intakes may range from 1  $\mu g/day$  to 6  $\mu g/day$  in remote areas to 11-160  $\mu g/day$  in urban areas. The highest non-occupational inhalation intakes (2.8 mg/day to 137 mg/day) would occur near drycleaning facilities. Use of coin-operated laundry facilities for 0.5 hours per day presents the second largest non-occupational intake (41 mg/day), but this exposure is not anticipated to occur on a daily basis. Occupational exposures were estimated to be in the 160-1150 mg/day range.

In general, drinking water does not appear to contribute greatly to overall exposure to PCE except perhaps in rural areas where it constitutes a greater portion of total exposure than in urban areas. However, certain incidents of contaminated water supplies have made drinking water an important route of exposure in some cases. A limited data base suggests a low level of exposure (  $1.2~\mu g/day$ ) via foodstuffs.

# 2. Quantitative Carcinogenic Risk Estimation

Below, the potential carcinogenic risk to humans due to tetrachloroethylene ingestion is estimated.

Ideally, this problem is approached on two fronts:

- 1) Application of various extrapolation models to occupational vs. ambient\* human exposure data (from retrospective epidemiological studies) to obtain an approximate dose/response relationship.
- 2) Application of these same models to data from controlled experiments on laboratory animals, and conversion of the animal/dose/response relationship to an estimated human dose/response.

In the first approach, the overriding uncertainty is in the data themselves: usually the exposure levels, lengths of exposure, and even response rates (responses per number exposed) are "best estimates," and, furthermore, unknown factors (background effects, etc.) may bias the data. In the second approach, the data are usually more accurate, but the relationship between animal and human response rates must be questioned, and at present there is no universally accepted solution to this problem. (In short, in the former case we have relevant data of questionable validity, whereas in the latter we have valid data of questionable relevance.) If both analyses can be performed and the results corroborate each other, we gain confidence in these results. If, on the other hand, data are not available for one of the analyses, it is assumed that some result is better than no result, and an analysis is performed that is based on the available data.

<sup>\*(</sup>or ambient, location A vs. ambient, location B)

In any case, a more important question is: which, if any, of the mathematical models is accurate? For the time being, though there is no firm basis for judgment, the models applied here are believed to tend to overestimated the true risk.

For PCE, the only quantitative carcinogenicity data currently available are from an NCI study on mice (discussed in U.S. EPA, 1979a). The available data concerning human and other mammalian effects are discussed in Chapter V. The data selected for extrapolation are listed in Table 29.

To deal with the uncertainties inherent in extrapolation, three commonly used dose/response models have been applied to the mouse data to establish a range of potential human risk. Additionally, the results from the CAG multistage model have been included. The assessment of potential human risk is subject to several important qualifications:

- Though positive carcinogenic findings exist, there have also been negative findings in tests with other species. Thus the carcinogenicity of PCE to humans is far from certain.
- Assuming that the positive findings indeed provide a basis for extrapolation to humans, the estimation of equivalent human doses involves considerable uncertainty.
- Due to inadequate understanding of the mechanisms of carcinogenesis, thee is no scientific basis for selecting among the several alternate dose/response models (as discussed above), which yield widely differing results.

# a. Calculation of Human Equivalent Doses

To obtain a quantitative human risk estimate based on animal data, it must first be determined what human dose is equivalent to a given animal dose. The approach recommended by the U.S. EPA (1979b) has been followed, which normalizes the dose rate according to body surface area. This approach is relatively conservative, in that it results in a lower equivalent dose than would be obtained from simple multiplication of animal dose rate (mg/kg/day) by human body weight. Whether the surface area or body weight ratio is the more appropriate normalization factor is still debatable. Since the weight ratio is roughly 14 times as large as the surface area ratio, the choice of a conversion method suggests an uncertainty of an order of magnitude at least.

TABLE 29. CARCINOGENIC RESPONSE IN MICE EXPOSED TO TETRACHCOROETHYLENE

		Time-Weighted Average Dose (mg/kg/day)	Equivalent Human Dose (mg/day)	Response	Percent	Percent Excess Over Averaged Controls*
	Male Mice	0	0	2/17	12	No.
		0 (vehicle control)	0	2/20	10	-
		536	1930	32/49	65	61
121		1072	3860	27/48	56	51
	Female Mice	0	0	2/20	10	-
		0 (vehicle control)	0	0/20	0	-
		386	1390	19/48	40	36
		772	2780	19/49	39	36

Source: U.S. EPA (1979a).

