EXTERNAL REVIEW
DRAFT

AQUEOUS AND TERPENE CLEANING

INTERIM REPORT

U.S. Environmental Protection Agency
Office of Toxic Substances
Washington, DC 20460

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November 15, 1990

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PESTICIDES AND TOXIC
SUBSTANCES

Dear Reader:

The Montreal Protocol, as recently amended last June in London, calls for a worldwide effort to phase out the use of all fully halogenated chlorofluorocarbons (CFCs), carbon tetrachloride, halons, and methylchloroform. In addition, the new Clean Air Act Amendments contain similar provisions for phasing out these substances domestically. An important key to phasing out these substances successfully is the development of functionally similar substitutes. An important key to the latter process is the development of information that can be used by chemical manufacturers, processors, equipment manufacturers, users, and others to make near-term decisions on which substitutes and technologies to pursue. To this end, EPA made a commitment during the Second International Conference on CFC and Halon Alternatives held in Washington, DC (October 1989) to prepare interim assessments on the most promising substitute chemicals.

The attached document represents EPA's first effort at interim assessments of the aqueous and terpene cleaners. As new information on these substitutes becomes available, the assessments will be revised. EPA is also releasing an interim assessment on the hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons. Additional substitutes, such as non-HCFC refrigerants and semi-aqueous cleaners, will be considered as data become available.

The interim assessments contain available information on the toxicity of the substitutes and on potential exposure levels to workers, consumers, and the general population from the manufacture, formulation, and use of these chemicals. Because some of these chemicals are not yet in commerce and are still undergoing toxicity testing, the assessment rests on incomplete data and, therefore, should not be interpreted as a final judgment. Nonetheless, the results of these preliminary analyses indicate that aqueous and terpene cleaners can be used in a manner safe to workers, consumers, and the general population given appropriate technological changes and exposure control practices.

In reaching this conclusion, we must emphasize the interim nature of these assessments in two respects. First, as more and better information becomes available on the toxicity of the alternatives and their likely exposures, a more definitive assessment can be conducted. Second, the data used in these analyses are, in many cases, limited and assumptions are often based more on analogy than direct measurement. As new equipment is developed that utilizes these chemicals and as work practices are modified to facilitate use of the substitute chemicals and to meet the needs of the new Clean Air Act Amendments, exposures are likely to be reduced. We urge all companies and workers involved with the production and use of CFC substitutes to take reasonable efforts to ensure that exposures to these chemicals are controlled while additional data are being developed.

We look forward to an increased level of communication with all parties that are affected by the phaseout of CFCs and other substances subject to the Protocol. We hope that these documents will serve as a good starting point for this dialogue at the Third International Conference in Baltimore, Maryland (November 27 through 29), as well as in the months ahead.

Sincerely,

Linda J. Fisher

Linda J. Fisher
Assistant Administrator

TABLE OF CONTENTS

1. EXECUTIVE SUMMARY

BACKGROUND

Over the past decade, there has been heightened concern worldwide over the slow but progressive depletion of the Earth's stratospheric ozone layer, the shield which protects the Earth from ultraviolet (UV-B) radiation. In the 1970s, scientists hypothesized that chlorine from chlorofluorocarbons (CFCs) could destroy stratospheric ozone, thus increasing the amount of UV-B radiation reaching the Earth's surface. Increased UV-B radiation can lead to increased cases of skin cancers and cataracts, and has been linked to crop, fish, and materials damage. Bromochlorofluorocarbons (halons) also destroy stratospheric ozone, and are believed to do so at a faster rate than CFCs.

In 1978, the United States banned the use of CFCs in non-essential aerosols (40 CFR 762) in an effort to halt ozone depletion. By 1982, however, the global production of CFCs had risen, thereby negating the decrease in use that had resulted from the 1978 aerosol ban in the U. S. and other nations. Uses of CFCs include refrigeration, metal and electronics cleaning, production of insulating foam, mobile air conditioning, and sterilization.

Montreal Protocol

The increase in CFC production prompted officials in the United Nations Environment Programme (UNEP) to develop and promote a multilateral response to stratospheric ozone depletion. These efforts resulted in the development of an international agreement -- the 1985 Vienna Convention To Protect the Ozone Layer -- which provided the framework for the eventual adoption of the Montreal Protocol on Substances That Deplete the Ozone Layer. The Montreal Protocol was signed in 1987, ratified in the U. S. in 1988, and became effective worldwide on January 1, 1989. To date, 64 nations, 28 of which are developing countries, have ratified the Protocol.

The Montreal Protocol, as initially ratified, requires a freeze in production and consumption, at 1986 levels, of the following chemicals:

CFC-11	Trichlorofluoromethane
CFC-12	Dichlorodifluoromethane
CFC-113	1,1,2-Trichloro-1,2,2-trifluoroethane
CFC-114	1,2-Dichlorotetrafluoroethane
CFC-115	Chloropentafluoroethane

The freeze is to be followed by a phased-in reduction to 80 percent of 1986 levels beginning in mid-1993 and 50 percent beginning in mid-1998. The Protocol also limits the production and consumption to 1986 levels of halons 1211, 1301, and 2402, beginning in 1992. These reductions are to be accomplished by allocating production and consumption allowances to firms that produced and imported these chemicals in 1986, based on their 1986 levels of activity.

On August 12, 1988, under the authority of the Clean Air Act, EPA promulgated regulations to implement the reductions called for in the Montreal Protocol (53 FR 20566).

London Amendments to the Montreal Protocol

Scientists measuring stratospheric ozone have concluded that the amount of global ozone in northern hemisphere mid-latitudes has decreased 1.7 to 3 percent from 1969 to 1986, with the lowest levels occurring in winter. This decrease is two to three times greater than had been predicted by atmospheric models. Several extensive scientific investigations also produced evidence that CFCs led to decreases in stratospheric ozone during the spring months in the area over the Antarctic pole (sometimes called the Antarctic ozone "hole").

Scientists believe that the naturally occurring atmospheric concentration of chlorine is 0.7 part per billion (ppb). When the Antarctic ozone hole was first observed in the mid 1970s, the chlorine concentration equalled approximately 2.0 ppb; it is currently at 3.0 ppb. EPA has concluded that levels of chlorine and bromine in the atmosphere will continue to increase measurably despite the reductions in CFCs required by the Montreal Protocol. Concentrations of chlorine are predicted to exceed 8 ppb by the year 2075.

Based on these assessments, the U.S. and other Parties to the Montreal Protocol determined that further restrictions, including controls on other chlorinated compounds and an eventual phaseout of CFCs, were warranted.

In June 1990, the Parties met again in London to formally amend the Montreal Protocol to include more stringent provisions. Under the revised Protocol:

- o all fully halogenated CFCs and carbon tetrachloride will be phased-out by 2000,

- o halons will also be phased-out by 2000 with exemptions for essential uses, and

- o methyl chloroform will be phased-out by 2005.

In addition, the Parties issued a non-binding declaration calling for HCFCs to be used only when other alternatives are not feasible, with phaseout by 2020 if possible, but no later than 2040. These restrictions are based on a series of recently completed scientific, economic, and technological assessments prepared by the Parties to the Protocol.

Clean Air Act Amendments

In November 1990, the Clean Air Act was amended to include a number of provisions that will eliminate the production of CFCs, halons, carbon tetrachloride, and methyl chloroform by the turn of the century. One key provision requires EPA to set "Lowest Achievable Emission Levels" for CFCs in the air-conditioning and refrigeration sectors and prohibits venting of HCFCs in these sectors within the next two years. In addition, the new Clean Air Act requires recycling of all refrigerants in mobile air-conditioning within the next five years.

INTERIM REPORTS

To increase the public's knowledge of the potential CFC replacement chemicals, EPA has been working to characterize the human health and environmental risks associated with the major substitutes for CFCs and halons. In late 1989, EPA released a draft strategy document, "CFC Substitutes Human Health and Environmental Effects Program," that outlined the Agency's approach to this task. Several offices within EPA, primarily the Office of Toxic Substances (OTS), the Office of Air and Radiation (OAR), and the Office of Water (OW), were involved in the creation of the strategy document.

A focal point of the strategy was the creation of interim reports which should help provide the public with an early indication of the health and environmental impacts of major chemical alternatives to the ozone depletors. Chemicals are selected for assessment in the interim reports based on projected use volumes and the potential for significant increases in exposures and releases, rather than because of specific toxicity problems associated with the chemicals.

The interim reports are to be based on data available at the time of publication, rather than being comprehensive documents. Although the data in the interim reports can be expected to change in these fast-moving fields, EPA believes that industry and the public should have access to the information as it becomes available. Where data for a particular chemical are not available, EPA relies on closely related chemicals and scientific judgment to estimate hazard and exposure factors. EPA will prepare future reports as new data on these chemicals become available or as other substitutes or exposure scenarios are identified.

This interim report focuses on eight terpenes and twenty aqueous cleaner chemicals as feasible substitutes for CFC-113 and methyl chloroform, another ozone-depleting chemical, in metal and electronics cleaning. These chemicals are:

Aqueous Cleaners

- Ammonium hydroxide (CAS # 1336-21-6), potassium hydroxide (CAS # 1310-58-3), sodium hydroxide (CAS # 1310-73-2)
- Diethylene glycol monobutyl ether (CAS # 112-34-5)
- Dodecanedioic acid (CAS # 693-23-2)
- Ethylenediaminetetraacetic acid (CAS # 60-00-4) and its tetrasodium salt (CAS # 64-02-8)
- Monoethanolamine (CAS # 141-43-5), diethanolamine (CAS # 111-42-2), triethanolamine (CAS # 102-71-6)
- Borax (CAS # 1303-96-4)
- Sodium carbonate (CAS # 497-19-8)
- Sodium gluconate (CAS # 527-07-1)
- Sodium silicate (CAS # 1344-09-8) and sodium metasilicate (CAS # 6834-92-0)
- Sodium tripolyphosphate (CAS # 7758-29-4), trisodium phosphate (CAS # 7601-54-9), tetrasodium pyrophosphate (CAS # 7722-88-5), tetrapotassium pyrophosphate (CAS # 7320-34-5)
- Sodium xylene sulfonate (CAS # 1300-72-7)

Terpene Cleaners

- d-limonene (CAS # 5989-27-5)
- anethole (CAS # 480-23-8)
- alpha-pinene (α-pinene) (CAS # 7785-70-8)
- beta-pinene (ß-pinene) (CAS # 18172-67-3)
- alpha-terpinene (α-terpinene) (CAS # 99-86-5)
- beta-terpinene (ß-terpinene) (CAS # 99-85-4)
- terpinolene (CAS # 586-62-9)
- dipentene (dl-limonene) (CAS # 138-86-3)

For purposes of this report, the term "hazard" refers to the potential for human health or environmental effects because of the inherent toxicity of a chemical. "Exposure" addresses potential exposures to workers who manufacture, process, or use aqueous or terpene cleaners, and the general public exposed to releases from industrial sites.

Aqueous and terpene cleaners are expected to become only partial replacements for CFC-113 and methyl chloroform in metal and electronics cleaning applications. Aqueous and terpene cleaners are not expected to be used in other CFC applications such as mobile air-conditioning, refrigeration, foam insulation, and sterilization. A separate EPA report, "Hydrofluorocarbons and Hydrochlorofluorocarbons Interim Report," presents EPA's assessment of the HCFCs and HFCs as substitutes in these major CFC use categories.

For purposes of this report, aqueous cleaners are assumed to replace 30% of the CFC-113 and methyl chloroform used in electronics cleaning and 40% of the CFC-113 and methyl chloroform used in metal cleaning. Terpenes are assumed to replace 25% of CFC-113 and methyl chloroform in electronics cleaning and 10% in metal cleaning. These estimates were developed to provide an indication of the order of magnitude of potential total releases. The actual replacement may be higher or lower in specific use areas.

Selection of the aqueous and terpene cleaners for this report was based on projected use volume aggregated from responses to letters sent by EPA's Office of Air and Radiation (OAR) to industrial and military installations under Section 114 of the Clean Air Act. At that time, these compounds were viewed as potential high-volume substitutes for the electronic and metal-cleaning uses of CFCs. In this quickly changing field, other substitutes, such as aliphatic hydrocarbons [e.g., Axeral (trade name)] and n-methyl-pyrrolidone are now also being considered by industry for these uses. These other substitutes also warrant a similar review, but due to time constraints, could not be included in this report. The absence of their review does not constitute an endorsement of their use over aqueous and terpene cleaners. Future assessments will include, but not be limited to, these other compounds. In the meantime, developers and users of CFC substitutes should consider the following:

- In developing and using alternatives to the ozone depletors, care must be taken that in solving one problem we do not create another. Any chemical or process that takes a significant portion of the market should be capable of being used in a safe and environmentally acceptable manner.

- In general, when making decisions about how to replace the ozone-depleting chemicals, EPA encourages industry to first

consider a preventive approach that will reduce overall use of chemicals through toxics use reduction, alternative processes, or conservation. In situations where these options do not exist, industry should avoid replacing ozone depletors with chemicals that possess known hazards and that cannot be used in a safe manner. EPA also cautions industry to be prudent in choosing any chemical for which there is a lack of hazard information and encourages those actions which would reduce exposure and release to the environment. Although chlorinated solvents such as methylene chloride, trichloroethylene, and perchloroethylene are also used in these applications, they are not considered good replacements for CFC-113 and methyl chloroform due to their potential adverse health effects.

Despite the limitations of this report due to lack of available information, there are several conclusions that can be drawn from this preliminary assessment. These findings are summarized below. This information should be provided to formulators, users, and the workforce handling these substitutes.

OVERALL FINDINGS OF THIS ASSESSMENT

The interim assessment evaluated the available information on the toxicity of the aqueous and terpene cleaners, as well as the potential exposure levels to workers and the general population from the manufacture, formulation, and use of these cleaners. Because many of these chemicals are not yet used widely in these applications, the assessment necessarily rests on incomplete data and, therefore, should not be interpreted as a final judgment. Nonetheless, the results of these preliminary analyses indicate that the aqueous and terpene cleaners can be used in a manner safe to workers, the general population, and the environment, given appropriate technological changes and exposure control practices.

