Chapter 5. Perchloroethylene

Five Chemicals Alternatives Assessment Study

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5.1 Overview – Perchloroethylene

5.1.1 Characteristics of the Chemical

Perchloroethylene, or PCE, is a non-flammable, man-made chlorinated hydrocarbon. The chemical contains two carbon atoms forming a double bond and each carbon has two chlorine atoms attached. The resulting chemical formula is C_2Cl_4 and the structure is represented in Figure 5.1.1 below.

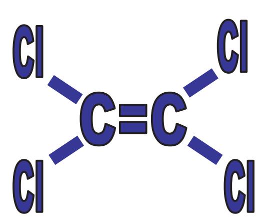

Figure 5.1.1

PCE's Chemical Abstract Series number is 127-18-4. This chemical has many additional synonyms, some of which are ethylene tetrachloride, tetrachloroethylene, perchloroethylene, carbon bichloride, carbon dichloride, perc, 1,1,2,2-tetrachloroethylene, and perchlor.

PCE is produced in the U.S. by three processes: the direct chlorination of ethylene dichloride, the oxychlorination of ethylene dichloride, and the chlorinolysis of hydrocarbons or their partially chlorinated derivatives. In the first two processes, PCE can be produced separately or as a co-product with trichloroethylene (TCE) with the raw material ratios determining the proportions of PCE and TCE. The third produces PCE as a co-product with carbon tetrachloride (Most 1989). Most PCE is produced from ethylene dichloride or other C_2 chlorinated hydrocarbons.

PCE is a clear and colorless liquid with an ether-like odor. It has low solubility in water, 0.015 g in 100 g of water, and has a specific gravity greater than water, 1.62. The vapors from PCE are 5.8 times denser than air, and its vapor pressure is 18 mm Hg at 25^{o} C making PCE heavier than air, which may allow it to collect at toxic levels in poorly ventilated spaces. While PCE is considered to be quite stable, at temperatures greater than 600º F (316º C), PCE breaks down to phosgene, and hydrogen chloride, which are dangerous respiratory irritants (ATSDR 1997). More physical properties are listed in the table 5.1.1 below.

Table 5.1.1: Chemical/Physical Characteristics of PCE ((United States Environmental Protection Agency (USEPA) 1994))	
Melting/Boiling Point	-19^{o} C / 121^{o} C
Vapor Pressure	18.47 mm Hg at 25^{o} C
Relative Vapor Density (air = 1)	5.8
Octanol/Water Partition Coefficient	Log Kow = 3.40
Specific Gravity/ Density	1.62 at 20^{o} C 1.6311 g/mL
Solubility	0.015 g in 100 g of water, low solubility in water
Soil Sorption Coefficient	Log Koc = 665
Bioconcentration Factor	39 (rainbow trout, Oncorhynchus mykiss) 49 (bluegill, Lepomis macrochirus)
Henry's Law Coefficient	1.8 x 10-2 atm m^{3}/mol
Biodegradation (days)	Water 60; Soil 120; Sediment 540; Air 96 (PBT profiler)

5.1.2 Health and Environmental Impacts

Exposure to PCE can be as a result of environmental contamination, presence in consumer products or occupational sources. PCE levels in the environment tend to be higher in urban and industrial areas. The ASTDR estimates that the most prevalent route of exposure to PCE is by inhalation and it is readily absorbed into blood through the lungs.

PCE can be detected by smell at levels ranging from 5 to 50 ppm. Therefore odor is a somewhat adequate detector for acute, high level exposures above the OSHA PEL of 100 ppm. In states that have a lower exposure limit (*e.g.,* California's PEL is 25 ppm), odor would not be an adequate detector. In addition, odor is not adequate for long term chronic exposures, because PCE can dull or desensitize the olfactory senses over a long period of time.

Other exposure routes of concern are oral via drinking water or contaminated food (Habeck 2003). Dermal exposure is generally considered a minor route of exposure but direct skin exposure to PCE in the liquid form can result in irritation and blistering. Target organs for PCE are the central nervous system and the liver (ATSDR 1997). Some studies suggest that frequent over-exposure to some organic solvents over months or years may cause lasting and possibly permanent central nervous system effects. Fatigue, lack of muscle coordination, loss of concentration as well as short term memory loss, and personality changes exhibited as nervousness, anxiety or irritability are some of the potential permanent long-term effects of chronic and frequent exposure (California Department of Health Services 1989). In addition, PCE inhaled by pregnant women can reach a developing fetus and has been found in breast milk of mothers exposed to the chemical (Habeck 2003).

Acute Exposure

For inhalation exposures, PCE can be irritating to the upper respiratory tract, cause giddiness, headache and intoxication. Nausea and vomiting may follow from inhalation of large amounts.

Concentrations of 200 ppm or more have been associated with dizziness, confusion, headache, nausea, and irritation of the eyes and mucous tissue. Exposure to extremely high levels (>1,500 ppm) may lead to unconsciousness due to anesthesia and, in extreme cases, death from respiratory depression. The IDLH for PCE has been set at 150 ppm (NIOSH 1996).

Skin contact with PCE can cause irritation. Symptoms can include redness, itching, and pain. Prolonged exposure can result in the removal of natural protective oils from skin resulting in irritation, dryness, cracking and dermatitis. Likewise, extended dermal contact can result in second- and third-degree chemical burns. Furthermore, contact of PCE vapors above 75 ppm with the eyes will result in irritation, redness, and pain (NIOSH 2000).