\*P (x) = 
$$\frac{P_{t}(x) - P_{c}}{1 - P_{c}}$$

The calculation of a human equivalent dose was performed using the following formula, assuming 70 kg for human weight and 0.025 kg for mouse weight:

Human Dose = Animal Dose x 
$$\frac{5 \text{ days}}{7 \text{ days}}$$
 x  $\frac{\text{Animal Weight x}}{\text{Animal Weight}}$   $\frac{2/3}{\text{Animal Weight}}$ 

From this, it was estimated that a dose of 1 mg/kg/day, 5 days per week for a mouse is equivalent to a dose of 3.6 mg/day for a human.

# b. Estimation of Human Risk

The three dose/response models used to extrapolate human risk were the linear "one-hit" model, the log-probit model, and the multistage model. The latter is actually a generalization of the one-hit model, in which the hazard rate is taken to be a quadratic rather than linear function of dose. All of these models are well known in the literature, and a theoretical discussion may be found in Arthur D. Little (1980). The one-hit and multistage models assume that the probability of a carcinogenic response is described by

P (response at dose X) = 
$$1 - e^{-h(x)}$$

where h(x) is the "hazard rate" function. The log-probit model assumes that human response varies with dose according to a log-normal distribution. Due to their differing assumptions, these dose/response models usually give widely differing results when effects data are extrapolated from relatively high doses to the low doses typical of environmental exposure.

For the linear one-hit model, the equation

$$P(x) = 1 - e^{-Bx}$$
, where  $P(x) = \frac{P_{t}(x) - P_{c}}{1 - P_{c}}$ 

P (x) is the excess probability of response at dose x and is solved for the parameter B. From our data, we find that B is approximately  $3 \times 10^{-4}$  based on the average of the dose/response data in male and female mice.

For the log-probit extrapolation, the "probit" intercept A was determined by the following equation:

$$P(x) = \Phi(A + \log_{10} [x])$$

where of is the cumulative normal distribution function.

This equation makes the assumption that the log-probit dose/response curve has unit slope with respect to the  $\log_{10}$ -dose. Using tables of the standard normal distribution, A is found approximately equal to 3.5, based on a mean value of A for all of the dose/response data. This value was used to determine the probability of a response at various concentrations according to the above equation.

The multi-stage model with a quadratic hazard rate function,

$$h(x) = ax^2 + bx + c,$$

was fit to the data. To estimate the parameters a, b, and c, a maximum likelihood method was used, aided by a computer program, which performed a heuristic search for the best fit. The parameter b dominates for small values of dose x and parameter a dominates for large values.

In Table 30 the risk estimates obtained from these three models, as well as EPA's CAG estimate, have been summarized. The expected number of cancers per million exposed population is shown for daily doses ranging from 0.1  $\mu$ g/day to 100 mg/day. These estimates represent probable upper bounds on the true risk, due to the conversative assumptions that were used. The gap between the estimates is large in the low-dose region; thus, there is a substantial range of uncertainty concerning the actual carcinogenic effects of PCE. However, present scientific methods do not permit a more accurate or definitive assessment of human risk.

Exposure levels and doses to individuals have been estimated for many different exposure conditions. These conditions consider inhalation of PCE in air and ingestion of PCE in food and water. The range of risks associated with body intakes for these exposure conditions, using four risk models, is summarized in Table 31. In addition to the assumptions previously mentioned, all of these risk estimates are based on the assumption that the daily exposures occur continuously over an individual's lifetime.

Estimated excess individual cancers due to continuous lifetime consumption of water contaminated with PCE at average concentration levels range from negligible to less than  $6 \times 10^{-7}$ . At the highest concentration observed in drinking water, the estimated risk of excess individual lifetime cancer is on the order of  $6 \times 10^{-3}$ .