In reaching this conclusion, we must emphasize the interim nature of this assessment in two respects. First, as more and better information becomes available on the toxicity of the alternatives and their likely exposures, a more definitive assessment can be conducted. Second, the data used in these analyses are, in many cases, limited, and assumptions are often based more on analogy than on direct measurement. As new equipment is developed that utilizes these chemicals, and as work practices are modified to facilitate use of the substitute chemicals, exposures are likely to be reduced. We urge all companies and workers involved with the production and use of CFC substitutes to take reasonable efforts to ensure that exposures to these chemicals are controlled while additional data are being developed.

Following are some general conclusions regarding toxicity and exposure for the aqueous and terpene cleaners.

TERPENES

Toxicity

Although the terpenes are generally of low to moderate toxicity, they are more biologically active than the CFCs, a class of chemicals that has long been recognized as having low toxicity. As discussed in Section 2, terpenes have been tested for some adverse effects in laboratory animals. Tests were conducted for general toxicity, developmental effects, neurotoxicity, and carcinogenicity. d-Limonene induced kidney toxicity and tumors in male rats only. The biological significance of these effects for humans is uncertain. At high doses, developmental effects were seen in mice and rabbits. Studies in rats provide a basis of concern for possible reproductive toxicity. Liver effects were seen in mice at high doses. In one study, α-pinene has been shown not to induce neurotoxicity. Dermal sensitization due to impurities is documented in humans. Undiluted terpenes are moderate skin irritants.

Exposure

For purposes of this report, 25% of the volume of CFC-113 and methyl chloroform used in electronic cleaning was assumed to be replaced with terpene cleaners. In addition, 10% of their use in metal cleaning is assumed to be replaced with terpenes.

General Population

The physical/chemical properties of these substances, together with known industrial use practices, indicate that exposures to the general population resulting from cleaning electronics and metals would be through water. Modeling estimates of exposures to the general population from these uses via drinking water and fish consumption do not indicate a basis for concern and are discussed later in this document. Measured values of terpenes in water and fish are needed to more fully characterize general population exposures.

Occupational

In an effort to understand occupational exposures, the Agency estimated preliminary exposures in two occupational settings: electronic printed circuit (PC) board and metal

cleaning. Because these compounds are not currently used for metal and electronics cleaning to a great extent, no measured occupational exposure data are available. EPA used exposure information on other metal and electronics cleaning chemicals (CFC-113 and methyl chloroform) as surrogate exposure data; in other situations, modeling information was used to infer potential occupational exposures. The Agency recognizes the limitations inherent in the occupational exposure analysis, in particular, the reliance on the existing CFC-113 and methyl chloroform data to predict exposures for terpenes. However, the results of this analysis can guide future and existing users of the terpenes. Use-specific exposure information is discussed in Section 3.

Traditionally, exposures to the CFCs have been relatively high, compared to other industrial chemicals, because of the well-known biological stability of the compounds. In contrast, the physical and chemical characteristics of the terpenes (e.g., odor and flammability) will dictate a need to use these substances in ways that reduce the potential for exposure. Nonetheless, an evaluation of the available toxicity data for most of the monoterpenes (excluding anethole, a flavoring and fragrance agent, which is not expected to be used in cleaning applications) and estimated occupational exposures are not problematic for all scenarios, except manufacturing. In the manufacturing situation, outerbound exposures could be reached during some practices, thus suggesting the need to further examine these levels and the need for appropriate controls.

It should be noted that terpenes will not be direct replacements for current CFCs in many cases. New technologies and equipment will be developed or existing equipment will be retooled to allow the use of these cleaners. New equipment may result in exposures that are lower than the estimated exposures summarized above and discussed in Section 3.

Environmental

Most environmental releases resulting from use of terpenes will be to water, based on the cleaning operation and their physical/chemical properties. Releases during manufacturing and formulation are to air and land (landfill or incineration) and appear to have minimal exposure potential.

The Agency believes that discharges containing terpenes will undergo gravity separation (pretreatment) in most instances, followed by wastewater treatment (see Section 4). Subsequent to these treatments, surface water concentrations resulting from electronics and metal cleaning uses of terpenes may reach levels that in worst case conditions (minimal dilution in receiving streams) have been shown to cause toxicity to aquatic organisms

in limited laboratory studies. Without efficient process controls (e.g., gravity separation, wastewater treatment, recycling, controlled disposal), surface water concentrations resulting from electronic and metal cleaning operations may exceed predicted aquatic toxicity levels.

AQUEOUS CLEANERS

Toxicity

Most of the 20 aqueous cleaner chemicals addressed in this report have been used widely in cleaning and other industrial applications for many years. As discussed in Section 2 and summarized below, some of the constituents used in aqueous cleaner formulations induce adverse effects in laboratory animals at low to moderate dose levels. These compounds include: diethylene glycol monobutyl ether (DGBE); monoethanolamine (MEA); diethanolamine (DEA); triethanolamine (TEA); and borax.

DGBE is currently the subject of an Agency test rule based on the concerns for potential toxicity and widespread exposure. Limited data on the ethanolamines indicate that liver and kidney effects and neurotoxicity occur at low dose levels in animals. The ethanolamines can be eye and skin irritants. However, they are used in cosmetic preparations and are also designed for intermittent applications (e.g., soaps and shampoos).

Exposure

General Population

The physical/chemical properties of these substances, together with known industrial use practices, indicate that exposures to the general population resulting from electronics and metal cleaning would be through water. Estimated exposures, using modeling techniques, to the general population via drinking water and fish consumption do not indicate a basis for concern and are presented later in this document. Measured values for aqueous cleaners in water and fish are needed to more fully characterize general population exposures.

Occupational

In an effort to understand occupational exposures, the Agency estimated exposures in occupational settings. Because insufficient monitoring data were found for all 20 chemicals, the Agency used monitoring data on surrogate chemicals (CFC-113 and methyl chloroform), OSHA permissible exposure limits (PELs), or modeling techniques to evaluate potential exposure, as

appropriate. The Agency recognizes the limitations inherent in these approaches to exposure analysis, particularly the reliance on existing CFC-113 and methyl chloroform data to predict exposures for aqueous cleaner components such as DGBE and the ethanolamines.

Although there is considerable uncertainty in the exposure estimates, the available data suggest that formulation and use of the cleaners represent the greatest potential exposures. Good workplace practices should be integrated into these operations to ensure that exposures are controlled. In the absence of protective equipment (e.g., gloves), exposure levels due to the formulation and use of DGBE and the ethanolamines in particular may be inappropriate.

The assessment does not consider any reduction of occupational or environmental exposures that would result from the use of personal protective equipment or the use of new cleaning processes using aqueous cleaners. Information on exposure estimates are presented in Section 3.

Environmental

Most environmental releases of the aqueous cleaners will be to water. Among the 20 compounds, surface water concentrations of MEA and TEA from electronics cleaning may reach levels, on some release days, that have been shown to cause chronic toxicity to algae, the most sensitive freshwater species for these chemicals.

In addition, sodium tripolyphosphate, trisodium phosphate, tetrasodium pyrophosphate, and tetrapotassium pyrophosphate have high potential to cause algal blooms and eutrophication in freshwater environments. Release of these compounds to water presents well known risks to aquatic species.

The use of appropriate process controls (e.g., wastewater treatment, recycling, controlled disposal) is recommended to ensure that surface water concentrations resulting from electronics cleaning operations do not exceed predicted aquatic toxicity levels.

NEXT STEPS

At this early stage in the project, it is unclear as to which terpene and aqueous cleaner chemicals will actually substitute for CFC-113 and methyl chloroform and the relative extent of substitution. As this situation becomes clearer, additional toxicity and exposure data may be needed.

OUTLINE OF THIS REPORT

Section 2, Hazard Assessment, presents a summary of EPA's hazard assessment for the 11 categories of aqueous cleaner chemicals and eight terpenes. The term "hazard" refers to the potential for human health or environmental effects because of the inherent toxicity of a chemical.

Section 3, Industrial Processes and Occupational Exposure, outlines the processes by which the aqueous and terpene cleaners are produced, formulated and used, and estimates potential occupational exposures of workers through dermal contact or inhalation, during manufacture, formulation, and use.

Section 4, Environmental Release, Fate, and Exposure, presents EPA's estimates of likely releases of the aqueous and terpene cleaners into the environment, discusses their patterns of persistence and accumulation in the environment, and presents an exposure analysis of industrial releases of these chemicals into water bodies.

More complete assessments of the human health and ecotoxicity effects of the aqueous and terpene cleaners can be found in EPA's support documents. The support documents and other references are listed at the end of this report. Additional copies of this document and EPA support documents can be obtained through:

TSCA Assistance Information Service
U.S. Environmental Protection Agency
Office of Toxic Substances (TS-799)
Washington, D.C. 20460

Telephone: (202) 554-1404

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2. HAZARD ASSESSMENT

This chapter provides an overview of the health and environmental hazard information of several candidate aqueous and terpene cleaner chemicals. This hazard assessment is based on readily available published literature and information obtained from EPA program office files. For more detailed evaluation and references, refer to EPA's support documents.

2.1 AQUEOUS CLEANERS

The 20 candidate aqueous cleaner chemicals presented in this section are grouped into 11 categories. They were selected from among the many chemicals that could be used in aqueous cleaner formulations based on production volume estimates obtained from industry.

Most of the aqueous cleaner candidates are well known, widely used industrial chemicals, and, as to be expected, all have some type of current application in soap or detergent formulations.

Because of the numerous possible combinations of chemicals present in cleaning formulations (see chapter 3 for more discussion), this document does not attempt to evaluate the human health or environmental effects of the aqueous cleaner formulations themselves. Rather, it assesses the effects of the 20 chemicals separately. Only a few of these chemicals have undergone extensive toxicity testing, and a number of these tests suffer from shortcomings that limit their use for hazard assessment. Nevertheless, the test data summarized below provide a general characterization of the toxicological properties associated with each chemical.

2.1.1 AMMONIUM HYDROXIDE, POTASSIUM HYDROXIDE, & SODIUM HYDROXIDE

NH_4OH, KOH, NaOH

These three strongly alkaline substances, which have wide current use as components of soaps or detergents, are well known for their caustic nature in the presence of moisture. These chemicals are expected to be used to clean metal surfaces. Contact of living tissue with the pure compounds by all routes of exposure usually produces immediate damage to living tissue, with the extent of damage being dependent on the pH of the solution and duration of exposure. The higher the pH (usually within the range 10 to 14), the greater the damage. There appears to be a latent period following skin contact to NaOH (the only compound with such data) during which no sensation of irritation occurs, and the duration of this period appears to be inversely related to pH.

There are instances (suicide attempts, accidents) in which massive oral exposure to NaOH has led to esophageal cancer, but available information suggests that the cancer is the result of extensive tissue destruction followed by tissue regeneration, rather than a genotoxic mechanism.

All three compounds have moderate to low acute toxicity to aquatic species, with vertebrates being more sensitive than invertebrates. Available data indicate that KOH and NaOH will not pose a hazard of chronic toxicity to aquatic organisms and that they will not bioaccumulate or persist in the environment. Indirectly, NH_4OH is most likely to cause chronic toxicity due to potential release of ammonia. Release of ammonia depends on the temperature, hardness, and pH of the ambient water. There is a chronic toxicity value of 85 µg/l (27-day EC_{50}) for NH_4OH and acute toxicity values of 80 mg/l (96-hour LC_{50}) for KOH and 43 mg/l (96-hour LC_{50}) for NaOH.

2.1.2 DIETHYLENE GLYCOL MONOBUTYL ETHER (DGBE)

$HOCH_2CH_2OCH_2CH_2O(CH_2)_3CH_2$

DGBE is widely used as a solvent for inks, dyes, enamels, and paints and, at low levels, for hard-surface cleaning agents. It is the subject of an Agency test rule [Federal Register Feb. 26, 1988] that requires manufacturers and processors of the chemical to perform testing for certain health effects based on concern for potential toxicity and concern for widespread exposure to workers and the general population by the dermal and

inhalational routes through manufacture, processing, and use. Because of technical difficulties in testing low-vapor-pressure compounds such as DGBE by inhalation, the recommended test route is dermal.

Animal data show that DGBE has low acute toxicity by the oral and dermal routes and is a slight skin irritant at 300 mg/kg. In undiluted form or in 50% solution, however, it is severely irritating to rabbit eyes. There is no information on the carcinogenicity of DGBE; three analogues are under consideration for cancer testing by the National Toxicology Program. The weight of available evidence indicates that DGBE is not mutagenic. Available studies of developmental toxicity, which suffer from various limitations, show no evidence of developmental toxicity, but they do provide evidence of maternal toxicity at doses as low as 25 mg/kg. Two studies of reproductive toxicity, also inadequate for complete hazard assessment, are negative for reproductive toxicity or parental systemic toxicity. Data on the neurotoxicity of DGBE are inadequate to draw any conclusions as to this effect.

Several subchronic (28- to 120-day) tests in rats and rabbits by the oral, inhalational, and dermal routes show that the blood is the target organ of DGBE toxicity. Dose levels at which adverse effects are seen are 51 mg/kg/day by the oral route, 13 mg/m^3 by inhalation (approximately equal to 2 mg/kg/day), and 30 mg/kg/day by the dermal route. Findings in inhalation toxicity studies indicate that DGBE may be toxic to the liver at exposure concentrations of 40 mg/m^3.

DGBE exhibits a low level of acute toxicity to aquatic organisms, with LC_{50} values for fish, daphnids, and algae being >1,000 mg/l. There are no data on the chronic aquatic toxicity of DGBE to fish and aquatic invertebrates (e.g., daphnids) or on the bioconcentration potential or persistence of DGBE in the environment.

DGBE is the subject of a test rule promulgated by EPA because of toxicity concerns and exposures resulting from all its many uses. The tests requested under the rule consist of a subchronic test with particular emphasis on reproductive, hematological, and kidney effects; neurotoxicity tests; a developmental neurotoxicity test; and a pharmacokinetics test, all by the dermal route. The satellite reproductive toxicity test and the pharmacokinetics test have been completed. Remaining data gaps are standard developmental and reproductive toxicity tests by the oral route, neurotoxicity tests by the inhalation route, and a subchronic (90-day) test for chronic toxicity by the oral route from which a NOAEL can be obtained. For ecological effects, data gaps are in the areas of chronic aquatic toxicity to fish and aquatic invertebrates and bioconcentration potential or persistence in the environment.