Chronic Exposure

Long term exposure to PCE may cause liver, kidney or central nervous system damage. Furthermore, the exposure can yield to an aggravation of pre-existing conditions. For example, persons with pre-existing skin disorders or eye problems or impaired liver or kidney function may be more susceptible to the effects of the substance. PCE can affect your brain and central nervous system as a whole, in a similar way as consumption of alcohol. Therefore the consumption of alcoholic beverages within a short time period of exposure to PCE enhances the toxic effects from PCE and alcohol. The two would have an additive effect on the central nervous system (California Department of Health Services 1989).

Overexposure may result in cumulative liver and central nervous system (CNS) damage or narcosis. Over all, PCE can affect the liver, kidneys, eyes, skin, respiratory system, and CNS.

Reproductive and Developmental Effects

There are conflicting data on the status as PCE as a reproductive and developmental toxin in both humans and animals. Some studies have reported adverse reproductive effects of PCE , including spontaneous abortions, menstrual disorders, altered sperm structure and reduced fertility, but the studies were limited and not conclusive (USEPA 1994).

Studies also have been conflicting regarding birth defects in animals, with some finding increased incidences in liver tumors and leukemia while others find no teratogenic effects. What is widely agreed upon is that PCE is able to transport across the placenta to the fetuses of pregnant women who have been highly exposed. In addition, PCE has been found in the breast milk of nursing mothers.

Carcinogenic Classification

Several agencies have investigated PCE's association with cancer. The National Toxicology Program NTP classifies PCE as "Reasonably anticipated to be human carcinogen" (National Toxicology Program 2005). IARC lists PCE as Group 2A, "Probably carcinogenic to humans." EPA specifies it as "Group B/C, probable/possible human carcinogen" (OSHA 2005) and ACGIH designates it as an A3, confirmed animal carcinogen (ACGIH 2006).

A recent Massachusetts-based research project from Cape Cod involved looking at PCE exposure through contaminated drinking water and found an association between PCE exposure and cancer rates (Aschengrau, et. al, 2003).

Table 5.1.2 summarizes the acute, chronic and cancer hazards associated with PCE.

Table 5.1.2: Perchloroethylene
Acute, Chronic and Cancer Hazards

Acute Effects (Short Term)	**Chronic Effects** (Long Term)	**Cancer Hazards**
• Single exposures can cause CNS effects such as dizziness, headache, sleepiness, confusion, nausea, difficulty speaking and walking. • High- level exposure may cause vomiting, unconsciousness & death • Not considered a significant skin irritant but prolonged exposure with undiluted liquid may cause skin irritation. • An eye irritant causing pain, redness and general inflammation.	• Long-term exposure may cause liver and kidney damage. • Prolonged and repeated exposure may cause dermatitis. • Increased health risks for people with pre-existing skin disorders and impaired renal or liver function.	• Reasonably anticipated to be a human carcinogen, sufficient evidence in animals, by NTP Animal testing has linked high exposure to liver and kidney cancer as well as leukemia. • NIOSH recommends handling it as a possible carcinogen

Worker Health

The OSHA PELs for PCE are 100 ppm for an 8 hour day and a maximum exposure level of 200 ppm for 5 minutes in any 3-hour period. California's state OSHA program has set the PCE permissible exposure level at 25 ppm, 75% lower than the national OSHA level. ACGIH has established a threshold limit value of 25 ppm, and a short term exposure limit of 100 ppm (OSHA 2005).

Public Health

The EPA has set a maximum contaminant level (MCL) in drinking water at 0.005 mg PCE/L water (USEPA 2006). The reference dose for PCE is 0.01 mg/kg/day.

Environmental Hazards

PCE most often enters the environment via fugitive emissions from dry cleaning and metal degreasing industries and by spills or accidental releases to air, soil or water (USEPA 2006). When released to soil, PCE will evaporate fairly rapidly into the atmosphere due to its high vapor pressure and low adsorption to soil. It can leach rapidly through sandy soil and therefore may reach groundwater.

When PCE is released in water, the primary loss will be by evaporation. Chemical and biological degradation are expected to be very slow. PCE should not accumulate in aquatic organisms nor absorb onto sediment (USEPA 2006). PCE is toxic to aquatic organisms.

For releases to the atmosphere, PCE will be expected to exist in the vapor phase and will degrade through reaction with photochemically produced hydroxyl radicals or chlorine atoms produced by photooxidation of PCE (USEPA) 2006).

5.1.3 Use and Functionality

Primary applications of PCE have been as a chemical intermediate or as a solvent, as most organic materials dissolve in PCE.

Nationally, since 1998 the major use of PCE has been as the basic raw material in the manufacture of hydrofluorocarbon (HFC) 134a, a popular alternative to chlorofluorocarbon (CFC) refrigerants. It also is used in the synthesis of several hydrochlorofluoro-carbons (HCFC 123 and 124 and HFC 125). In 2004 over 66% of the 355 million pounds of PCE use was in this application.