The range of individual predicted excess lifetime cancers associated with non-occupational inhalation intakes extends from negligible additional risks to 9.1 x  $10^{-5}$  for maximum urban exposures (Table 31). For non-occupational intakes due to inhalation near drycleaning facilities, the estimated excess individual risks due to continuous lifetime exposure are on the order of 5.6 x  $10^{-4}$  to 8.5 x  $10^{-2}$ . Continuous lifetime exposures to concentrations likely to occur in coin-operated laundry facilities would result in an estimated excess individual risk of lifetime cancers between 8.2 x  $10^{-3}$  to 8.5 x  $10^{-2}$ , but exposure at these levels is not anticipated to occur continuously throughout an individual's lifetime.

Extrapolation	Exposure		Estimated No. Excess Lifetime Cancers (per Million Population Exposed) <sup>1</sup>				
Model	Level (mg/day): 0.0001	0.001	0.01	0.1	1	10	100
Linear Model	0.03	0.3	3	30	300	3000	30,000
Log-Probit Model	*	*	<0.02	3	233	6200	67,000
Multi-Stage Model	0.02	0.2	2	20	200	2000	22,000
CAG Multi-Stage Mode	0.057	0.57	5.7	5.7	570	5700	57,000

The number of lifetime excess cancers represents the <u>increase</u> in number of cancers over the normal background incidence, assuming that an individual is continuously exposed to tetrachloroethylene at the indicated daily intake over their lifetime. There is considerable variation in the estimated risk due to uncertainty introduced by the use of laboratory rodent data, by the conversion to equivalent human dosage, and by the application of hypothetical dose-response curves. In view of several conservative assumptions that were utilized, it is likely that these predictions overestimate the actual risk to humans.

TABLE 31. RANGES OF CARCINOGENIC RISK TO HUMANS DUE TO ESTIMATED EXPOSURE TO TETRACHLOROETHYLENE<sup>1</sup>

Exposure Route	Estimated Exposure (µg/day)	Range in no. estimated excess lifetime cancers (per Million Population Exposed)
rinking Water		
General Population - Surface Water	< 0.4	$neg^2 = 90.2^3$
Cround Water	< 1	$\frac{2}{\text{neg}^2} - <0.6^3$
Smaller Subpopulation - Surface Water	2-6	$neg^2 - 0.3^3$
- Ground Water	6-8	$neg^2 \sim 0.5^2$
ood	1.2	$neg^2 - 0.07^3$
nhalation		
Rural Remote	1.1-6	$\log^2 - 0.3^3$
Urban	11-160	neg <sup>2</sup> - 91 <sup>3</sup>
- Near Manufacturing Site/Industrial Areas	1.3-2,300	$neg^2 - 1,300^3$
- Near Drycleaning Facilities	2,800-135,000 <sup>6</sup>	$560^4 - 85,000^2$
- Use of Coin-Op Facilities with Drycleaning Equipment	41,000 <sup>6</sup>	$8,200^4 - 30,000^2$
- Occupational	165,000-1,150,000 <sup>6</sup>	$33,000^4 - 481,000^3$
solated Exposures		
Orinking Water - contaminated wells	>50	. >104
- contamination in distribution system	10,000	2,000 <sup>4</sup> - 6,200 <sup>2</sup>

A range of probability is given, based on several different dose-response extrapolation models. The lifetime excess incidence of cancer represents the increase in incidence of cancer over the normal background incidence, assuming that an individual is continuously exposed to tetrachlorocthylene at the indicated daily intake over their lifetime. There is considerable variation in the estimated risk due to uncertainty introduced by the use of laboratory rodent data, by the conversion of equivalent human dosage, and by the application of hypothetical dose-response curves. In view of several conservative assumptions that were utilized, it is likely that these predictions overestimate the actual risk to humans.

Log-probit extrapolation model.

CAG multistage extrapolation model.

<sup>4</sup> Multistage extrapolation model.

<sup>5</sup> Assuming a respiratory flow of 1.2 m<sup>3</sup>/hr while awake (16 hr), 0.4 m<sup>3</sup>/hr while asleep, and respiratory retention of 50%.

<sup>6</sup>Assumed continuous lifetime daily exposure; the resulting risk estimates probably tend to be higher than actually occur because exposure for a given individual is unlikely to be continuous.

Occupational exposures might be much higher, with a corresponding increase in excess lifetime risk to populations exposed in this way.

The total number of excess lifetime cancers resulting from all possible PCE exposure situations cannot be determined, and the results presented above should be considered along with the following: first, the human carcinogenicity of PCE is as yet unproven, second, the size of some of the subpopulations is unknown, and third, the "median" levels for ingestion are not statistically valid for the entire U.S. population.