2.1.3 DODECANEDIOIC ACID (DDA)

$$HOOC(CH_2)_{10}COOH$$

DDA is used as an intermediate in the manufacture of plasticizers, lubricants, adhesives, polyesters, corrosion inhibitors, and bleaching agents. Virtually no information was found on the toxicity of DDA in the literature. Based on a consideration of structure-activity relationships using data on structural analogues and based on professional judgment, DDA is not expected to be significantly toxic to humans.

With respect to environmental toxicity, estimations of maximum toxicity derived from QSAR (quantitative structure-activity-relationship) equations for neutral organics indicate that DDA may be moderately to highly toxic to aquatic organisms. Maximum fish 96-hr LC_{50} values range from 6 to 17 mg/l, the mysid shrimp 96-hr LC_{50} is 2 mg/l, and the daphnid 16-day EC_{50} is 1.5 mg/l.

It is important to note that these values are based on the un-ionized form of DDA; in water, where DDA will be ionized, toxicity is expected to be reduced. There is no information on the chronic aquatic toxicity of DDA or on its bioconcentration and persistence in the environment.

2.1.4 ETHYLENEDIAMINETETRAACETIC ACID (EDTA) & ITS TETRASODIUM SALT

$$(HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)_2, \quad (NaOOCCH_2)_2NCH_2CH_2N(CH_2COONa)_2$$

EDTA and its tetrasodium salt were selected as components for aqueous cleaner formulations because of their well-known ability to form chelates with di- and trivalent metal ions. In addition, EDTA is used as an antioxidant in foods (at an acceptable level of use of 0.01%), and both compounds are used as chelating agents in the treatment of metal poisoning, at doses ranging from 16 to 50 mg/kg/day.

On the basis of available data, EDTA and its tetrasodium salt are not expected to exhibit high acute toxicity by the oral route. EDTA has been implicated as an inducer of hypersensitivity when used as an antimicrobial agent in cosmetics, but a sensitization study in guinea pigs was negative. There are four oral cancer bioassays of EDTA salts in rats and mice that are inadequate for hazard assessment for various reasons. Nevertheless, three of the assays were negative. The fourth showed an increased incidence of neoplasms in female rats, but

the increase was attributed to the longer lifespan of the EDTA-treated animals. These feeding studies do show that EDTA salts have low systemic toxicity by the oral route at doses as high as 2,500 mg/kg/day for rats. The only treatment-related effects in rats fed this dose were reduced body weight gain and increased blood coagulation time. Mutagenicity data are sparse and inconclusive, and there is no information on neurotoxicity.

Several studies demonstrate that EDTA is maternally and developmentally toxic and, additionally, that it may have adverse effects on the reproductive system. Data are from studies in which only one or two doses were tested, most of the test doses are high, treatment did not occur throughout organogenesis, and assessment of fetal development was incomplete. Doses in the oral studies (diet and gavage) ranged from approximately 950 to 1,375 mg/kg/day. The only exception is a study in which EDTA was applied to the eyes of pregnant rabbits (an unusual route of administration), at an approximate dose of 3 mg/kg; this dose resulted in 70% embryo/fetal mortality.

The apparent discrepancy between the results of the four oral lifetime studies in rats and the oral developmental toxicity studies in rats, at comparable dose levels, can probably be attributed to the sensitivity of pregnant animals or to strain differences.

Available data show that EDTA and its salts have low to moderate acute toxicity to aquatic organisms (i.e., acute toxicity values are >100 mg/l for freshwater fish and aquatic invertebrates and >1 but <100 mg/l for green algae), and they are expected to have low chronic toxicity based on a chronic value of approximately 1 mg/l for inhibition of algal growth.

Information gaps are noted in the following areas: extent of gastrointestinal absorption, mutagenicity, developmental and reproductive toxicity, acute toxicity to algae.

2.1.5 MONOETHANOLAMINE (MEA), DIETHANOLAMINE (DEA), & TRIETHANOLAMINE (TEA)

$NH_2CH_2CH_2OH$, $NH(CH_2CH_2OH)_2$, $N(CH_2CH_2OH)_3$

MEA, DEA, and TEA are strong bases that are widely used in the chemical and pharmaceutical industries as intermediates for the production of emulsifiers, detergents, solubilizers, cosmetics, drugs, and textile-finishing agents.

At high solution concentrations, all three compounds are moderate to severe skin and eye irritants, and data from one study with humans indicate that TEA (2% solution) may be a weak

skin sensitizer. In rats, single oral doses of ≥200 and ≥400 mg/kg produced effects on the liver and kidney, respectively.

There is no information on the carcinogenicity of MEA and DEA; a dermal bioassay of DEA is planned for 1990. There is limited evidence that TEA has human carcinogenic potential, based on the finding of an increased tumor incidence in mice and equivocal results in rats. A dermal bioassay of TEA with rats and mice is in progress. The weight of evidence for all three amines indicates that none represents a mutagenicity hazard to humans. It should be noted that DEA and TEA can be converted to the carcinogen N-nitrosodiethanolamine (NDELA) in the presence of nitrosating agents. The reaction can occur in the stomach, by the reaction of ingested amines with nitrosating agents in foods or medications. It can also occur in other, nonbiological environments, as NDELA has been detected in consumer or industrial products containing ethanolamines.

A developmental toxicity study of MEA shows that this compound is maternally and developmentally toxic in rats; the lowest effect level is 50 mg/kg for developmental effects in rats by the oral route. Data on DEA and TEA suggest that these compounds are also developmentally toxic. There are no reproductive studies of MEA, DEA, or TEA but, in a subchronic inhalation study of MEA, suppressed spermatogenesis was found in guinea pigs and dogs exposed to 75 to 102 ppm MEA for up to 30 days.

Given available data, the most significant health effects for these amines are neurotoxicity, organ toxicity, and ecotoxicity. Neurotoxicity was noted in dogs, rats, and guinea pigs exposed continuously by inhalation to MEA at concentrations as low as 11 mg/kg/day for rats. TEA produced neurotoxic effects in rats and guinea pigs fed doses as low as 200 mg/kg/day. Although there are no data on the neurotoxicity of DEA, based on structural analogy, DEA is also expected to elicit this effect.

The target tissues for all three amines, in repeated-dose studies by the oral, dermal, and inhalational routes, are the liver and kidney. Dose levels at which effects are seen in animals are 170 mg/kg/day by the oral route (DEA), 145 mg/kg/day by the inhalational route (MEA), and 4 mg/kg by the dermal route (MEA).

MEA, DEA, and TEA show low to moderate acute toxicity (i.e., values are >1 but <100 mg/l) and moderate chronic toxicity to aquatic organisms. Average chronic toxicity values for freshwater green algae, the most sensitive freshwater aquatic species, are 0.850 mg/l for MEA; 6.6 mg/l for DEA; and 1.8 mg/l for TEA. The compounds have a low potential to bioconcentrate and, thus, food-chain transport should be minimal.

Areas lacking adequate information are absorption and metabolism (DEA and TEA), carcinogenicity (DEA and MEA), mutagenicity, developmental and reproductive toxicity, organ toxicity (i.e., 90-day test data), neurotoxicity, acute toxicity to saltwater organisms, chronic toxicity to fish or aquatic invertebrates, and bioconcentration in fish.

2.1.6 BORAX

$$Na_2B_4O_7.10H_2O$$

Borax, or sodium tetraborate decahydrate, is primarily used in soaps and detergents, with lesser amounts being used in fertilizers and pharmaceuticals. Toxicity data on boric acid are included here because both borax and boric acid dissociate in the presence of body fluids to the borate ion and both compounds are considered toxicologically equivalent. Boron is an element normally consumed by humans in quantities ranging from 0.02 to 0.3 mg/kg/day, depending on the diet.

Human and animal data show that borax has moderate acute toxicity by the oral route. Based on data from several animal bioassays, there is no reason to suspect that borax has human carcinogenic potential. The compound is not mutagenic in bacteria, weakly mutagenic and cytotoxic in cultured mammalian cell assays, and negative in a cell transformation assay. There is no information on the developmental toxicity of borax or boric acid.

Chronic and subchronic oral exposure of animals to borax or boric acid produces toxicity to the testes, blood, kidney, liver, spleen, brain, and adrenals, with these effects being noted in at least two species and effects on the testes and blood being noted in rats, mice, and dogs. In addition, there is a case study in which an infant exposed to 43 mg boron/kg/day for 12 weeks developed anemia. Nine case reports document neurotoxic signs in infants at doses as low as 8 mg boron/kg/day over a 5-week period.

The most significant effect seen in animals is reproductive toxicity (i.e., testicular atrophy). Doses at which no effects were noted in chronic studies are 17.5 mg boron/kg in rats and 8.8 mg boron/kg in dogs.

Borax shows low acute toxicity to aquatic organisms, with 24-hr LC_{50}'s ranging from 162 mg/l to 111 g/l in tested species. The boron equivalent range is 4.6 to 3,145 mg/l. It is moderately toxic upon chronic exposure. Chronic exposures to aqueous solutions of borax at concentrations >3.5 mg/l (boron equivalent concentration >0.1 mg/l) produced teratogenic effects

in fish. Because of the relatively high water solubility of borax, it will remain in the water column in dissociated form.

Areas lacking adequate information include: pharmacokinetics, acute inhalation toxicity, mutagenicity, developmental and reproductive toxicity, and systemic effects (i.e., a 90-day test).

2.1.7 ADDITIONAL SODIUM & POTASSIUM SALTS

Of the remaining nine aqueous cleaner chemicals, only the phosphates appear to be associated with significant toxicity. The current intended use of all of these salts except sodium xylene sulfonate is in cleaning of metal surfaces; sodium xylene sulfonate may find application in cleaning of metal surfaces and electronic components (e.g., PC boards).

Sodium tripolyphosphate ($Na_5P_3O_{10}$), trisodium phosphate (Na_3PO_4), tetrasodium pyrophosphate ($Na_4P_2O_7$), and tetrapotassium pyrophosphate ($K_4P_2O_7$) have high potential to cause algal blooms and eutrophication in freshwater environments, and they should never be released to water. The concentration of concern is 100 ng/l (ppt), and it is based on a phosphate concentration of 10 µg/l that was correlated to algal blooms and oxygen depletion (eutrophication). Available information on health effects does not point to any significant toxicity, but no information was found on the carcinogenicity, developmental/reproductive system toxicity, or neurotoxicity of these compounds.

Data on **sodium carbonate (Na_2CO_3)** and **sodium gluconate [$HOCH_2(COH)_4COONa$]** show that these compounds are not highly toxic to human health or the environment and, even though these data are not complete, both compounds are not expected to pose any significant toxicity. The only concern is over the alkalinity of sodium carbonate and, thus, for irritation to skin or mucous membranes at high solution concentrations of the chemical.

Data on **sodium metasilicate (Na_2SiO_3)** and **sodium silicate ($Na_2Si_3O_7$)** show that they, too, are not highly toxic to human health or the environment. However, data are inadequate in the areas of subchronic toxicity and developmental/reproductive system toxicity, and uncertainty remains as to the toxicity of the compounds in these areas. Although there are also no data on carcinogenicity, mutagenicity, and neurotoxicity, there is low concern for these health effects based on a consideration of the physicochemical properties of the two compounds. Finally, the same caution applies for irritation to skin or mucous membranes at high concentrations of these strongly alkaline compounds in solution.

From the sparse available toxicity data on **sodium xylene sulfonate** ($C_8H_{10}O_3S.Na$) and on the basis of analogue data, the compound is not expected to be carcinogenic and it is expected to have low toxicity to aquatic organisms. It should be noted, however, that there are no data on the acute toxicity, developmental/ reproductive system toxicity. neurotoxicity, or ecotoxicity of this compound, and some uncertainty remains as to its potential toxicity in these areas.

2.2 TERPENE CLEANERS

This section presents a summary of the evaluation of the potential hazards of eight terpene compounds with respect to human health and aquatic toxicity.

The toxicity database for most of the terpenes under review is inadequate for a full evaluation of their potential effects to human health and aquatic organisms. However, the available information indicates that d-limonene and anethole are hepatotoxic in mice and rats, respectively. In addition, the existing data indicate that d-limonene is a developmental toxicant in mice and rabbits, however, neither of the available studies are adequate for establishing LOAELs and NOAELs. Based on limited data in rats, there is also a basis for concern about the potential reproductive toxicity of d-limonene and other terpenes. d-Limonene has also been shown to induce kidney toxicity and kidney tumors in the male rat only. The biological relevance of the male rat kidney response to humans is uncertain.

Evidence suggests that contact dermatitis, or dermal sensitization, may develop when the terpenes are used in a commercial formulation or oxidation products are formed. The pure terpenes themselves do not appear to cause dermal sensitization. In addition, there is a concern for aquatic toxicity for all the terpenes of interest based on test data and Structure Activity Relationship (SAR) analysis. Additional information concerning the chronic toxicity, oncogenicity, mutagenicity, developmental/reproductive effects, neurotoxicity, and acute/chronic aquatic toxicity is needed for most of these terpenes for a complete assessment. More details are given below.

Absorption/Metabolism: Absorption and metabolism data are not available for all the terpenes of interest. The data reviewed are inadequate to fully characterize the pharmacokinetics of the terpenes. However, based on available data on d-limonene, anethole, α- and β-pinene and an analogue, p-cymene, the terpenes are expected to be absorbed from the skin, lungs and gastrointestinal (GI) tract. The available data on d-limonene, α- and β-pinene, and anethole indicate that the terpenes may be metabolized to give hydroxy-substituted and

carboxylic acid derivatives. These derivatives may be conjugated with glucuronic acid or excreted free in the urine.

Acute toxicity: Available acute toxicity studies show that d-limonene is slightly to moderately toxic following a single oral exposure (LD_{50} values range from 3.4-7.9 g/kg). Similarly, α-pinene and anethole are moderately acutely toxic (LD_{50} = 3.7 and 3.2 g/kg, respectively). Whereas, β-pinene and dipentene are not acutely toxic by the oral route (LD_{50} > 5 g/kg). Additional data on these five terpenes show that none are acutely toxic by the dermal route. No acute toxicity data are available for α- and β-terpinene and terpinolene.