The second most common use of PCE in 2004, dry cleaning, constituted 12% of the total PCE usage nationally. This is down from about 25% of the 344 million pounds in 1998. The decrease can be attributed to the improved efficiency of dry cleaning machines in the industry as well as the emergence of alternative cleaning processes and chemicals. PCE constitutes 70% of all commercial dry cleaning solvents.

In 2004, aerosol products (for cleaning tires, brakes, engines, carburetors and wire as well as an anti-seizing agent) made up 12% of the total use of PCE. Automotive aerosols use has remained about the same or declined slightly since 1998.

As an industrial metal cleaning and degreasing agent, the trend has been a slight decrease in the overall usage. The portion of PCE used as a vapor degreaser is now 8%. Table 5.1.3 A lists the shift in PCE usage from 1998 to 2004.

Table 5.1.3 A: Shift in National PCE Usage from 1998 to 2004
(Halogenated Solvents Industry Alliance, Inc. 2005)

PCE Use Category	% in 1998	% in 2004
Chemical intermediate	50	66
Dry Cleaning/textile processing	25	12
Automotive aerosols	10	12
Metal cleaning/degreasing	10	8
Miscellaneous	5	2

PCE Regulations

Table 5.1.3 B lists various regulations and requirements that are associated with PCE.

Table 5.1.3 B: PCE Regulations and Requirements (National Toxicology Program 2005)

Agency	Regulation and Requirements
CPSC (Consumer Product Safety Commission)	Visual novelty devices containing PCE have labeling requirements
DOT (Department of Transportation)	PCE is considered a hazardous material and a marine pollutant and special requirements have been set for marking, labeling, and transporting this material
EPA	• Clean Air Act NESHAP: Listed as a Hazardous Air Pollutant (HAP) • NSPS: Manufacture of substance is subject to certain provisions for the control of • Volatile Organic Compound (VOC) emissions • Urban Air Toxics Strategy: Identified as one of 33 HAPs that present the greatest threat to public health in urban areas • Clean Water Act • Effluent Guidelines: Listed as a Toxic Pollutant • Water Quality Criteria: Based on fish/shellfish and water consumption = 0.69 μg/L; based on fish/shellfish consumption only = 3.3 μg/L • Comprehensive Environmental Response, Compensation, and Liability Act • Reportable Quantity (RQ) = 100 lb • Emergency Planning and Community Right-To-Know Act • Toxics Release Inventory: Listed substance subject to reporting requirements • Resource Conservation and Recovery Act • Listed Hazardous Waste: Waste codes in which listing is based wholly or partly on substance - U210, F001, F002, F024, F025, K019, K020, K073, K116, K150, K151 • Characteristic Toxic Hazardous Waste: TCLP Threshold = 0.7 mg/L • Listed as a Hazardous Constituent of Waste • Safe Drinking Water Act • Maximum Contaminant Level (MCL) = 0.005 mg/L
FDA	Maximum permissible level in bottled water = 0.005 mg/L

5.2 Perchloroethylene Use Prioritization

Uses in Massachusetts Manufacturing

In Massachusetts, three of the above mentioned applications for PCE - aerosol packaging, metal degreasing and garment cleaning - were also reported in the Toxics Use Reduction Act (TURA) data for 2003. In addition, use in plating masks was reported. The maskant is used to protect areas during certain plating steps and is removed before the process is finished. This masking agent does not appear in the final manufactured product. The largest national use, manufacturing of refrigerants or HCFC's, was not reported in the TURA data, and is not a significant manufacturing use in Massachusetts.

Six companies reported use of PCE in the 2003 TURA data. This does not represent the total number of companies using PCE in Massachusetts, because small businesses (< 10 employees) and those using less than 10,000 lb of PCE are not required to report. For example, there is only one facility in the state reporting PCE used in dry cleaning (15,000 lb total use). The Massachusetts DEP works with dry cleaning facilities through their Environmental Results Program, (ERP). Under this program, DEP has identified over 550 dry cleaning facilities that use PCE. Total usage is estimated to be over 1 million pounds.

Metal cleaning and degreasing was responsible for 6% of total PCE use reported under TURA in 2003. Again, this is not representative of all PCE usage for metal cleaning and degreasing because of the high reporting threshold (10,000 lb) relative to the amount used in most facilities.

Two companies reported PCE usage in distribution, accounting for just over half of the approximately 304,000 lb of PCE used in the state. This activity typically consists of repackaging chemicals from tank wagons into smaller containers. The smaller containers are then sold to users in Massachusetts and other states for a specific end use. This study focuses on alternatives for the specific end uses, rather than for the distribution of the chemical.

The second largest reported use in the state is for custom blending of raw material, reported by one aerosol packaging facility. This use made up 34% of the PCE reported. When contacted, this facility reported that they were not packaging PCE for use in automotive aerosols at this time, but had done so in the past. While some industry experts stated that PCE was no longer used widely in many automotive aerosols, the *Household Products Database* (National Library of Medicine 2004) reports PCE being used in automotive and specialty consumer aerosol cleaners.

Total pounds of reported PCE usage in Massachusetts and the percentage from 2003 are listed in the Table 5.2 A.