# 3. Other Human Risks Associated with PCE Exposure

Other than carcinogenic risks, the risks associated with chronic exposure to PCE cannot be quantified. The effects of chronic exposure to PCE in humans have not been well characterized, making assessment of long-term, low-level exposure to PCE difficult.

Tests with laboratory animals have established lowest observedeffect levels of 386 mg/kg body weight over a two-year period. These levels are orders of magnitude above estimated human exposure levels. No indications of teratogenic effects of PCE have been reported.

Acute human exposure to PCE is of concern at high exposure concentrations. In general, little or no effects occur at a concentration of  $700~\text{mg/m}^3$  PCE. Minimal effects (lightheadedness, impaired coordination) become evident at 1,300  $\text{mg/m}^3$ , with more definite indications of CNS depression (mental confusion, lassitude) observed as the concentration increases. Kidney impairment and liver damange have been reported in humans following accidental exposure to PCE but are not well documented.

# B. RISKS TO AQUATIC SYSTEMS

Although no in situ tests have been performed to evaluate the effects of PCE on aquatic organisms, some insight may be gleaned from the laboratory experiments. The lowest concentrations at which toxic effects on a freshwater species were observed was 840  $\mu g/l$  for the fathead minnow. This concentration is two orders of magnitude larger than typical unremarked ambient concentrations (STORET data average was 8.5  $\mu g/l$ ), while the highest level observed was 142  $\mu g/l$ . Effluent concentrations reported in STORET average 57  $\mu g/l$ ; however, the high concentration was 5500  $\mu g/l$  (5.5 mg/l). These latter levels exceed the chronic value cited above.

Lethal concentrations (LC $_{50}$ 's, 96 hours) were similarly well above observed ambient levels of PCE; the LC $_{50}$ 's ranged from 3.5 to 52.2 mg/l for marine organisms and 4.8-21.4 mg/l for freshwater species.

Thus, the maximum effluent concentration exceeds the  $LC_{50}$  for some of the more sensitive species and the chronic value for the species tested. The risks to aquatic organisms, based upon limited laboratory data, do not appear to be widespread. However, risks in the vicinity of an effluent may be significant as evidenced by the fish kills reported.

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#### APPENDIX A

# DESCRIPTION OF OCCUPATIONAL ENVIRONMENTS IN WHICH TETRACHLOROETHYLENE IS USED\*\*

### A. INTRODUCTION

Tetrachloroethylene is, at room temperature, a colorless, sweet-smelling, volatile liquid. It is about 1.5 times heavier than water, and its vapor is about five and three quarters times as dense as air. PCE is an effective solvent for a large number of natural and synthetic organic substances. It is these good solvent properties, low fire hazard, and ability to form an azeotropic mixture with water that have made PCE popular for use in the cleaning of garments and textile fabrics. Approximately 45% of domestic tetrachloroethylene consumption occurs in the drycleaning and textile industries, with approximately 19% used as a metal cleaning solvent (Arthur D. Little, Inc., 1977). Table A-1 is materials balance for occupational use of PCE; the data have been used in this report as a basis for fate modeling.

Tetrachloroethylene is used in drycleaning at approximately 35,000 facilities throughout the United States (NIOSH, 1979). Most of these tetrachlorethylene users are small, independent retail drycleaners. Most retail (commercial) drycleaning is done with equipment that requires the manual transfer of garments damp with solvent. In the textile industry, PCE is used in wool scouring and dye scouring of knits, as well as in laboratory-scale simulation of drycleaning operations for testing of fabric wear characteristics.

The extent of use of PCE in metal cleaning is small as compared with the use of trichloroethylene. The higher boiling point of tetrachloroethylene(121°C versus 87°C) requires the use of substantially more heating for vapor degreasing than is needed with trichloroethylene. The resultant hotter vapor may be desirable for selected applications (e.g., dewaxing) but is generally undesirable as the cleaned material has to be removed at a higher temperature. Tetrachloroethylene is also utilized to a limited extent as a cold cleaning solvent.

PCE is a raw material in the production of some fluorocarbon materials, e.g., Freon 113. In this application, it is utilized in a closed chemical system.

<sup>\*</sup>This appendix is a compilation of information derived from the seven sources listed in the References.