Undiluted d-limonene and α-pinene have been reported to cause moderate skin irritation in primary dermal irritation studies with rabbits. However, diluted samples of α- and β-pinene, anethole and dipentene (10-20% in petrolatum) were found not to produce skin irritation in human volunteers. These results indicate that the undiluted terpenes are moderate skin irritants and that diluted or formulated terpenes may not be skin irritants. There is no information on the dermal irritation of α- and β-terpinene and terpinolene. Eye irritation information is not available for any of the eight terpenes.

No data are available on the dermal sensitization potential of α- and β-terpinene and terpinolene. Purified d-limonene, α- and β-pinene, anethole and dipentene have been found not to induce contact dermatitis in humans. However, the oxidative product of a contaminant of some formulated terpenes, delta-3-carene, is a sensitizer. In view that delta-3-carene may be a contaminant in the preparation of some terpenes, and that terpenes are expected to be used in an oxidizing environment, sensitization is a potential problem with commercially available preparations of terpenes contaminated with delta-3-carene.

Subchronic and chronic toxicity: The subchronic and chronic oral toxicity of d-limonene has been adequately tested in rats and mice and has been shown to induce renal toxicity in the male rat. In addition, there were indications of liver toxicity in male mice and general toxicity in female mice at high doses. In a two-year feeding study by the National Toxicology Program (NTP report No. 347), dose-related kidney toxicity was observed in male rats fed with d-limonene at the two doses tested (75 and 150 mg/kg/day). The apparent lowest observed adverse effect level (LOAEL) for kidney toxicity being 75 mg/kg/day. In a subchronic toxicity study (NTP report) and several short-term oral toxicity studies with d-limonene, similar toxic effects to kidneys were observed in male rats. The significance of the kidney toxicity seen in male rats and its relevance to humans is unclear. This is further discussed in the carcinogenicity and mutagenicity section below.

In the chronic toxicity study of d-limonene in mice, signs of general toxicity, such as body weights 5-15% lower than vehicle controls, were observed at the high dose (500 mg/kg/day) in females after week 28. Signs of liver toxicity were seen in the high dose males at 1000 mg/kg/day. Based on the two-year mouse study, there is an apparent no observed adverse effect level (NOAEL) of 250 mg/kg/day for general toxicity in female mice and an apparent NOAEL of 500 mg/kg/day for liver toxicity in male mice.

Anethole has been reported to cause liver toxicity in two subchronic oral toxicity studies. In one study, anethole fed to rats for 90 days at doses of 50, 150, 500, or 1500 mg/kg/day induced liver toxicity in the form of hepatocellular edema and degeneration at the 150-1500 mg/kg/day dose levels. No effects were seen at 50 mg/kg/day. Based on the results of this first study, the apparent NOAEL for liver toxicity is 50 mg/kg/day. In the second study, slight liver toxicity was found in rats fed anethole at 500 mg/kg/day for 15 weeks.

No subchronic or chronic toxicity studies have been conducted on any of the other terpenes.

Carcinogenicity and mutagenicity: Anethole, the only terpene of interest with an aromatic configuration, has been tested in four limited (one year or less) cancer bioassays. No tumorigenic responses were found in any of the available studies. However, there are indications that anethole is a gene mutagen in prokaryotes when tested with metabolic activation.

d-Limonene has been found to induce kidney tumors in the male rat. In a two-year feeding study (NTP report No. 347), a dose-related increased incidence of kidney tumors was seen in male rats at 75 and 150 mg/kg/day. This same study showed no evidence for tumorigenic responses in female rats or male and female mice.

The mechanism by which d-limonene induces nephrotoxicity and kidney tumors in male rats, is not fully understood, and the biological relevance to humans is unclear. However, current data suggest that d-limonene-induced nephropathy and renal neoplasia occur via excessive accumulation of α-2u-globulin in renal tubules. It has been hypothesized that male rat kidney tumors should not be considered as relevant to human risk as other tumors. This is because concentrations of protein homologues in human urine are well below those found for α-2u-globulin in male rats. Given this situation, it is unlikely that enough protein could accumulate in the human kidney following exposure to d-limonene to result in hyaline droplet formation containing this protein. In addition, these human proteins appear to have low binding affinity to d-limonene. The Agency is currently addressing this issue.

No carcinogenicity or mutagenicity data are available for any of the other terpenes of interest.

Reproductive and developmental effects: The available information on the developmental toxicity of the terpenes is limited to one developmental toxicity study in mice and a second one in rabbits which were conducted with d-limonene. Neither study is adequate for establishing LOAELs or NOAELs, due to the small sample sizes. In addition, in the mouse study, only two dose levels were tested, and dosing did not occur throughout the entire period of organogenesis. However, the mouse study does provide evidence of maternal toxicity as demonstrated by a significant reduction in body weight after exposure to 2363 mg/kg/day d-limonene by gavage. Exposure to this level also resulted in developmental toxicity as manifested by a significant increase in the incidence of fetuses with skeletal abnormalities including lumbar ribs, fused ribs, and delayed ossification of several bones in the paws.

In dams allowed to give birth, there was a significant reduction in body weight of male progeny from week 5 to week 7 at the high dose level (2363 mg/kg). However, a similar effect was not seen in females. In addition, a significant increase in absolute and relative weights of the heart, liver, and ovaries in the female pups was observed at the high dose level. Histopathology revealed no gross lesions of the testes or ovaries from pups in all dose groups. No maternal or developmental toxicity was observed after exposure to 591 mg/kg/day (the only other dose tested).

In the rabbit study maternal toxicity was observed after exposure to 500 and 1000 mg/kg/day of d-limonene by gavage; exposure to either dose resulted in a significant reduction in food consumption and body weight, while exposure to 1000 mg/kg/day also led to death. There was no indication of maternal toxicity at the lowest dose tested, 250 mg/kg/day, and there was no significant evidence of developmental toxicity at any dose level. However, a significant increase in the fetal body weight of males in the low dose group was observed. In addition, an increased incidence of fetuses with incomplete lobulation of the lungs and lumbar ribs in all treated groups was noted, although this increase was not statistically significant.

No reproductive toxicity studies have been conducted on terpenes. However, in a 28-day toxicity study in which rats were administered d-limonene by gavage at 277, 554, 1385, or 2770 mg/kg/day, a significant dose-related reduction in absolute ovarian weight in rats after exposure to doses 554-2770 mg/kg/day, and a significant reduction in relative ovarian weight after exposure to 2770 mg/kg/day, were reported. These effects were not noted in a 6-month study at comparable doses. The reasons for this conflicting finding are not known but these

results do provide a basis for concern for possible reproductive toxicity for d-limonene and other terpenes.

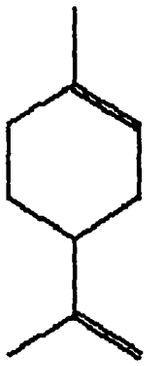
Neurotoxicity: The available neurotoxicity studies on d-limonene and α-pinene showed no compound-related neurotoxic effects. The study on α-pinene was well designed, executed, and analyzed. A functional observational battery (FOB) and neurochemical analysis were performed. No neurotoxic effects were reported in 40 rats exposed via inhalation to 200 mg/kg/day (approximately 300 ppm) of commercial turpentine containing 95% α-pinene for 8 weeks.

A study on a commercially available pet flea and tick dip, containing 78.2% d-limonene and unspecified additional chemicals, reported several neurotoxic signs and symptoms. However, since the neurotoxic effects noted, such as muscle tremors, ataxia, and hypersalivation, are all associated with hyperactivity in the cholinergic system, and most insecticides formulated for use on pets contain small amounts of cholinesterase inhibitors, it is reasonable to conclude that the neurotoxic effects observed are associated with a component of the remaining 21.8% of the mixture, not d-limonene. No data are available to evaluate the neurotoxic potential of the other terpenes.

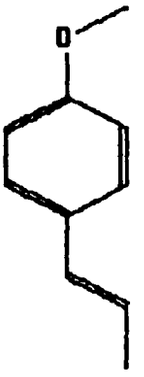
Environmental effects: Analysis of measured (where available) acute and chronic toxicity values of the terpenes to freshwater aquatic organisms, along with predictions which were based on SAR analysis, indicate that the terpenes present a moderate (1-100 mg/L) to high (< 1 mg/L) hazard to aquatic organisms. Based on the lowest measured acute toxicity value for fish and daphnids, and using an assessment factor (AF) of 100, the Concentration of Concern (COC) for the terpenes is less than 1 ppm, which means that the terpenes exhibit high ecotoxicity.

The COC for a chemical is that concentration in the aquatic environment below which there is a low probability of harm to organisms within the environment. COCs are derived from effective concentrations by the application of AFs (USEPA, 1984), which are similar to uncertainty factors (HCN, 1989). Since the AF reflects uncertainty, its magnitude depends on the amount and quality of toxicity data available. In general, the greater the amount of toxicity data and the higher the quality of the data, the smaller the factor. Four AFs, ranging from 1 to 1000, are used by the Agency to set a COC for chronic aquatic toxicity risk. A more detailed discussion on the derivation of COCs and AFs can be found in the terpene hazard support document.

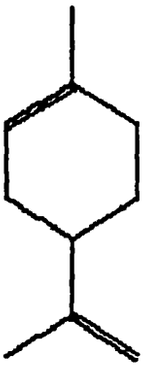
The chemical structures of the eight terpenes under review and of p-cymene, a close analogue, are shown below.



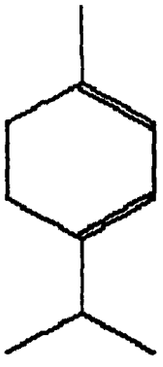
d-Limonene



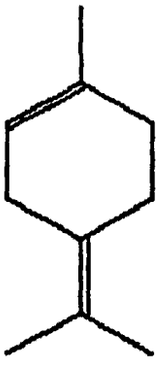
Anethole



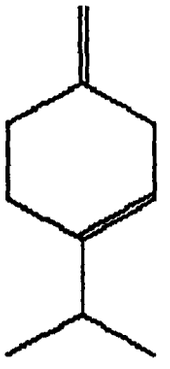
Dipentene (dl-limonene)



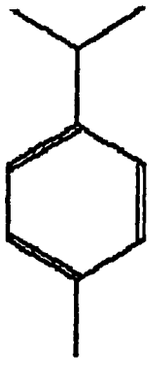
α-Terpinene



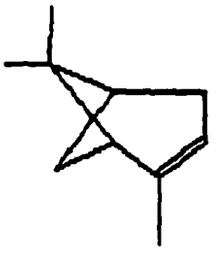
Terpinolene



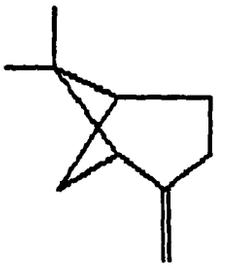
β-Terpinene



p-Cymene



α-Pinene



β-Pinene

3. INDUSTRIAL APPLICATIONS AND OCCUPATIONAL EXPOSURE

This section characterizes potential occupational exposures that may result from the increased manufacture, formulation, and use of aqueous and terpene-based cleaning formulations as substitutes for CFC-113 and methyl chloroform in PC board and metal cleaning. The information presented in this section is discussed in more detail in the two support documents on occupational exposure and environmental release (PEI, 90a; PEI, 90b). The following occupational exposures scenarios are addressed in this section: manufacture of terpenes; formulation of aqueous and terpene cleaners; and use of aqueous and terpene cleaners in PC board cleaning, warm immersion cleaning, and cold immersion cleaning.

Both aqueous and terpene-based cleaners are mixtures, comprised of components which enhance the cleaning product's performance in a specific application. The most common aqueous cleaners generally consist of three components: alkalis or alkaline salts which provide alkalinity, reduce hardness, and act as buffering and chelating agents in the cleaning solution; chemical additives which may provide additional cleaning, surface modification properties, rust inhibition or water softening depending on the specific use application; and surfactants which improve detergency, emulsification, and surface wetting properties. Terpene cleaners generally consist of: a terpene which provides a high solvency of greases and oils; chemical additives, depending on the sensitivity of the materials cleaned and degree of cleanliness required; and surfactants. Because there are a number of possible cleaner formulations, for purposes of this report, four model aqueous cleaner formulations and two model terpene cleaner formulations were used to screen potential occupational exposures. These formulations are intended to be representative of cleaners as a whole. The composition of the model formulations are described in sections 3.2.1 and 3.3.2.

Occupational exposure assessments require information that is representative of the variability in the industrial sector under review, on: the populations exposed; worker activities and industrial practices leading to exposure; routes of exposure; and the frequency, duration, and levels of exposure to the chemicals under review. A comprehensive exposure assessment would relate

worker activities to exposures measured, and then present the range and distribution of the monitoring data. In the case of aqueous and terpene-based cleaners, there were no personal monitoring data available to characterize potential exposures, primarily because these cleaners are not currently in extensive use in these applications. In the absence of any monitoring data, exposure levels were estimated using techniques frequently used in EPA occupational exposure analyses.

Both typical and outerbound potential occupational exposures were estimated. Typical exposures are presented to provide a sense of what likely or average exposures may potentially be. EPA has some degree of confidence that potential exposures are likely to be less than the outerbound levels presented. There is more uncertainty in the estimates of typical exposures because typical conditions are more difficult to establish. It should be noted that the exposure estimates presented do not take into account the use of personal protective equipment, such as gloves and respirators, or the use of equipment, such as closed-loop systems and nitrogen blankets, which may help to reduce exposures in future uses of aqueous and terpene cleaners.

The routes of occupational exposure assessed for the aqueous and terpene cleaners were the inhalation and dermal routes. The major sources of information used to develop this assessment include:

- Permissible Exposure Limits (PELs) promulgated by the Occupational Safety and Health Administration (OSHA);
- A database maintained by OSHA which contains records on 1400 chemicals regulated by OSHA and monitored mostly for enforcement purposes) since 1981;
- Information from National Institute of Occupational Safety and Health (NIOSH) studies such as Health Hazard Evaluations and Industry Wide Surveys;
- Information voluntarily submitted to the Agency by manufacturers and users of aqueous and terpene-based cleaners during the development and review of this document.