Table 5.2 A: PCE TURA Reported Use 2003

(Toxic Use Reduction Institute (TURI) 2005)

PCE TURA Reported Use 2003	Total Use (lbs)	% of total
Distribution	154,207	51
Aerosol packaging	103,529	34
Metal cleaning/degreasing	19,600	6
/textile processing	15,697	5
Plating Mask	11,184	4

Uses in Products

In addition to previously mentioned applications, there are many smaller volume industrial and consumer uses of PCE. Industrial uses include paint stripping, adhesive and ink formulations, insulating fluid in electrical transformers and paper coatings. Consumer uses for PCE include furniture polish/cleaners, oven cleaners, lubricants and pesticides. Some uses frequently listed in references have been determined to be historical and are marked below as "not a current practice." Table 5.2 B lists general product types that may utilize PCE.

Table 5.2 B: Industrial and Consumer Use/Applications of PCE

Industrial Use/Application	Consumer Use/Application
Paint stripping; paint & varnish removers; consumer – not a current practice	Furniture polish/cleaners household rug & upholstery cleaners
Adhesive formulations	Non structural caulking
Printing inks	Oven cleaners
Solvent for de-inking paper	Lubricating oils & greases
Paper coatings	Laundry starch products – not a current practice
Insulating fluid in electrical transformers	Waterproofing compound Shoe polish
Silicones	Compounds & sealants
Process solvent for desulfurizing coal	Silver polish, spray
Heat-exchange fluid	Rubber coatings
Remove soot from industrial boilers	Pesticides – not a current practice

Summary of Stakeholder Input

Stakeholders raised several issues concerning the use of PCE. One of the major concerns was the exposure of workers (especially in automotive repair facilities) using aerosol PCE products for cleaning and repair work. In addition, there were concerns that many products were available to consumers and were used with limited awareness or health warnings about the potential for exposure.

In addition to automotive applications, there was strong stakeholder interest in learning more about the health implications of various dry cleaning alternative solvents that are currently available on the market. There have been several other organizations such as the Institute for Research and Technical Assistance (IRTA), California Environmental Protection Agency Air Resources Board (CARB) and the state of North Carolina that have done reports on dry cleaning alternatives in the past few years. Stakeholders were eager to have that body of information expanded upon and related to conditions in Massachusetts.

Priority Uses

Based on the analysis of national and state PCE use, stakeholder input and exposure potentials, three high priority use categories were selected. PCE is widely used in dry cleaning of garments in Massachusetts with exposure potential to workers. This combined with strong stakeholder interest led to its selection as a high priority use. Automotive aerosols were determined to be a high priority because of exposure to both workers and the general public and because of the strong interest by stakeholders.

Vapor degreasing was selected as a high priority because of its prevalence nationally and in Massachusetts and because of industry's interest in learning more about the alternatives. The Institute has a great deal of expertise in cleaning technologies and through the TURI Laboratory's work had heard from several Massachusetts companies that were searching for vapor degreasing alternative chemistries. From this work, there was an identified need to identify drop-in replacements for PCE in existing closed-loop, air-tight vapor degreasing equipment.

5.3 PCE Alternatives Prioritization

5.3.1 Alternatives Associated with Dry Cleaning

Available Alternatives for Dry Cleaning

Since the 1960s, the dry cleaning industry has predominantly used PCE as its cleaning solvent. In Massachusetts, there are over 550 dry cleaning facilities that report under DEP's Environmental Results Program. These facilities use over 73,000 gallons of PCE resulting in 600,000 pounds of hazardous waste (Peck 2005).

Currently several dry cleaning alternative chemicals and processes are available on the market, summarized in table 5.3.1. The most widely used alternatives are hydrocarbon-based systems from three manufacturers. Capitalizing on the success of these hydrocarbon systems, one manufacturer created a mixture of hydrocarbons (isoparaffins) with a hydrofluoroether and a perfluorocarbon to further enhance performance (expanded cleaning capabilities) and improve safety (by raising the flash point). Another option uses volatile methyl siloxane as the cleaning solvent. Glycol ether-based alternatives are also used to a lesser extent.

Non-solvent based alternative dry cleaning systems currently on the market include carbon dioxide and wet cleaning. Carbon dioxide, as either a liquid or a supercritical fluid, can also be used to clean garments utilizing specialized equipment. Typically, liquid carbon dioxide is maintained under a pressure of 700 pounds per square inch and uses detergents specifically designed for this process. Companies are also using wet cleaning processes for more dry-clean-only garments. These processes rely on water, detergent, conditioners and/or degreasers to clean the garment. Wet cleaning processes sometime use specialized equipment designed to minimize temperature and agitation or to create a fine mist to deliver the water-based detergents to the materials to be cleaned.

Table 5.3.1 A: Dry Cleaning Alternatives

Classification	Sample Product Names
Hydrocarbons	Exxon DF 2000 Fluid
	Chevron EcoSolv
	Shell Shellsol
	Drylene 800
Hydrofluoroether (HFE), perfluorocarbon (PFC), hydrocarbon (isoparaffins)	Pure Dry
Volatile methyl siloxane (VMS) (decamethyl cyclopentasiloxane); GE Cyclopentasiloxane	GreenEarth
Substituted aliphatic glycol ethers (dipropylene glycol tertiary-butyl ether DPTB)	Rynex
Traditional wet cleaning	Laidlaw Corporation PowerBrite detergent
Cold Spray Washing	Icy Water: DWX-44 detergent
Spray Washing	Green Jet : DWX-44 detergent
Carbon dioxide	Liquid carbon dioxide

Alternatives Screening

All eleven dry cleaning chemistries passed the initial EH&S screen for carcinogens, PBTs and TURA More Hazardous Chemicals.