TABLE A-1 MATERIAL BALANCE OF TETRACHLOROETHYLENE USED IN OCCUPATIONAL ENVIRONMENTS

	ľ	Dry C	leaning	<del></del>	1	Degreasing		Fabric	r
	Commercial	Industrial	Coin-Op	Subtotal	Vapor	Cold	Subtotal	Scour ing	Grand Total
References	(4)(6)	(5)(7)	(4)(6)		(1)(3)	(1)(3)		(1)(3)	Grain Total
Number of Facilities	18,750	270	14,500	33,520	3,600	45,800	49,400	2,522	85,442
Pounds PCE Lost per Year	128 x 10 <sup>6</sup>	28.8 x 10 <sup>6</sup>	48.4 x 10 <sup>6</sup>	205.2 x 10 <sup>6</sup>	94.8 x 10 <sup>6</sup>	41 x 10 <sup>6</sup>	135.8 x 10 <sup>6</sup>	120.4 x 10 <sup>6</sup>	461.4 x 10 <sup>6</sup>
PCE Lost Through Solid Waste	21.6 x 10 <sup>6</sup>	0.13 x 10 <sup>6</sup>		21.73 x 10 <sup>6</sup>	1.9 x 10 <sup>6</sup>	2.05 x 10 <sup>6</sup>	3.95 x 10 <sup>6</sup>	0.54 x 10 <sup>6</sup>	26.22 x 10 <sup>6</sup>
PCE Lost Through Incineration					7.6 x 10 <sup>6</sup>	8.2 x 10 <sup>6</sup>	15.8 x 10 <sup>6</sup>		15.8 x 10 <sup>6</sup>
PCE Lost Through Atmosphere	106.4	28.67 x 10 <sup>6</sup>	48.4 x 10 <sup>6</sup>	183.47 ×10 <sup>6</sup>	85.3 x 10 <sup>6</sup>	30.75 x 10 <sup>6</sup>	116.05 x 10 <sup>6</sup>	119.86 x 10 <sup>6</sup>	419.38 × 10 <sup>6</sup>
% Loss in Solid Waste	17	<1		11	2	5	3	<1	6
% Loss in Incineration					8	20	12		3
Z Loss in Atmosphere	83	>99	100	89	90	75	85	>99	91

## 1. Degreasing

# a. Vapor Degreasing

Vapor degreasing is a cleaning process in which organic soil is dissolved and removed through the condensation of hot solvent vapors on the cold, soiled work. Industry sources confirm that a total of 30,000 vapor degreasers are currently operating in the United States, and a fraction of these machines employ tetrachloroethylene.

The most recent and comprehensive survey of the vapor degreasing industry was presented by Dow Chemical Company in a recent EPA report. This survey involved contacting 2,578 plant sites engaged in a manufacturing activity with the metalworking industries and employing more than 20 people. (Most vapor degreasers are believed to be employed in these industries.) When the results of the survey are extrapolated to the entire industry, the population of vapor degreasers in the United States can be defined as shown in Table A-2. Dow Chemical reported that 85% of the vapor degreasers surveyed were using open-top equipment; the remainder were using enclosed, with conveyor systems machines. The distribution of open-top versus enclosed machines did not appear to be correlated with plant sizes in the United States (EPA, 1979).

On the basis of communications with vapor degreaser operators and suppliers, it is estimated that an average of three operating personnel and three maintenance personnel are associated with each opentop vapor degreaser. Twice as many people are likely to be associated with each enclosed machine. These estimates account for rotation and turn-over of personnel and occasional extensive maintenance or cleanout requirements (Arthur D. Little, Inc., 1977).

# b. Cold Cleaning

Cold cleaning (solvent degreasing) involves the use of liquid solvent to remove soil, with solvent being directly hand-applied (rubbing or wiping) in some cases, while spraying or soaking is utilized in other cases. A survey of solvent producers by Dow indicated that 41 million pounds of PCE are utilized in solvent degreasing.

# c. Textile Industry Applications

Tetrachloroethylene is utilized in several processes within the textile industry. It is found as a component of some carrier solvents in the dyeing of synthetics, is employed as a solvent in scouring wool and synthetics, and is utilized in simulated drycleaning operations in order to evaluate fabric wear characteristics.