For solid components of aqueous cleaners, the OSHA PEL for nuisance dust, 15 mg/m^3 total dust, 8-hour time-weighted average (TWA), was used to estimate the outerbound inhalation exposure during formulation and use, if that component does not have a chemical-specific OSHA PEL. Assuming a breathing rate of 1.25 m^3/hour and an 8-hour work day, the estimated worker inhalation exposure to all of the solid constituents during formulation or use is not expected to exceed 150 mg/day. Concentrations of chemicals that have PELs are expected to be controlled by their

chemical-specific PEL rather than by the nuisance dust PEL. Exposures to individual components may be less than 150 mg/day when more than one component is present as airborne dust. Sufficient data are not available to estimate a typical dust exposure.

For liquid components, two approaches were taken to estimate levels of exposure: a theoretical modeling approach, and a surrogate data approach. The modeling approach required an estimate of source strength, such as the amount of chemical that might volatilize from a liquid surface. The chemical's airborne concentration was then estimated considering dilution from mixing and ventilation in the workplace air. Finally, worker exposure was estimated based on the chemical concentration, the worker's breathing rate, and the duration of exposure. Engineering judgment was used to estimate typical values of model input variables. The surrogate data approach used actual exposure monitoring data for a chemical other than the chemical under review but one used in a similar industrial setting. The surrogate chemicals used in this exposure assessment were CFC-113 in PC board cleaning and methyl chloroform in metal cleaning. Workplace concentrations of the surrogate chemical were converted to concentrations of the chemical under review by taking into account differences in vapor pressures and use concentrations. The surrogate data approach does not take into account differences in work practices and equipment which may change due to chemical substitution.

Greater reliance is placed on use of the modeling approach based on past experience with other chemicals where comparisons with actual data could be made. However, there is uncertainty with the modelled exposures. This uncertainty originates predominantly in the assumptions used for model input variable values. Generally, beyond ventilation of indoor work areas, controls that might limit exposure were not considered in the modeling. In addition, the extent to which future differences in work practices and equipment design will reduce exposures is also unknown and not considered. The surrogate data approach provides greater certainty when the only difference in the exposure scenario is the chemical itself. Because the surrogate chemicals are not close analogues to the aqueous and terpene substitutes, there are differences in equipment and work procedures between the use of the surrogates and the use of aqueous and terpene cleaners, which add considerable uncertainties to the exposures estimated from the surrogate data approach. Thus, only the modeling approach results are presented in this report. Surrogate data approach exposure estimates range from 2 to 54 percent of modeling approach exposure estimates. A more complete discussion of the two approaches is presented in the support documents (PEI, 90a; PEI, 90b).

Dermal exposures were estimated from a model using an estimate of hand surface area in contact with the substance, surface concentration of the substance, and concentrations of specific chemicals in the substance. This model generated outerbound estimates of the amount of a chemical that might be available at the skin's surface for dermal absorption. Sufficient data were not available to estimate a typical dermal exposure.

3.1 SUMMARY AND CONCLUSIONS

Tables 3-1 and 3-2 summarize the results of this preliminary assessment which are described in more detail in the following sections. Monitoring studies of actual worker activities associated with the use of aqueous and terpene-based cleaners would reduce uncertainties associated with this exposure characterization. The monitoring studies could also serve to show the extent exposures might be lowered through equipment designs and workplace practices established for these cleaners.

3.2 AQUEOUS CLEANERS

Aqueous solutions have been used in the metal parts cleaning industry for over twenty years. They have also found acceptance in maintenance cleaning activities. In the electronics industry, widespread use of these cleaners has found acceptance only in the past five years. It is anticipated that aqueous cleaners will serve as feasible substitutes for CFC-113 and methyl chloroform in a fraction of all electronics (20 - 35 percent) and metal cleaning practices (30 to 50 percent). To estimate exposures, it was assumed that aqueous cleaners will replace CFC-113 and methyl chloroform in 30 percent of PC board cleaning operations and in 40 percent of metal cleaning operations.

Aqueous cleaners are available in many chemical formulations, depending on the substrate being cleaned, the type of surface contaminant, and the degree of cleanliness required. These formulations can be generic multi-purpose cleaning solutions or be formulated for the needs of a specific industry.

There are three general types of aqueous cleaning solutions: alkaline cleaners; acidic cleaners; and solvent emulsion cleaners, which include terpene cleaners, also discussed in this report. Since alkaline cleaners are the most likely to serve as substitutes for CFC-113 and methyl chloroform, they are the focus of the aqueous formulations discussed in this report.

TABLE 3-1 SUMMARY OF ESTIMATED OCCUPATIONAL EXPOSURES TO AQUEOUS CLEANER CONSTITUENTS

Use	Estimated number of sites at estimated substitution rate	Estimated number of exposed employees per site	Chemical category	Physical state	Exposure duration, hr/day[b]	Typical inhalation exposure, mg/day[c]	Outerbound inhalation exposure, mg/day[c,d]	Outerbound dermal exposure mg/day[c]
Formulation-metal cleaner	20[a]	10	Alkaline salts	Solid	4	N/A	150	18000
			Additives	Solid	4	N/A	150	18000
			Surfactants	Liquid	8	4	21	3900
Formulation-electronics cleaner	20[a]	10	Alkaline salts	Solid	N/A	N/A	N/A	N/A
			Additives	Liquid	8	11	55	2300
			Surfactants	Liquid	8	3	13	3900
Warm immersion cleaning	2000	7	Alkaline salts	Solid	1	N/A	150	10000
			Additives	Solid	1	N/A	150	730
			Surfactants	Liquid	8	<1	<1	550
Cold immersion cleaning	3100	4	Alkaline salts	Solid	1	N/A	150	10000
			Additives	Solid	1	N/A	150	730
			Surfactants	Liquid	8	<1	<1	550
PC board cleaning	210	25	Alkaline salts	Solid	N/A	N/A	N/A	N/A
			Additives	Liquid	8	<1	<1	2300
			Surfactants	Liquid	8	<1	<1	200

[a] Total number of formulation sites for both metal cleaning and electronics cleaning formulations.

[b] Duration of exposure is a function of worker activities.

[c] Exposure estimates do not account for personal protective equipment or enhancements to equipment design which may reduce exposures.

[d] Concentrations of chemicals that have PELs, such as sodium hydroxide and borax, are expected to be controlled by their chemical-specific PEL rather than by the nuisance dust PEL, and resulting exposures may be lower than 150 mg/day.

TABLE 3-2 SUMMARY OF ESTIMATED OCCUPATIONAL EXPOSURES TO TERPENE CLEANER CONSTITUENTS

Use	Estimated number of sites at estimated substitution rate	Estimated number of exposed employees per site	Chemical category	Physical state	Exposure duration, hr/day[a]	Typical inhalation exposure, mg/day[b]	Outerbound inhalation exposure, mg/day[b]	Outerbound dermal exposure mg/day[b]
Manufacturing-terpenes	35	10	Terpene	Liquid	<8	600	1500	3900
Formulation-metal cleaner	10	10	Terpene	Liquid	<4	9	92	3900
			Additives	Solid		N/A	150	3900
				Liquid		<1	8	3900
			Surfactants	Liquid		<1	8	3900
Formulation-electronics cleaner	1	10	Terpene	Liquid	<4	140	720	3900
			Surfactants	Liquid		7	34	3900
Warm immersion cleaning	510	7	Terpene	Liquid	<4	3	13	3600
			Additives	Solid		N/A	N/A	550
				Liquid		<1	<1	1100
			Surfactants	Liquid		<1	<1	1500
Cold immersion cleaning	770	4	Terpene	Liquid	<4	17	84	3600
			Additives	Solid		N/A	N/A	550
				Liquid		2	8	1100
			Surfactants	Liquid		2	8	1500
PC board cleaning	180	25	Terpene	Liquid	<4	84	420	3500
			Surfactants	Liquid		3	17	390

[a] Duration of exposure is a function of worker activities.

[b] Exposure estimates do not account for personal protective equipment or enhancements to equipment design which may reduce exposures.

3.2.1 FORMULATION OF AQUEOUS CLEANERS

Formulation refers to the blending of chemicals to result in a cleaning formulation. Formulation is accomplished using physical mixing and blending operations. Alkaline-based cleaners, the most common type of formulation, are produced in concentrated form as either liquids or powders. These alkaline-based cleaners are largely comprised of three types of components: alkalis or alkaline salts, builders, and surfactants. Typical aqueous formulations for metal and electronics cleaning are presented in Tables 3-3 and 3-4, respectively. These formulations provide a basis for occupational exposures and environmental release estimates presented later in this report. Table 3-5 presents OSHA PELs for aqueous cleaner constituents for which exposure limits have been adopted. Concentrations of these constituents would be expected to be limited to their PELs. Resulting estimates of exposure to solids in aqueous cleaners, based on chemical-specific PELs, are not presented in this report.

There are an estimated 20 companies that produce aqueous cleaners for metal and electronics cleaning. No information was available on the average daily throughputs for these facilities; however, sufficient production capacity seems to exist to meet potential increases in demand.

These formulators are believed to employ from 10 to 33 employees per site, with an average of 20 total employees. It is expected that less than 10 employees would be directly exposed during aqueous formulation at a typical facility. Potential points of worker exposure include: raw materials handling; activities at the blending tanks; and product packaging. Workers may be exposed during 250 days per year.

Rubber gloves are probably used by workers formulating the cleaners. Information on the use of other forms of personal protective equipment was not available. General ventilation is the only engineering control believed to be typically used in formulating facilities.

Inhalation and dermal exposure estimates, summarized in Table 3.1, were determined from the models described in the introduction to section 3. Open-top mixing vessels were assumed for estimating inhalation exposures to liquid constituents of metal cleaning formulations. Closed mixing vessels were assumed for estimating exposures to liquid constituents of electronics cleaning formulations. Inhalation exposures to surfactants are estimated to be 4 mg/day in the typical case, 21 mg/day outerbound. Outerbound dermal exposures are estimated to be 18,000 mg/day for alkaline salts and additives, the solid components, and 3,900 mg/day for surfactants, the liquid components available for absorption.

TABLE 3-3 TYPICAL AQUEOUS METAL CLEANING FORMULATIONS

Chemical	CAS Number	Weight percentage in formulation
Formulation 1: Powder Alkaline Metal Cleaner		
Sodium carbonate	497-19-8	45
Trisodium phosphate	7601-54-9	15
Sodium tripolyphosphate	7758-29-4	20
Borax	1303-96-4	17
Linear alkyl aryl sulfonate[a]	-	2
Anionic surfactant[b]	-	1
		100
Formulation 2: Liquid Alkaline Metal Cleaner		
Water	7732-18-5	30
Sodium metasilicate	6834-92-0	33
Sodium hydroxide	1310-73-2	7
Tetrasodium pyrophosphate	7722-88-5	5
Trisodium phosphate	7601-54-9	22
Alkyl aryl sulfonate	25155-30-0	2
Anionic surfactant[b]	-	1
		100
Formulation 3: Non-phosphated Alkaline Aluminum Cleaner		
Sodium carbonate	497-19-8	55
Sodium metasilicate	6834-92-0	35
EDTA	60-00-4	4
Linear alkyl aryl sulfonate	25155-30-0	3
Anionic surfactant[b]	-	3
		100

[a] An example of a linear alkyl aryl sulfonate is sodium dodecylbenzene sulfonate, CAS Number 25155-30-0.
[b] Typical anionic surfactants include ethoxylated octyl phenol and ethoxylated nonyl phenol.

Sources: Bennett, 75; Kirk-Othmer, 83; Pappalardo, 85; Pettit, 89d.

TABLE 3-4 TYPICAL AQUEOUS ELECTRONICS CLEANING FORMULATION

Chemical	CAS Number	Weight percentage in formulation
Formulation 4: Alkaline Electronics Cleaner		
Monoethanolamine	141-43-5	60
Diethylene glycol monobutyl ether	112-34-5	35
Anionic surfactant[a]	-	5
		100

[a] Typical anionic surfactants include ethoxylated octyl phenol and ethoxylated nonyl phenol.

Sources: Bennett, 75; Kirk-Othmer, 83; Pappalardo, 85; Pettit, 89d.

TABLE 3-5 AQUEOUS CLEANER CONSTITUENTS FOR WHICH EXPOSURE LIMITS HAVE BEEN ADOPTED

Chemical	OSHA, PEL	ACGIH, TLV
Sodium hydroxide	2 mg/m^3, ceiling[a]	2 mg/m^3, ceiling
2-Butoxyethanol	120 mg/m^3, TWA[b,c]	121 mg/m^3, TWA with "skin" notation
Borax (sodium tetraborate)	10 mg/m^3, TWA	5 mg/m^3, TWA
Dipropylene glycol methyl ether	600 mg/m^3, TWA	606 mg/m^3, TWA with "skin" notation
Tetrasodium pyrophosphate	5 mg/m^3, TWA[d]	5 mg/m^3, TWA
Monoethanolamine	8 mg/m^3, TWA[d]	7.5 mg/m^3, TWA

[a] The OSHA final limit, effective December 30, 1992, is 2 mg/m^3, ceiling. The transitional limit, in effect until December 30, 1992, is 2 mg/m^3, TWA.
[b] TWA = time-weighted average.
[c] Transitional limit is 240 mg/m^3.
[d] There is no transitional limit.

Source: ACGIH, 89.

3.2.2 PC BOARD CLEANING WITH AQUEOUS CLEANERS

Methyl chloroform and CFC-113 are the predominant solvents used in the electronics industry today. However, aqueous cleaning is an accepted method of defluxing PC boards in some applications. Although DOD standards do not currently allow for the use of terpene cleaners in PC board manufacture for military use, revision of those standards is underway. It is expected that the new specifications will discourage use of CFCs and other ozone-depleting chemicals and will allow any method of cleaning that satisfies certain cleaning performance criteria. There are four general types of aqueous cleaning equipment used to remove fluxes from PC boards: mechanical brushing; low-throughput batch; high-throughput batch; and in-line conveyorized.

There are an estimated 705 PC board manufacturers in the U.S. using 5,000 to 7,000 cleaning units. Based on a 30 percent conversion to aqueous cleaners, 210 sites may substitute aqueous cleaners for methyl chloroform and CFC-113. At each of these sites, an average of 24 workers could potentially be exposed based on estimates of 3 workers per cleaning unit and 8 units per site.