Alternatives Prioritization for Dry Cleaning

In order to limit the number of alternatives studied, alternatives were prioritized using information about which alternatives were being used in Massachusetts and preliminary EH&S and technical feasibility data. Input from stakeholders was also a key factor in determining priority alternatives.

Stakeholders felt that it would be valuable to assess as many classes of commercially available alternatives as possible. Therefore, an important criterion for prioritization was to have each type or class of alternative represented in the list for final assessment.

One product, Pure Dry, was eliminated from further assessment because two of its components, hydrofluorocarbon and hydrofluoroether, had PBT concerns. Specifically, both chemicals exceed EPA's very persistent criteria for water, soil, sediment and air. In addition, HFE was in the bioaccumulative range and of moderate concern for aquatic toxicity.

Because several of the hydrocarbon alternatives were similar in their make-up, one was selected as representative of that class of alternatives. Based on the Institute's survey of Massachusetts dry cleaners, Exxon DF2000 is used more frequently than the other hydrocarbon alternatives. It is important to note that while the other two hydrocarbon alternatives (Chevron EcoSolv and Shell Shellsol) were not included in the following assessment, they would be worthy of consideration as feasible alternatives.

Drylene 800, a petroleum distillate product, was not chosen for further study because very little information could be obtained on this product. In addition, the Institute did not identify any dry cleaners in Massachusetts using Drylene 800.

Traditional wet cleaning is used by many dry cleaners in Massachusetts for some garments or when requested by customers. There are also some dry cleaners that use wet cleaning exclusively. The product options for the wet cleaning alternatives include traditional wet cleaning, Icy Water and Green Jet. Icy Water and Green Jet both use the same DWX 44 detergent.

Rynex, which is increasing used by dry cleaners in Massachusetts according to the Institute's survey, is based on substituted aliphatic glycol ethers (dipropylene glycol tertiary-butyl ether DPTB). Rynex did not approach any levels of concern in the EH&S screening.

GreenEarth was found to have some PBT levels of concern with half-lives of 340 in sediment and 31 days in air. However, due to the interest of stakeholders in GreenEarth as an alternative, and because it is the second most popular alternative for dry cleaning, behind DF 2000, based on the Institute's survey of Massachusetts dry cleaners, it was included for further assessment.

Liquid carbon dioxide is currently not as popular as many other alternatives, but was included because of its potential as a minimal-waste option with no traditional solvent used.

The screening and prioritization processes narrowed the field of possible dry cleaning alternatives to assess to the five listed on Table 5.3.1 B. These were, DF 2000, GreenEarth, Rynex, Wet cleaning with DWX 44 (including sub categories of Icy water and Green Jet processes) and liquid carbon dioxide. Products with their corresponding classifications are listed in the next table.

Table 5.3.1 B: Selected Dry Cleaning Alternatives and Classifications

Dry Cleaning Alternatives	Classification
DF 2000	Isoparaffin Hydrocarbon
Rynex	Substituted Aliphatic Propylene Glycol Ether
GreenEarth	Volatile methyl siloxane
Traditional Wet Cleaning	Aqueous based
Icy Water	Aqueous based
Green Jet	Aqueous based
Carbon Dioxide	Liquid carbon dioxide

5.3.2 Alternatives Associated with Vapor Degreasing

Available Alternatives for Vapor Degreasing

Over the years, the preferred solvent used in vapor degreasing has changed many times. Vapor degreasing solvents have included chloro-fluoro-carbons (CFCs), trichloroethane (TCA), trichloroethylene (TCE) and perchloroethylene (PCE). CFCs and TCA were found to be ozone depleting and have been phased out under the Clean Air Act. Currently, the major solvent used in vapor degreasing operations is TCE. PCE is used less often than TCE, but is still used in significant quantities.

There are many reasons why companies continue to use vapor degreasing. Many do so because of concerns about the ability of aqueous-based alternative cleaning processes to produce clean and dry parts. Further obstacles of cleaning with water based cleaning may be associated with the design and complexity of parts shapes. Due to the high surface tension of water, aqueous cleaning formulations can not always get into small, blind holes without implementing a significant process change. Solvents in the vapor form are more successful at cleaning these hard to reach areas. In some instances, the costs associated with new equipment required for alternative processes are a barrier.

n-Propyl Bromide (nPB)

Several different cleaning formulations have been developed to address the need for alternatives to PCE in vapor degreasing. The most widely used alternatives have been products based on n-propyl bromide (nPB). It should be noted that nPB was found to be a developmental toxin by the State of California and was added to their Proposition 65 list on December 2005. The chemical is also currently undergoing carcinogenicity testing by the EPA. At the same time, however, EPA has proposed allowing the use of nPB, under the Significant New Alternatives Policy program (SNAP), as a replacement for ozone depleting substances such as CFC 113, trichloroethane, HCFC 141b and more recently, TCE and PCE in vapor degreasing and other applications. Since nPB is a relatively new solvent to the global market to replace higher ozone depleting substance (ODS) solvents, new data about its toxicity is still emerging.