TABLE A-2. USE OF SOLVENTS IN VAPOR DEGREASING

	Solvent	Trichloroethyene	<u>Tetrachloroethylene</u>	Methyl Chloroform
	Number of Degreasing Tanks	1,500	4,095	5,310
132	Number of Facilities	885	2,700	350
	Number of Exposed Personnel	8,400	23,169	32,174

SOURCE: Arthur D. Little, Inc., estimates based on Dow Survey and conversations with degreaser vendors and operators and solvent manufacturers.

# 2. Drycleaning

## a. Overview

The "drycleaning" process, whereby garments are cleaned in a solvent that is primarily non-aqueous, originated in Paris, France, in the mid-19th century. This process has undergone many refinements and changes since its origin, as gasoline, and carbon tetrachloride have been replaced as drycleaning solvents by Stoddard solvent, tetrachloroethylene, and fluorocarbon 113.

The drycleaning industry encompasses three types of firms. "Commercial drycleaners" are those engaged primarily in drycleaning or dyeing of apparel and household fabrics other than rugs. This segment of the industry is characterized by a large number of independent businessmen, each of whom operates his own small plant. "Industrial drycleaners" are those engaged in supplying laundered or drycleaned work uniforms, wiping towels, dust control items, etc., to industrial and commercial users. "Coin-operated" dry cleaning installations are those that are often found in conjunction with coin-operated laundries. Although the equipment utilized for coin-operated drycleaning is designed to require no attendant operator, many coin-operated installations are manned with an attendant who both conducts routine maintenance procedures and assists customers.

The drycleaning process utilized by both commercial establishments and industrial plants entails removing soils from garments through the use of a non-aqueous solvent. The drycleaning solvents currently in use can be classified as "petroleum" solvents and "synthetic" solvents, with the synthetic category including tetrachloroethylene and trichlorotrifluoroethane (fluorocarbon 113), and the petroleum category including Stoddard solvent and 140F solvent.

On the basis of available census data and communications with industry sources, it is estimated that there are currently 25,000 commercial drycleaners (SIC code 7216) in the United States and that approximately 75% of these establishments utilize tetrachloroethylene as their drycleaning solvent. Approximately 125,000 workers are employed in commercial drycleaning, with an estimated 30,000 of these employees actually operating the drycleaning machinery. While all employees in a commercial drycleaning plant may be exposed to solvent vapors, the drycleaning machine operators are most directly exposed.

Industrial drycleaners (SIC code 7218) are those industrial launderers who operate their own cleaning facilities. Industry sources estimate that there are approximately 500 industrial establishments with drycleaning operations, and these plants utilize either tetrachloroethyleneor petroleum solvents in their drycleaning operations. Industrial drycleaners employ approximately 25,000 workers, with an estimated 2,000 employees directly exposed to solvent as either cleaning machine operators or maintenance personnel.

In each drycleaning plant (commercial or industrial), several discrete operations are performed. The following section describes these operations and the potential of each for exposing employees to PCE and other chemicals.

# b. Process Description

# i. Garment Marking

"Marking" is the process of identifying garments by attaching tags to each garment or stamping an identification code onto an inner surface of the garment. Marking is the first operation performed upon garments entering a cleaning plant and is a necessary prerequisite to garment processing. As garments are delivered to the cleaning plant, they are bundled; before processing can begin, garments must be identified so that, at the conclusion of the drycleaning process, orders can be properly assembled for return to their owners. The marking process usually involves the sorting of garments, both by "due date" and by garment type (light or dark color, fragile or durable garments, etc.).

There are no hazardous chemical or physical agents inherent in the marking process. However, marking areas are often adjacent to the drycleaning area, and marking personnel may be exposed to diffusing solvent emissions that originate from the drycleaning equipment.

# ii. Spotting

"Spotting" involves the selective application of chemicals, steam, detergent, and/or water to loosen or remove specific stains from soiled garments. Spotting is sometimes done prior to drycleaning (pre-spotting), but may also be necessary following the drycleaning step to remove stubborn stains. Depending upon the size of the drycleaning plant and the nature of the drycleaning process, spotting can require a full-time employee; however, this step is usually handled by the drycleaning machine operator. Industrial drycleaning plants generally do not conduct spotting operations.