Workers can be exposed to aqueous cleaners in PC board cleaning during transfer of the cleaner to the cleaning bath and, to a much lesser extent, from handling the PC boards after the boards have been rinsed with water. Workers may be exposed during 250 days per year. Handling of the PC boards during cleaning and draining of dirty cleaner and rinse water is usually an automated, closed process with most unit designs. Gloves are typically used when handling the cleaned PC boards.

Inhalation and dermal exposure estimates, summarized in Table 3.1, were determined from the models described in the introduction to section 3. Enclosed heated immersion baths were assumed for estimating inhalation exposures to liquid constituents of the aqueous PC board cleaners. Typical and outerbound inhalation exposures to all constituents were estimated to be less than 1 mg/day. Outerbound dermal exposures were estimated to be 2,300 mg/day for additives and 200 mg/day for surfactants available for absorption.

3.2.3 WARM IMMERSION CLEANING WITH AQUEOUS CLEANERS

Aqueous cleaning has found wide usage in the manufacturing sector as an alternative to open-top vapor degreasing for cleaning metal parts. Cleaning is accomplished by using heated solutions in immersion tanks or by spraying. Finishing steps include rinsing, drying, and wastewater disposal. Systems may be batch, which often require more manual handling of parts, or in-line, which are used when higher throughput is needed.

An estimated 9,070 open-top vapor degreasers operate in the U.S., of which 5,106 use methyl chloroform or CFC-113. It was assumed that there would be up to a 40 percent conversion to aqueous cleaners, thus resulting in an estimated 2,000 sites which may substitute aqueous cleaners for methyl chloroform and CFC-113. The number of workers exposed to aqueous cleaners per degreaser was assumed to be seven, the same as for open-top vapor degreasers.

Worker exposure to aqueous cleaners in warm immersion systems may occur during transfer of the cleaner to the cleaning bath, handling of the parts during the cleaning operation, handling of the cleaned parts, and disposal of the dirty cleaning solution. Workers may be exposed during 250 days per year.

The use of dermal protection is currently recommended by aqueous cleaner formulators and is probably employed by many aqueous cleaner users.

Inhalation and dermal exposure estimates, summarized in Table 3.1, were determined from the models described above. Open-top warm immersion baths were assumed for estimating inhalation exposure to liquid constituents of the aqueous metal cleaners. Outerbound inhalation exposures to alkaline salts and additives when handled as solids during warm immersion cleaning were estimated to be 150 mg/day based on the OSHA PEL for nuisance dust. Typical and outerbound inhalation exposures to surfactants were estimated to be less than 1 mg/day. Outerbound dermal exposures were estimated to be 10,000 mg/day for alkaline salts and 730 mg/day for additives, the solid components, and 550 mg/day for surfactants, the liquid components available for absorption.

3.2.4 MAINTENANCE COLD CLEANING WITH AQUEOUS CLEANERS

Cold batch immersion systems dominate as a method of metal cleaning in various industrial/manufacturing settings and service settings such as automotive garages and repair shops. These cleaning operations can include spraying, flushing, brushing, and immersion. Drying will also be necessary if remaining water could cause rust to form.

An estimated 9,740 cold degreasers operate in the U.S., of which 7,689 use methyl chloroform or CFC-113. Assuming up to 40 percent conversion to aqueous cleaners, 3,100 sites may substitute aqueous cleaners for methyl chloroform and CFC-113 units.

The number of workers potentially exposed per unit is the same as for cold cleaners using chlorinated solvents, or four workers.

Workers can be exposed to aqueous cleaners in cold cleaning during: transfer of the cleaner to the cleaning bath; handling of parts during the cleaning operation; handling of the cleaned parts; and disposal of the dirty cleaning solution. Workers may be exposed during 250 days per year.

The use of dermal protection is currently recommended by aqueous cleaner formulators and is probably employed by many aqueous cleaner users.

Inhalation and dermal exposure estimates, summarized in Table 3.1, were determined from the models described above. Open-top cold aqueous baths were assumed for estimating inhalation exposures to liquid constituents of the aqueous metal cleaners. Outerbound inhalation exposures to alkaline salts and additives when handled as solids during cold cleaning were estimated to be 150 mg/day based on the OSHA PEL for nuisance dust. Typical and outerbound inhalation exposures to surfactants were estimated to be less than 1 mg/day. Outerbound dermal exposures were estimated to be 10,000 mg/day for alkaline salts and 730 mg/day for additives, the solid components, and 550 mg/day for surfactants, the liquid components available for absorption.

3.3 TERPENE CLEANING

Terpenes are a class of natural products commonly found in the odorous components of plants. Recently, the demand for certain terpenes has risen as a result of their increased use in cleaning applications. Of the many terpenes available for use in industrial applications, monoterpenes, those terpenes which contain ten carbon atoms, offer the best potential for increased use in metal and electronics cleaning.

Current consumption of terpenes is estimated to range from about 157 to 193 million kilograms (about 125 to 161 million kilograms are derived from pine; 32 million kilograms are derived from citrus fruits). Assuming terpene-based cleaner substitution for current methyl chloroform and CFC-113 usage of up to 25 percent in PC board cleaning and up to 10 percent in metal cleaning, incremental terpene demand could be up to 1.8 million kilograms per year.

3.3.1 MANUFACTURE OF TERPENES

Most terpenes are obtained from the distillation or extraction of citrus oils and wood turpentine. Citrus oils are obtained most commonly from the distillation of discarded orange and lemon pulp and peels. Turpentines are obtained from extraction or distillation of stumps and resinous wood wastes and from the wood-cooking step of the kraft pulping process.

There are an estimated 30 to 35 manufacturers of d-limonene and four major manufacturers of other terpenes. Florida's production of d-limonene is approximately 6.8 million kg (15 million lb) per year. Production of α- and ß-pinene was 71 million kg (156 million lb) in 1987. Estimates of production quantities of other terpenes were not found.

One terpene manufacturer/formulator reported that they had 35 total employees. Less than 10 employees would be expected to be exposed to terpenes during manufacture at a site. This estimate was extrapolated to all terpene manufacturers.

During terpene manufacture, workers may be exposed to terpenes during: production operations; quality control sampling; tank truck and drum filling; packaging of product; and maintenance activities. Sampling and product loadout operations have the highest potential for exposure. Workers may be exposed from 26 to 250 days per year.

One manufacturer stated that their workers use "solvent-resisting" gloves and safety glasses where exposure is likely. Exposures to terpene concentrations greater than 100 ppm (556 mg/m^3) may be very irritating, so it is likely that air concentrations would be controlled to below this level. It may be noted that estimated workplace concentrations in this assessment do not exceed 50 ppm during manufacture of terpenes or during formulation or use of terpene cleaners.

No monitoring data were found for worker exposure to terpenes during manufacture. Inhalation and dermal exposure estimates, summarized in Table 3.2, were determined from the models described in the introduction to section 3. Inhalation exposures to terpenes at manufacturing sites for drumming of terpenes were estimated to be 600 mg/day typically, and 1500 mg/day outerbound. Outerbound dermal exposures were estimated to be 3900 mg/day terpenes available for absorption.

3.3.2 FORMULATION OF TERPENE CLEANERS

Formulation of terpene cleaners involves mechanical blending of raw materials. Typical formulations consist of the terpene, a surfactant, and may include other performance enhancers. Formulation is done on a batch basis, usually in closed mixing vessels, but open tanks may be used. Loading of large-quantity components to the mixer may be manual or automated. Typical formulations for metal and electronics cleaning are presented in Table 3-6. These formulations provide a basis for occupational exposures and environmental release estimates in this assessment. It may be noted that d-limonene is the only terpene used as a basis for exposure and release estimates because d-limonene is believed to have the highest potential to be commercialized.

Future assessments may better address other terpene mixtures which may be developed for these cleaning operations.

TABLE 3-6 TYPICAL TERPENE-BASED CLEANERS

Chemical[a]	CAS Number	Percent in formulation
Formulation 1: Electronics Cleaner		
d-Limonene	5989-27-5	90
Anionic surfactant	---	10
Formulation 2: Metal Cleaner		
Water	7732-18-5	60
d-Limonene	5989-27-5	20
Diethanolamine	111-42-2	3
Sodium xylene sulfonate	1300-72-7	3
Dipropylene glycol methyl ether	34590-94-8	6
Anionic surfactant	---	8

[a] All pure chemicals are liquids except diethanolamine and sodium xylene sulfonate.

Sources: Hayes, 88; Barnett, 89; Pettit, 89

There are an estimated 100 formulators of terpene cleaners in the U.S. Of these, 10 are formulators of terpene metal cleaners, and one formulates terpene electronic cleaners. One terpene manufacturer/formulator reported that they had 35 total employees. Less than 10 employees would be expected to be exposed to terpenes during formulation at a site, and this estimate was extrapolated to all terpene formulators.

During formulation, workers may be exposed to terpenes and other formulation components during raw material unloading, transferring, weighing, blending, sampling, product packaging, and maintenance. Workers may be exposed during 250 days per year.

Because terpenes remove skin oils, it is likely that terpene cleaner formulators will wear impervious gloves when contact is likely.

Inhalation and dermal exposure estimates, summarized in Table 3.2, were determined from the models described in the introduction to section 3. Closed tanks were assumed in estimating inhalation exposure during terpene electronics cleaner formulation. For terpene metal cleaning formulation, the closed

tank assumption was used to estimate typical exposure, and an outerbound estimate of exposure was made assuming the use of open tanks. Inhalation exposure during the formulation of the metal cleaner was estimated to typically be 9 mg/day terpene with an outerbound estimate of 92 mg/day terpene. For other liquid constituents, inhalation exposures were estimated to be less than 1 mg/day typically and up to 8 mg/day as an outerbound. Outerbound inhalation exposure to the single solid constituent, diethanolamine, was estimated to be 150 mg/day based on the OSHA PEL for diethanolamine (DEA). DEA is the only solid constituent of terpene cleaners with a chemical-specific OSHA PEL; this PEL happens be identical to the OSHA PEL for nuisance dust. For formulation of the electronics cleaner, typical inhalation exposures were estimated to be 140 mg/day terpene and 7 mg/day surfactant, with outerbound estimates of 720 mg/day terpene and 34 mg/day surfactant. Outerbound dermal exposures to any constituent during formulation are estimated to be 3,900 mg/day available for absorption.

3.3.3 PC BOARD CLEANING WITH TERPENE CLEANERS

Methyl chloroform and CFC-113 are the predominant solvents used in the electronics industry today. Although DOD standards do not currently allow for the use of terpene cleaners in PC board manufacture for military use, revision of those standards is underway. It is expected that the new specifications will discourage use of CFCs and other ozone-depleting chemicals and will allow any method of cleaning that satisfies certain cleaning performance criteria. Most new terpene cleaning units are in-line conveyorized, although some batch units are in use.

There are an estimated 705 PC board manufacturers in the U.S. using 5,000 to 7,000 degreasers. Based on a 25 percent conversion to terpene cleaners, 176 sites would substitute terpene cleaners for methyl chloroform and CFC-113. These PC board manufacturers would average 12 exposed workers per site based on 3 workers per cleaning unit and 4 units per site.

Workers can be exposed to terpene cleaners in PC board cleaning during transfer of the cleaner to the cleaning bath and, to a much lesser extent, from the PC boards after the boards have been rinsed with water. Handling of the PC boards during cleaning and draining of dirty cleaner and rinse water is usually an automated, closed process. Workers may be exposed during 250 days per year.

Because terpenes remove skin oils, it is likely that terpene cleaner users wear impervious gloves when contact is likely. It is a common practice to wear gloves when handling PC boards that have been cleaned.

Inhalation and dermal exposure estimates, summarized in Table 3.2, were determined from the models described earlier. Enclosed conveyorized PC board cleaning units were assumed for estimating inhalation exposures to liquid constituents of terpene cleaners. Typical inhalation exposures during PC board cleaning were estimated to be 84 mg/day terpene and 3 mg/day surfactant, and outerbound inhalation exposures were estimated to be 420 mg/day terpene and 17 mg/day surfactant. Outerbound dermal exposures were estimated to be 3,500 mg/day terpene and 390 mg/day surfactant available for absorption.

3.3.4 WARM IMMERSION CLEANING WITH TERPENE CLEANERS

Terpene cleaning may be used as an alternative to open-top vapor degreasing for cleaning metal parts in various industrial settings. Warm immersion terpene cleaning is accomplished by using heated solutions in immersion tanks or by spraying. Finishing steps include rinsing, drying, and wastewater disposal. Systems may be batch, which often require more manual handling of parts, or in-line, which are used when higher throughput is needed.

An estimated 9,070 open-top vapor degreasers operate in the U.S., of which 5,106 use methyl chloroform or CFC-113. At 10 percent conversion to terpene cleaners, 510 sites will substitute terpene cleaners for methyl chloroform and CFC-113. The number of workers exposed to terpene cleaners per degreaser was assumed to be seven, the same as for open-top vapor degreasers.

Worker exposure to terpene cleaners in warm immersion systems may occur during transfer of the cleaner to the cleaning bath, handling of the parts during the cleaning operation, handling of the cleaned parts, and disposal of the dirty cleaning solution. Workers may be exposed during 250 days per year.

Because terpenes remove skin oils, it is likely that terpene cleaner users wear impervious gloves when contact is likely.

Inhalation and dermal exposure estimates, summarized in Table 3.2, were determined from the models described earlier. Enclosed warm immersion degreasing units were assumed for estimating inhalation exposures to liquid constituents of terpene cleaners. Typical inhalation exposures are estimated to be 3 mg/day terpene and less than 1 mg/day for additives and surfactants. Outerbound inhalation exposures are estimated to be 13 mg/day terpene and less than 1 mg/day for additives and surfactants. Outerbound dermal exposures are estimated to be 3,600 mg/day terpene, 550 mg/day solid additives, 1,100 mg/day liquid additives, and 1,500 mg/day surfactant available for absorption.

3.3.5 MAINTENANCE COLD CLEANING WITH TERPENE CLEANERS

Cold batch immersion systems dominate as a method of metal cleaning in industrial/manufacturing settings and service settings such as automotive garages and repair shops. These cleaning operations can include spraying, flushing, brushing, and immersion. Drying may also be necessary if remaining water could cause rust to form.