Halogenated Organic Alternatives

Other classes of products include those based on hydrochlorofluorocarbons (HCFCs) or hydrofluorocarbons (HFCs), which are available from a few manufacturers in varying forms. Hydrofluoroethers (HFEs) have also shown some success in vapor degreasing applications and are available in multiple formulations.

Siloxane-Based Alternatives

The last class of solvent-based alternatives identified is volatile methyl siloxanes (VMS). These products have not been as widely used for vapor degreasing but have many of the necessary physical proprieties such as surface tension and Kb[6] value.

Aqueous-Based Process Change

Switching to aqueous systems is a potentially feasible alternative to solvent-based vapor degreasing, though this option may involve additional time and capital investment. The Institute's Surface Solutions Laboratory (TURI Lab) has worked with companies to help them switch from traditional chlorinated solvents to aqueous based cleaning or alternative solvent based vapor degreasing. Each company's cleaning needs are unique and a cleaning process should be specifically tailored for those needs. Information on the success of the TURI Lab's efforts in alternative, less toxic cleaners can be found at www.cleanersolutions.org.

In a related effort to eliminate chlorinated solvent degreasing in Massachusetts, the Institute worked with the Massachusetts Office of Technical Assistance on an EPA funded grant to help companies replace chlorinated solvents in their cleaning processes. One company that received assistance during the study had switched from TCE to an nPB based cleaner but then approached the TURI Lab for help in making the next step to an aqueous cleaner. This was accomplished in 2004 and was fully integrated and implemented throughout the company and its plating lines in 2005. Details about this process are included in Appendix E.

[6] Kauri butanol value (Kb) is a measure of the cleaning strength of a solvent. The higher the Kb, the more aggressive the solvent. For more information, see the Technical Assessment for vapor degreasing alternatives.

Table 5.3.2 A summarizes the products identified as alternatives to PCE-based vapor degreasing.

Table 5.3.2 A: Vapor Degreasing Alternatives

Classification	Sample Products
Propylbromide (nPB)	Tech Spray Solvon (IP or PB)
	Petroferm Lenium (GS, CPor ES)
	EnviroTech Ensolv
	Kyzen Metalnox 6960
Hydrochlorofluorocarbon (HCFC)	Asahi AK 225
Hydrofluorcarbon (HFC)	DuPont Vertrel MCA
	MicroCare Heavy Duty Degreaser C
	MicroCare Heavy Flux Remover C
Hydrofluoroether (HFE)	3M HFE 7100, 7200 or 71DE
Volatile methylsiloxane (VMS)	Dow OS 10, OS 20, or OS 30
Process Change	Aqueous based alternatives and systems (see case study of multi-step phase out of vapor degreasing)

Alternatives Screening

All identified vapor degreasing alternatives passed the initial EH&S screen for carcinogens, PBTs and TURA More Hazardous Chemicals. However, there were some concerns brought up during this phase of screening. The manufacturing of 2-propanol (isopropyl alcohol – an ingredient in some of the formulations) by the strong acid process is listed as a Group 1 carcinogen (carcinogenic to humans) by IARC while the chemical itself is listed as a Group 3 (not classifiable as to its carcinogenicity). The screening methodology for this project only applies to substances in the product, not to upstream or downstream processes, feedstocks or waste materials. Therefore, alternatives with 2-propanol were not screened out (because the carcinogenicity is with the manufacture of the 2-propanol only, not the chemical as it exists in the cleaning formulations), however that information was considered during the prioritization process.

Alternatives Prioritization for Vapor Degreasing

Since there were several similar products within some of the chemical classes, representative products were selected for further assessment. In addition, several products contained chemicals with high Persistence Bioaccumulation or Toxicity values or had potential carcinogenicity concerns associated with the life cycle. This information was considered during the prioritization process, noted below, when final decisions were made about which alternatives to assess.

n-Propyl Bromide (nPB)

Serious concerns regarding the toxicity of nPB were identified during the prioritization process. Even so, when stakeholders were consulted they indicated that including it in the assessment would be valuable in their efforts to compare potentially safer substitutes for PCE. Because of the pending approval of nPB under the SNAP program, products based on nPB are now frequently considered as alternatives for chlorinated solvents in many applications including vapor degreasing. Therefore, the Institute decided to include an nPB-based product in the assessment. The one nPB product that did not contain 2-propanol (EnviroTech's Ensolv) was selected for assessment.

Halogenated Organic Alternatives

The HFEs and the HCFC-based AK 225 were dropped from further review based on their high persistence. Each HFE product contained at least two components with half-lives that exceeded the EPA very persistent criteria. In addition, AK 225 contained a component that also exceeded the EPA very persistent criteria. As a result, the Institute did not consider these alternatives for further evaluation. Two of the three HFC products (the Vertrel product and one of the Microcare products) were prioritized for further assessment.

Siloxane-Based Alternatives

The Dow OS 10 VMS product was determined to be the safest alternative within the VMS category and was therefore selected for assessment. Specifically, the Dow OS20 and OS30 products exceeded the persistence criteria for sediment and air.

Aqueous-Based Process Change

TURI's Lab has had great success in helping companies change from vapor degreasing to aqueous based cleaning. Through TURI's Lab assistance and database of testing, aqueous based alternative cleaning products have been found for nearly 90% of all companies that the lab has worked with. Appendix E.1 contains a description of aqueous-based alternatives previously tested at TURI's Lab that could be used in a vapor degreasing multi-phase process change.