### iii. Drycleaning

Equipment/Process Categories: Drycleaning is a process during which batches of garments are immersed in solvent and agitated within a horizontally mounted cylinder. This "washing" step is followed by a spin cycle to extract solvent and a drying operation to evaporate any remaining solvent from the damp clothing.

Most commercial PCE equipment involves the use of two machines, the first to wash and extract garments, and the second to dry. This "transfer" equipment requires the manual handling of damp garments. Some PCE drycleaning equipment combines the washing, extraction, and drying steps into a single unit. This type of equipment, known as

"dry-to-dry," is utilized by only a small number (less than 20%) of commercial drycleaners; the need for larger capacity units to achieve production comparable to that of a transfer plant (due to longer residence of a load in a dry-to-dry machine) has limited its spread.

Employee Exposures from Cleaning Operations: The drycleaning machine operator generally is exposed to the highest concentration of solvent within each plant. One major source of direct employee exposure to solvent vapor is the transfer of garments. Garment transfer usually is done manually and typically involves holding garments wet or damp with tetrachloroethylene directly in the employee's breathing zone. Most drycleaners comply with OSHA's current permissible exposure levels of 100 ppm tetrachloroethylene over an 8-hour time-weighted average; however, manual transfer operations result in employee exposures which exceed the peak allowable concentration (300 ppm) specified for PCE by OSHA in 29 CFR 1910.1000. Furthermore, it is unknown how many drycleaners currently meet the exposure levels recommended by the recent NIOSH criteria documents on tetrachloroethylene.

There are several solvent sources compounding the employee exposures that occur during garment transfer operations. Among the common sources of solvent emissions are leaking washer and tumbler door gaskets, tumbler aeration dampers, lint trap and button trap doors, improperly operating water separators, and pump gaskets. These emission sources are generally indicative of inadequate maintenance programs; however, they highlight the need for equipment design that minimizes routine maintenance requirements.

Another source of emissions is the premature removal of garments from the drying cycle. This problem may result from attempts to shorten the cycle for increased productivity or from the presence of solvent-retaining items such as comforters.

Employee Exposures from Solvent Treatment: Other recognized emission sources result from the techniques utilized by drycleaners to maintain the purity of their solvents. During normal operation, solvent is continuously filtered. The filter medium typically consists of either a series of wire mesh strips coated with diatomaceous earth or of a replaceable filter cartridge. Periodically, the filter medium must be replaced. Where cartridge filters are utilized, they must be drained and discarded, a process that often results in excessive employee exposures to residual solvent. Where diatomaceous earth is employed, the filter medium is removed from its mesh carrier by a back wash system, by air bubbling, or by mechanical agitation. The collected filter medium is then either discarded (presenting a handling problem) or, as is usually done at PCE plants, is "cooked" to recover solvent from the filter "muck." Muck cooking can result in significant solvent emissions since the cooker itself contains gaskets that may leak and, if the cooking process is not properly carried out, large amounts of residual solvent may escape into the plant environment when the cooker is opened.

Most drycleaners also employ distillation to purify their solvent. Tetrachloroehylene cleaners utilize a batch atmospheric distillation process. In addition to the potential leak points (gaskets, joints, etc.) in the still itself, misadjustment of the still's water separator can result in the presence of solvent in open-top wastewater containers.

Tetrachloroehylene stills have another potential emission source; the still's relief vent is often located inside the plant building, and may discharge small quantities of air saturated with tetrachloroethyleneval

Activated carbon adsorbers ("sniffers") are utilized by most industrial cleaners and by approximately one-third of the commercial PCE drycleaners to recover solvent from washer and tumbler exhaust lines and from the general plant environment. However, if the carbon bed is not regenerated frequently by steam stripping, significant quantities of solvent may be lost.

# iv. Garment Finishing

The term "finishing" is employed in the drycleaning industry to indicate the "pressing" of garments to remove wrinkles and restore each garment to its original size, shape, and appearance. Pressing equipment is heated with super-heated steam, and pressers may be exposed to elevated heat levels throughout their work shifts. In addition, the application of heat during the garment finishing step will drive off any residual solvent from the garment, so that pressers may be exposed to solvent vapor.

## v. Assembly

Following the finishing step, garments are sorted and assembled, generally in plastic bags. Employees engaged in assembly operations are exposed to the background levels of solvent and heat found throughout the plant.

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