An estimated 9,740 cold degreasers operate in the U.S., of which 7,689 use methyl chloroform or CFC-113. At 10 percent conversion to terpene cleaners, 770 sites will substitute terpene cleaners for methyl chloroform and CFC-113. The number of workers potentially exposed per unit is the same as for cold cleaners using chlorinated solvents, or four workers.

Workers can be exposed to terpene cleaners in cold cleaning during transfer of the cleaner to the cleaning bath, handling of parts during the cleaning operation, handling of the cleaned parts, and disposal of the dirty cleaning solution. Workers may be exposed during 250 days per year.

Because terpenes remove skin oils, it is likely that terpene cleaner users wear impervious gloves when contact is likely.

Inhalation and dermal exposure estimates, summarized in Table 3.2, were determined from the models described in the introduction to section 3. Open-top cold immersion baths were assumed for estimating inhalation exposures to liquid constituents of terpene cleaners. Typical inhalation exposures are estimated to be 17 mg/day terpene, and 2 mg/day for both additives and surfactants. Outerbound inhalation exposures are estimated to be 84 mg/day terpene and 8 mg/day for both additives and surfactants. Outerbound dermal exposures are estimated to be up to 3,600 mg/day terpene, 550 mg/day solid additives, 1,100 mg/day liquid additives, and 1,500 mg/day surfactant available for absorption.

4. ENVIRONMENTAL RELEASE, FATE, AND EXPOSURE

This section analyzes the likely environmental releases and impacts that may be associated with a conversion from CFC-113 and methyl chloroform to aqueous or terpene cleaners. The section begins by estimating the quantity of chemicals likely to be released at each site where the cleaners are manufactured, formulated, or used, and the number of potential release sites. These releases assume both uncontrolled releases and releases using control technologies (Section 4.1).

Section 4.2 summarizes the likely fate of aqueous and terpene cleaners in the environment, based on their physical and chemical properties. Section 4.3 presents the results of exposure analyses conducted by EPA which estimate the concentrations of aqueous and terpene cleaners in the aquatic environment. Details on the assumptions and calculations used in this chapter are available in EPA's environmental exposure support document.

4.1 RELEASES

4.1.1 AQUEOUS CLEANERS

The major environmental impact from converting existing cleaning operations to aqueous-based systems is the potential increased discharge to wastewater. The water release estimates presented in this section represent release to treatment, receiving stream, or sewer in the absence of pollution prevention techniques or recycling systems. Closed loop-cleaning systems or systems that substantially recycle aqueous cleaning solutions have been developed and may be employed. These types of systems may have water releases that are significantly less than the estimates presented in this assessment.

Releases to water are calculated using mass balance by estimating total consumption and subtracting releases to all other media. In the case of recycling and treatment of the water, some of the filter or sludge waste would require solid waste disposal.

Wastewater discharged from an aqueous system contains both the material cleaned from the parts and the chemicals contained in the cleaning formulation. The release of constituents in the cleaners is mitigated somewhat if the water release is treated; however, even after treatment large quantities may still be released to sewers or receiving streams. This report does not attempt to address the constituent releases and assumes existing regulations will control the concentration of these constituents in the waste stream.

Table 4-1 summarizes the release of aqueous cleaner constituents to water; Table 4-2 presents the releases of aqueous cleaners to air. Releases to air are expected to be low for aqueous cleaners due to the low vapor pressures of the constituents. For air releases, a model was used to predict vapor generation rates upon which release estimates were based. These calculations provide an upper bound release scenario.

TABLE 4-1 ESTIMATED AQUEOUS CLEANER RELEASES TO WATER[a]

Chemical	Warm Immersion Cleaning	Cold Immersion Cleaning	PC Board Cleaning	Total
Sodium carbonate	47	367	0	414
Sodium metasilicate	32	250	0	282
Sodium hydroxide	4	26	0	29
Sodium tripolyphosphate	9	74	0	83
Trisodium phosphate	17	135	0	152
Tetrasodium pyrophospate	2	19	0	21
Borax	8	62	0	70
EDTA	2	15	0	17
Surfactants	5	43	30	78
Ethanolamines	0	0	360	360
DGBE	0	0	210	210

[a]Based on typical formulation and once-through use without treatment; estimates presented in 1000 kg/yr.
Number of aqueous cleaner sites:
Formulation: 20 PC board cleaning: 212
Warm immersion: 2042 Cold immersion: 3076

TABLE 4-2 ESTIMATED AQUEOUS CLEANER RELEASE TO AIR[a]

Category	Chemical	Total, kg/yr
Alkalies/Salts	Sodium carbonate	0
	Sodium metasilicate	0
	Sodium hydroxide	0
	Sodium tripolyphosphate	0
	Tetrasodium pyrophosphate	0
	Borax	0
Additives	EDTA	0
	Ethanolamines	50
	DGBE	2
Surfactants	Alkyl aryl sulfonate	<790
	Anionic Surfactants	<440

[a] Based on typical formulation; released during formulation, transfer, and use.

4.1.2 TERPENE CLEANERS

Similar to aqueous cleaners, the most significant releases to the environment resulting from increased terpene cleaner use are expected to be the releases to wastewater--as much as 0.6 million kg of terpenes to wastewater per year without the use of on-site control technologies.

Terpene releases to water represent the release to treatment, stream, or sewer and do not estimate the efficiency of wastewater treatment. However, due to concerns for biological oxygen demand (BOD) and chemical oxygen demand (COD) from terpenes, terpene wastestreams may require pretreatment before discharge to a wastewater treatment plant or stream. The consideration of wastewater treatment is discussed in section 4.2.2. The releases to water of terpenes and the other constituents of the cleaning solution can be mitigated by recycle and reuse of the cleaner using filtration and other means to remove contaminants from the cleaner. Closed loop-cleaning systems or systems that substantially recycle terpene cleaning solutions have been developed and may be employed. These types of systems may have water releases that are significantly less than the estimates presented in this assessment. The BOD and COD of terpenes may also limit the release to wastewater treatment and/or streams. This will usually result in the disposal of removed wastes by landfill or incineration. Water release estimates were made based upon total terpene usage, number of sites, and days of operation per year.

Terpene releases to air were estimated using a vapor generation rate model for evaporation losses and volume

displacement for transfer losses. Table 4-3 summarizes the release of terpenes to water. Table 4-4 presents the release of terpenes to the air.

4.1.3 DATA NEEDS

Amounts of solid and hazardous wastes generated by aqueous and terpene cleaners, and the composition of those wastes, were not addressed in detail in this assessment. Solid waste data from users of aqueous and terpene cleaners would be useful supplements to the data in this assessment. Additionally, actual data on releases to all media from operating facilities would be useful to improve on the estimates in this assessment.

4.2 ENVIRONMENTAL FATE AND TRANSPORT

This section describes the fate of various compounds of aqueous and terpene cleaning formulations following release into aquatic environments. It is based on readily available information obtained from the published literature and from EPA files. Several of the compounds have limited data bases available to assess their fate in the environment. In these cases, estimates are based on known physical and chemical properties and by the behavior of similar chemicals.

4.2.1 AQUEOUS CLEANERS

A brief description of the environmental fate is provided here. The environmental fate of the aqueous cleaner constituents in aquatic systems is similar for many of the potential compounds of the cleaning formulations.

ALKALIS, SILICATES, AND BORATES

These compounds are very soluble in water and tend to freely dissociate in aqueous systems under environmental conditions. Once the salt has dissolved, the dissociated ions produced may participate in several reactions described in the technical support document for this section. Therefore, the fate of and transformations of the individual dissociated ions, rather than the compounds, must also be investigated.

As an example, with an alkali such as ammonium hydroxide, the ammonium ion will form an equilibrium in water with the ammonium hydroxide parent compound (Morel, 83). Ammonium (NH_4^+) is a usable form of nitrogen by plants and is not considered a pollutant at concentrations within the assimilative capacity of the system (Morel, 83). However, ammonium can undergo oxidation to form nitrate and nitrite through nitrification.

TABLE 4-3 ESTIMATED TOTAL TERPENE RELEASE TO WATER

Operation	# Sites	Sites using no treatment[a] million kg/yr	Sites using no treatment[a] kg/site/day[b]	Sites using gravity separation[a] million kg/yr	Sites using gravity separation[a] kg/site/day[b]
Manufacture	35	0[c]	0[c]	0[c]	0[c]
Formulation	11	0[c]	0[c]	0[c]	0[c]
PC board cleaning	176	0.06	6.5	0.05	1.3
Cold immersion	769	0.1	3.0	0.09	0.6
Warm immersion	511	0.2	6.5	0.1	1.3

[a] Based on 80% of sites using gravity separation and 20% using no treatment.
[b] Based on 250 operating days for formulation and use, and 350 for manufacture.
[c] Negligible quantities are released.

TABLE 4-4 ESTIMATED TOTAL TERPENE RELEASE TO AIR[a]

Operation	# Sites	Release from operations (kg/yr)	Release from gravity separation[b] (kg/yr)	Per site release from operations (kg/site/day)	Per site release from gravity separation (kg/site/day)
Manufacture	35	3,750	na	0.30	na
Electronic formulation	1	35	na	0.14[d]	na
Metal formulation	10	280	na	0.11[d]	na
PC board cleaning	176	35,000	91,000	0.8[e]	5.2[f]
Cold immersion	769	32,000	180,000	0.17[e]	2.4[f]
Warm immersion	511	6,100	260,000	0.05[e]	5.2[f]

[a] Based on a 25% substitution rate for PC board cleaners and a 10% rate for metal cleaners.
[b] It is estimated that an equal quantity would be recycled or sent off-site for disposal.
[c] Release from vacuum distillation, wastewater treatment, spills, and transfer to drum and tank car.
[d] Release from closed lid formulation represents the typical value.
[e] Release from evaporation and transfer.
[f] Release from 50% of those sites using gravity separation allowing evaporation of terpene phase during gravity separation.

PHOSPHATES

Organic and inorganic phosphates are the predominant forms of phosphorus in the environment. The fully reduced form of phosphorus, phosphine (PH_3), has been found in polluted springs and the hypolimnion of lakes and marshes under highly reducing conditions (Bodek et al, 88).

Orthophosphates and polyphosphates complex with metal ions. These metal phosphates are poorly soluble (Bodek et al, 88). In many water environments, complexation with iron (III) and calcium oxides in the sediment is the primary sink for phosphates. There the phosphates will remain unless the sediment becomes anaerobic, resulting in conditions which convert insoluble iron phosphates and calcium phosphates to soluble forms (Bohn, 79).

ETHANOLAMINES

The ethanolamines are highly water soluble (pH dependent). There is very little loss of the compounds from water as a result of non-biological degradation (Gannon et al, 78). Biological degradation in wastewater treatment, ranged from 25-90 percent depending on the number of ethanol groups. Discharges of high concentrations of DEA and TEA have resulted in dissolved oxygen depletion (Gannon et al, 78).

Diethanolamine (DEA) and triethanolamine (TEA) can react with nitrite to form N-nitrosodiethanolamine (Yordy and Alexander, 81). This phenomenon has been reported in bench-scale experiments (Gannon et al, 78), but not in field experiments, to date.

ETHYLENEDIAMINETETRAACETIC ACID

EDTA and its salts should be biodegradable in aquatic and terrestrial ecosystems (days to weeks) provided sufficient organic matter is present to support microbial growth and the residence time of EDTA is adequate.

SURFACTANTS

Very limited information is available on the environmental fate of sodium xylene sulfonate, dodecanedioic acid, and sodium gluconate. Most surfactants, however, are up to 99 percent biodegradable in water.

DIETHYLENE GLYCOL N-BUTYL ETHER

Based on an analysis of the properties of DGBE, it is considered likely to biodegrade in both water and soil environments, with days to weeks required for ultimate degradation.

4.2.2 TERPENE-BASED CLEANERS

Limited fate and transport information is available for the eight terpenes addressed in this report. The physical and chemical properties may be found in the technical support documents for this section. With the exception of anethole, the terpenes exhibit similar properties, both measured and estimated. Because of this characteristic, the environmental fate of these compounds is expected to be similar.

AIR

During daylight hours, terpenes will form smog by photochemical oxidation and ozone by its reaction with hydroxyl radicals. However, nighttime reactions of terpenes will reduce the available terpene and nitrate radicals for the daytime formation of smog and ozone.

WATER

The fate of terpenes in the aqueous environment has been estimated using physical/chemical properties generated by AUTOCHEM and QSAR. Volatilization of the terpenes, except for anethole, is expected to be moderate to high in flowing water and moderate in systems such as lakes. The EXAMS II model (discussed later in this section) predicts an 80 percent removal after 36 miles downstream due to volatility from a river. In natural flowing waters the volatilization half-life is estimated to be 1.2 hours for all the terpenes except anethole (5.7 hours). In lakes, the estimated half-life of the terpenes is 111 hours except anethole (156 hours).

All the terpenes should sorb fairly strongly to soil and sediment (log K_{oc} values >3). Ultimate biodegradation is expected to require weeks under aerobic conditions and months or more under anaerobic conditions. Based on the volatility and sorption of terpenes, migration to groundwater is expected to occur slowly. The presence of terpenes over time in the groundwater would be due to their fairly low biodegradability aerobically and quite low biodegradability anaerobically.

In a wastewater treatment simulation model, all the terpenes, with the exception of anethole, are expected to be removed, principally through volatilization, at an overall efficiency of approximately 90 percent (Clark et al, 89).

In a bench-scale study conducted for EPA by Versar, the removal rate of dipentene and anethole were investigated in a simulated biological treatment system (Versar, 90). The results of the study show that at least 90 percent of the dipentene and 98 percent of the anethole were removed by the bench-scale activated sludge system. A separate control showed that dipentene was removed to below the analytical detection limit (at least 90 percent removal) by air stripping alone. Therefore, the amounts removed by biodegradation or sorption, if any, could not be determined. The control also showed that anethole could be removed to the extent of approximately 90 percent by air stripping alone. Therefore, in the biologically active system at least 8 percent of the anethole was removed by biodegradation and/or sorption onto waste sludge. It is concluded that, for the purposes of exposure assessment, terpenes should be at least 90 percent removed under typical treatment conditions.