This approach to assisting companies in adopting alternatives is necessary because there are many possible choices for chemistries and process equipment, and the optimum alternative is dependent on the particular parts, materials and soils. Because of this, and based on the Institute's extensive experience in this field, it was determined that while aqueous cleaning remains a technically and economically feasible and safer alternative for many vapor degreasing situations, trying to choose a representative alternative for this study would not result in a meaningful comparison with the other vapor degreasing alternatives. Therefore, companies using this report to investigate alternatives are encouraged to review the materials in Appendix E.1 and contact the Institute for more specific information regarding aqueous cleaning options.

Summary of Vapor Degreasing Alternatives Prioritization

As a result of the prioritization process, the following alternative formulations were selected for further assessment and comparison to PCE: one nPB product (Ensolv), one VMS product (DOW OS 10), and two HFC products (Flux Remover C and Vetrel MCA). These products were selected as representative products of their chemical classes in order to assess a diverse set of alternatives. Products with their corresponding classifications are listed in Table 5.3.2B.

Table 5.3.2 B: Selected Vapor Degreasing Alternatives and Classifications

Vapor Degreasing Alternatives Evaluated	Classifications
Ensolv	n-propyl bromide (nPB)
DOW OS 10	Volatile methyl siloxane
Flux Remover C	Hydrofluorcarbon
DuPont Vertrel MCA	Hydrofluorcarbon

5.3.3 Alternatives Associated with Automotive Aerosols

Available Alternatives

The use of PCE in aerosols is widespread. The chemical can be found in applications ranging from adhesive applications to graffiti removal. PCE is used in aerosol cleaning products, many of which have been designed for various automotive needs. The three main uses of PCE in automotive shops include brake cleaning, engine cleaning and tire cleaning. Engine cleaning can be further broken down to products used externally and those used for more sensitive internal engine parts (*e.g.,* carburetors and fuel injection systems). This further classification in the engine cleaner category is necessary to ensure that the alternatives evaluated are appropriate for the intended engine cleaning application.

While immersion and other methods of cleaning are also available for some automotive repair applications, this study only included aerosol delivery systems and formulations. Automotive aerosols were a high priority for stakeholders because of their use and by both consumers and small businesses and strong potential for exposure. In addition, some of these products were identified through the Household Products database to contain upwards of 85 % PCE (National Library of Medicine 2004).

The list of potential alternatives identified represents a wide range of formulations. Many are based on non-halogenated solvents including toluene, heptane, acetone or petroleum distillates. Others use terpenes, glycol ethers, or aqueous surfactants. Specific information on each alternative is included in Appendix C.3 in the Alternatives EH&S Screening tables.

Table 5.3.3 A: Automotive Aerosols Alternatives

Classification	Sample Products
Brake	AMREP Inc, Misty Brake and Parts Cleaner EF
	AMREP Inc, Misty Brake Parts Cleaner II
	Bio Chem Systems BioBrake
	CRC Industries Brakleen Brake Parts Cleaner-Non-Chlorinated
	Mirachem 500 Foaming Aerosol
	ZEP Manufacturing Company Brake Wash
Engine - External	3M Citrus Base Cleaner (Aerosol)

Table 5.3.3 A: Automotive Aerosols Alternatives

Classification	Sample Products
	American Polywater Corporation Type HP™ Cleaner/ Degreaser
	AMREP Inc, Misty Coil Cleaning Foam
	AMREP Inc, Misty Safety Solvent 2000
	AMREP Inc, Misty Solvent Cleaner & Degreaser
	AMREP, Inc. Misty Heavy Duty Butyl Degreaser
	Berryman Products, Inc, New Engine Degreaser
	Bio Chem Systems Bio T Foammax
	Citrus Engine Brite Engine Cleaner & Detailer
	ECOLINK 3005 High Purity Contact & Precision Parts Cleaner
	LPS Micro X
	MicroCare Flux Remover C
	MicroCare Heavy Duty Degreaser C
	Mirachem 500 Foaming Aerosol
Engine - Internal	AMREP Inc, Misty Choke & Carburetor Cleaner II
	Malco Carburetor Cleaner Aerosol
	Malco Foamy Air Intake Cleaner Aerosol
	Malco Fuel Injector Air Intake Cleaner (Aerosol)
	ZEP Manufacturing Company Choke & Carburetor Cleaner
	ZEP Manufacturing Company ZEP Carb X (Aerosol)
Tire	AMREP Inc, Misty Detailing & Dressing Spray
	Armor All STP® Son of a Gun® One Step Tire Care
	Armor All Tire Foam (Aerosol)
	Bio Chem Systems Bio T General Purpose Foam
	Mirachem 500 Foaming Aerosol

Alternatives Screening

None of the automotive aerosols were eliminated due to the initial screening. Many, however, contain chemicals with serious environmental or health concerns; this information was taken into account during the prioritization process.

Alternatives Prioritization

For brake, engine and tire cleaners, where similar products existed within a particular chemical class, representative products were selected for further assessment. In addition, to arrive at a reasonable number of alternatives for assessment, products that contained chemicals with high values for P, B or T, or that have carcinogenicity indications, were considered a lower priority for assessment.