4.3 EXPOSURE ANALYSIS

This section estimates the exposure of humans and aquatic organisms to aqueous and terpene cleaners released into water bodies from industrial operations. The exposure estimates are based on the typical cleaning formulations for metal and electronics cleaning and the physical and chemical properties.

The release estimates used in these analyses ranged from releases without control technology or wastewater treatment to releases with some degree of on-site (gravity separation) control along with biological (secondary) wastewater treatment.

EPA uses computer models to estimate the concentrations and impacts of chemicals released into aquatic environments. The Probabilistic Dilution Model (PDM) estimates the days of exceedance of the Concentration of Concern (COC) for the 10 percent of those facilities in an industrial group that will have the worst number of exceedances.

The ambient water concentrations were estimated for the mean and low flows for the 50th and 10th percentile streams in an industrial grouping. The concentrations were estimated by a simple dilution calculation using the chemical loadings in the various release scenarios. Table 4-9 provides these results. These numbers can be compared to the COC of 7 ppb.

Human exposure to drinking water and fish ingestion were estimated using the above stream concentrations. For drinking

water the estimates were based on 2 liters of water consumption per day. Fish ingestion estimates were based on the bioconcentration factor (BCF) and the ingestion of 16.9 grams of fish per day. The formulae and results can be found in the technical support documents for this section. Exams II was used to estimate the impact various fate processes would have on the terpene after release into an aquatic environment.

4.3.1 PROBABILISTIC DILUTION MODEL (PDM)

PDM is a computer model developed by EPA to conduct surface water exposure assessments. PDM estimates the days of exceedance of the COC for the 10 percent of those facilities in an industrial group that will have the worst number of exceedances.

PDM analysis was performed for all the terpenes and for those aqueous cleaners which had release estimates available. Table 4-5 contains the COCs for the aqueous and terpene cleaners.

All three use scenarios were examined. The operations were broken down into the following categories, based on Standard Industrial Classifications (SIC) codes:

- electronic components manufacture
- metal can manufacture
- electroplating
- metal finishing
- motor vehicle manufacture
- large household appliance and parts manufacture

The average days of exceedance of the 10 percent worst streams was calculated for each industrial group using the various release scenarios. The release quantities associated with wastewater treatment were estimated using a 90 percent treatability level estimated by EPA using the "Toronto Sewage Treatment Plant Simulation Model" developed by Clark et al (Clark et al, 89) and verified by a bench scale treatability study.

AQUEOUS CLEANERS

The COC for the aqueous cleaners was exceeded less than one day per year except for the following: sodium silicate in all industry groupings, maximum 10 days; dodecanedioic acid in Electronic Component Manufacturing, 7 days; and all three ethanolamines in Electronic Component Manufacturing, 2 days for MEA, 17 for DEA, 54 for TEA.

TERPENE CLEANERS

d-Limonene was selected as the focus of the terpene analysis because it is anticipated to be the most likely terpene used in the formulation of these cleaners. The COC was derived from measured data on acute toxicity to fish and daphnids. Data on the toxicity to algae will be available at a later date and may lower the COC for terpenes.

TABLE 4-5 CONCENTRATIONS OF CONCERN (COC) FOR THE CONSTITUENTS OF TERPENES AND AQUEOUS CLEANERS

Chemical	COC (ppb)
Terpenes	
α-Pinene	3
β-Pinene	5
d-Limonene	7
Terpinolene	12
α-Terpinene	20
Anethole	70
Dipentene	300[a]
Aqueous Cleaners	
Ammonium hydroxide	8
Potassium hydroxide	800
Sodium hydroxide	400
Borax	300
Sodium silicate	5,000
Sodium metasilicate	100
Sodium carbonate	1,000
Phosphate	0.1
Sodium gluconate	10,000
Dodecanedioic acid (freshwater)	200
(saltwater)	60
DGBE	10,000
EDTA	100
Sodium xylene sulfonate	1,000
Monoethanolamine	90
Diethanolamine	700
Triethanolamine	200

[a] The COC for dipentene was generated using a commercial grade product, unlike the other terpenes which were tested using a pure grade material. The impact, if any, on the measured COC is unknown.

Analysis of the days of exceedance for terpenes released untreated into a receiving stream was also performed to estimate the effects of no controls. However, due to the BOD and COD of terpene-based cleaning formulations, it is anticipated that discharge into a stream untreated may be prohibited under certain provisions of the Clean Water Act or an approved state NPDES program. Thus, discharge to a municipal wastewater treatment plant or use of an on-site control technology is likely.

To estimate the effectiveness of control technologies, the exceedance of the COC was estimated using gravity separation prior to release of the terpene to a receiving stream, wastewater treatment without gravity separation, and gravity separation followed by wastewater treatment.

Tables 4-6 and 4-7 show a summary of the results of PDM (the 10 percent worst-case streams) for a COC of 7 ppb (7 ug/L) under the four release scenarios. The worst-case release of terpenes to water (no gravity separation or wastewater treatment) resulted in 212-248 day of exceedance per year. With wastewater treatment the COC was exceeded 52-178 day per year. When gravity separation is used prior to discharge the COC is exceeded 101-208 days per year. When both gravity separation and wastewater treatment are used the exceedance is 9-81 days per year. The days of exceedance for the remaining terpenes may be found in the technical support documents for this report.

The level of treatment required to avoid exceeding the COC 20 or more days per year will range from 95 to 99 percent depending on the industrial category from which the release originates.

4.3.2 STREAM CONCENTRATIONS

A search of the open literature and the data base STORET did not find any reference to ambient levels of terpenes in surface waters. Additional efforts are on-going to ascertain if ambient levels of terpenes in surface waters exist in other sources.

The stream concentrations were estimated for the mean and low stream flows for the 50th and 10th percentile stream within each SIC. Results after wastewater treatment ranged from <1 ppb to 83 ppb depending on stream flow and industrial grouping. For release after gravity separation the concentration ranged from <1 ppb to 167 ppb and after both gravity separation and wastewater treatment the concentration ranged from <1 ppb to 17 ppb. Table 4-8 provides the results for each scenario by SIC code. These results would indicate that the COC may be exceeded under certain, but not all, stream flow and release conditions and do not indicate the frequency at which the COC will be exceeded.

TABLE 4-6 DAYS OF EXCEEDANCE OF THE COC FOR D-LIMONENE BY SIC CODE AND OPERATION WITHOUT GRAVITY SEPARATION

SIC Code	Operation	Days Per Year Exceedance Percent Treatment 90	0
Motor Vehicle Manufacture	Cold Immersion Cleaning	133	237
	Warm Immersion Cleaning	178	247
Metal Finishing	Cold Immersion Cleaning	79	229
	Warm Immersion Cleaning	135	246
Large Household Appliances and Parts Manufacture	Cold Immersion Cleaning	66	222
	Warm Immersion Cleaning	119	243
Electroplating	Cold Immersion Cleaning	66	222
	Warm Immersion Cleaning	121	243
Metal Can Manufacture	Cold Immersion Cleaning	52	212
	Warm Immersion Cleaning	108	240
Electronic Component	PC Board Cleaning, etc	139	248

TABLE 4-7 DAYS OF EXCEEDANCE OF THE COC FOR D-LIMONENE[a] BY SIC CODE AND OPERATION WITH GRAVITY SEPARATION[b]

SIC Code	Operation	Days Per Year Exceedance Percent Treatment 90	0
Motor Vehicle Manufacture	Cold Immersion Cleaning	42	174
	Warm Immersion Cleaning	81	208
Metal Finishing	Cold Immersion Cleaning	14	129
	Warm Immersion Cleaning	35	185
Large Household Appliances and Parts Manufacture	Cold Immersion Cleaning	9	113
	Warm Immersion Cleaning	26	172
Electroplating	Cold Immersion Cleaning	9	114
	Warm Immersion Cleaning	27	174
Metal Can Manufacture	Cold Immersion Cleaning	3	101
	Warm Immersion Cleaning	15	162
Electronic Component Manufacture	PC Board Cleaning	40	189

[a] COC: 7ppb (7 ug/L) for d-limonene.
[b] Release without gravity separation represents approximately 20 percent of use sites.

For the above stream flow conditions, the treatability of the terpenes would need to range from 96.5 to 99.2 percent to avoid exceeding the COC of 7 ppb more than 20 days per year.

TABLE 4-8 STREAM CONCENTRATION (ug/L)

Terpene Cleaners Results after wastewater treatment only. (Results after gravity separation and WWT). [Results after gravity separation only].

	%tile	Plant Flows Mean	Low[a]
Electronic Component Manuf.	50	0.6(0.1)[1.2]	6.6(1.3)[13.2]
	10	5.7(1.1)[11.4]	51.6(10.3)[103]
Warm Immersion Cleaning			
Metal Can Manuf.	50	0.2(0.1)[0.5]	3.4(0.7)[6.8]
	10	3.1(0.6)[6.2]	61.3(12.3)[123]
Electroplating	50	0.9(0.2)[1.8]	2.1(0.4)[4.3]
	10	3.1(0.6)[6.2]	40.1(8.1)[81.3]
Lg. Household Appliance Manuf.	50	0.5(0.1)[1.0]	4.5(0.9)[9.0]
	10	4.1(0.8)[8.1]	48.9(9.8)[98.0]
Metal Finishing	50	0.7(0.1)[1.3]	3.8(0.8)[7.6]
	10	4.1(0.8)[8.2]	50.8(10.2)[102]
Motor Vehicle Manuf.	50	0.5(0.1)[1.0]	4.3(0.9)[8.8]
	10	6.3(1.3)[12.7]	83.3(16.7)[167]
Cold Immersion Cleaning			
Metal Can Manuf.	50	0.1(0.0)[0.2]	1.6(0.3)[3.1]
	10	1.4(0.3)[2.8]	28.3(5.7)[56.6]
Electroplating	50	0.4(0.1)[0.8]	1.0(0.2)[2.0]
	10	1.4(0.3)[2.8]	18.8(3.8)[37.5]
Lg. Household Appliances Manuf.	50	0.2(0.0)[0.4]	2.1(0.4)[4.1]
	10	1.9(0.4)[3.8]	22.6(4.5)[45.1]
Metal Finishing	50	0.3(0.1)[0.6]	1.7(0.4)[3.5]
	10	1.9(0.4)[3.8]	23.4(4.7)[46.9]
Motor Vehicle Manuf.	50	0.2(0.1)[0.5]	2.0(0.4)[4.1]
	10	2.9(0.6)[5.8]	38.5(7.7)[76.9]

[a]low flow is the 7Q10 flow.

4.3.3 EXPOSURE ANALYSIS MODELING SYSTEM (EXAMS II)

In an attempt to quantify the loss of terpenes due to the various fate processes after release to an aquatic system (river), EXAMS II was performed. EXAMS II estimates the change in the surface water concentration after accounting for fate and persistence for a selected stream segment. EXAMS incorporates various fate, transport, and transformation processes, which include hydrolysis, biodegradation, photolysis, oxidation, reduction, adsorption, volatilization, and ion exchange. The change in surface water concentration with distance as a result of the various fate processes, was estimated at 80 percent after 36 miles (60km).

4.3.4 DRINKING WATER AND FISH INGESTION ESTIMATES

No measured levels of aqueous and terpene compounds in drinking water and fish were identified in the open literature or EPA files. Modeled drinking water and fish ingestion estimates indicated maximum exposures would be approximately 3 mg/yr and 26 mg/yr respectively from terpenes and approximately 50 mg/yr for drinking water from aqueous cleaner formulations. As aqueous and terpene cleaner compounds are substituted for CFCs, measured data would add additional characterization of the exposure to aquatic and human populations. The results are summarized in Tables 4-9 and 4-10 for terpenes and aqueous cleaners, respectively.

TABLE 4-9 HUMAN EXPOSURE TO TERPENE CLEANERS IN DRINKING WATER, BY OPERATION AFTER TREATMENT

Operation	Drinking Water (mg/yr)[a] 50th%tile[a]	10th%tile[a]	Fish Ingestion (mg/yr)[a] 50th%tile	10th%tile[a]
PC Board Cleaning				
Electronic Component Manufacture	0.31	2.85	2.53	23.54
Warm Immersion Cleaning				
Metal Can Manufacture	0.11	1.54	0.95	12.72
Electroplating	0.45	1.54	3.69	12.72
Large Household Appliances and Parts Manufacture	0.24	2.03	1.99	16.77
Metal Finishing	0.33	2.04	2.76	16.88
Motor Vehicle Manufacture	0.23	3.16	1.90	26.06
Cold Immersion Cleaning				
Metal Can Manufacture	0.05	0.71	0.44	5.87
Electroplating	0.21	0.71	1.70	5.87
Large Household Appliances and Parts Manufacture	0.11	0.94	0.92	7.74
Metal Finishing	0.15	0.94	1.28	7.79
Motor Vehicle Manufacture	0.11	1.46	0.88	12.03

[a]50%tile indicates that 50% of those facilities within the SIC code will have exposure estimates lower than those reported. The 10%tile indicates that 90% of those facilities within the SIC code will have exposure estimates lower than those reported.

TABLE 4-10 HUMAN EXPOSURE TO AQUEOUS CLEANERS IN DRINKING WATER, BY OPERATION BEFORE TREATMENT

Operation	Drinking Water (mg/yr) 50th%tile[a]	10th%tile[a]
PC Board Cleaning		
Electronic Component Manufacture	5.33	49.56
Warm Immersion Cleaning		
Metal Can Manufacture	0.05	0.71
Electroplating	0.21	0.71
Large Household Appliances and Parts Manufacture	0.11	0.94
Metal Finishing	0.15	0.94
Motor Vehicle Manufacture	0.11	1.46
Cold Immersion Cleaning		
Metal Can Manufacture	0.25	3.32
Electroplating	0.96	3.32
Large Household Appliances ans Parts Manufacture	0.52	4.38
Metal Finishing	0.72	4.40
Motor Vehicle Manufacture	0.50	6.80

[a]50th%tile indicates that 50% of those facilities within a SIC code will have exposure estimates lower than those reported. The 10th%tile indicates that 90% of those facilities within the SIC code will have exposure estimates lower than those reported.

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