<u>Brake Cleaners</u>

Two products, ZEP Manufacturing Company Brake Wash and AMREP Inc Misty Brake Parts Cleaner II, contain 2-propanol. Due to the carcinogenicity of one manufacturing method for 2-propanol, and because there are numerous other alternatives available for assessment, these products were eliminated from further consideration.

The remaining four aerosol brake cleaner products, Bio Chem Systems BioBrake, CRC Industries Inc Brakleen Brake Parts Cleaner-Non-Chlorinated, AMREP Inc, Misty Brake and Parts Cleaner EF and Mirachem 500 Foaming Aerosol, were selected for further assessment. It should be noted that some of these products contain constituents with known hazards, for example, one product contains 43% toluene. These issues will be addressed in the EH&S assessment.

Table 5.3.3 B: Brake Cleaning Aerosol Alternatives and Classifications

Brake Cleaning Aerosol Alternatives Evaluated	Classifications
AMREP Inc, Misty Brake and Parts Cleaner EF	Heptane-Acetone mix with Carbon Dioxide propellant
Bio Chem Systems BioBrake	C9-C12 hydrocarbons; Propanol ,2-methoxymethylethoxy; Acetone;
CRC Industries Brakleen Brake Parts Cleaner-Non-Chlorinated	Toluene; Methanol; Acetone; Xylene; Heptane; n-hexane; with Carbon Dioxide propellant
Mirachem 500 Foaming Aerosol	Aqueous based with propane-isobutane propellants

<u>Engine - External</u>

Two products, both from MicroCare, were eliminated from further analysis as an engine cleaner because of high persistence values for the constituents tetrafluoroethane (aerosol only), pentafluorobutane and decafluoropentane. One product, Ecolink 3005 High Purity Contact & Precision Parts Cleaner was eliminated from further study because one of its constituents exceeded the EPA criteria for water, soil, sediment and air persistence.

In addition, several products were considered a lower priority for assessment based on the presence of 2-propanol or mineral seal oil (some "mineral oils, untreated and mildly treated" are an IARC Class 1 carcinogen). For the case of mineral seal oil, there was not enough information available to determine whether the mineral oils in these products are highly treated or not. For each of these alternatives, there were other products based on similar formulations, but without 2-propanol and mineral oil, that were included in the assessment. Therefore several products were eliminated: AMREP Inc, Misty Safety Solvent 2000 (2-propanol), LPS Micro X (2-propanol), and Bio Chem Systems Bio T Foamaxx (Mineral Seal Oil).

This still left seven products that represented a range of different mixtures. It was decided to include them all for final assessment. These products were Misty Heavy Duty Butyl Degreaser, Citrus Engine Brite Engine Cleaner & Detailer, 3M Citrus Base Cleaner (Aerosol), AMREP Inc, Misty Solvent Cleaner & Degreaser, AMREP Inc, Misty Coil Cleaning Foam, Mirachem 500 Foaming Aerosol and Berryman Products Inc New Engine Degreaser.

Table 5.3.3 C: External Engine Cleaning Aerosol Alternatives and Classifications

External Engine Cleaning Aerosol Alternatives Evaluated	Classifications
Misty Heavy Duty Butyl Degreaser	Aromatic Petroleum Distillates; 2-Butoxyethanol; with an Isobutane-Propane propellant blend
Citrus Engine Brite Engine Cleaner & Detailer	2-Butoxy Ethanol; Methyl Esters of C16–C18 and C18; Unsaturated Fatty Acids; Petroleum Sulfonate; Kerosene; Orange Peel Oil Sweet Cold Pressed; Nonyl Phenol Ethoxylate; Carbon Dioxide
3M Citrus Base Cleaner (Aerosol)	D-Limonene with propane propellant
Misty Solvent Cleaner & Degreaser	Monocyclic Terpene Methyl Esters Of Soybean Oil
Misty Coil Cleaning Foam	Aqueous with propane-isobutane propellants
Mirachem 500 Foaming Aerosol	Aqueous with propane-isobutane propellants
Berryman Products Inc New Engine Degreaser	Aqueous cleaner with nitrogen propellant

Engine - Internal

Again the two products from MicroCare were dropped from further analysis based on the higher persistence values for the constituents Tetrafluoroethane (aerosol only), 1,1,1,3,3-Pentafluorobutane and 1,1,1,2,3,4,4,5,5,5-decafluoropentane. Similarly, many products were considered a lower priority for assessment because of the presence of 2-propanol, mineral oil or other substances with carcinogenicity concerns. These products and constituents of concern were ZEP Manufacturing Company Choke & Carburetor Cleaner (Methylene Chloride, Ethyl Benzene), AMREP Inc, Misty Choke & Carburetor Cleaner II (2-propanol), Malco Foamy Air Intake Cleaner Aerosol (2-propanol).

Three products, ZEP Manufacturing Company ZEP Carb X (Aerosol) American Polywater Corporation Type HP™ Cleaner/ Degreaser, and Malco Fuel Injector Air Intake Cleaner (Aerosol), were selected for final assessment.

Table 5.3.3 D: Internal Engine Cleaning Aerosol Alternatives and Classifications

Internal Engine Cleaning Aerosol Alternatives Evaluated	Classifications
ZEP Manufacturing Company ZEP Carb X (Aerosol)	Toluene; Methanol; Xylene; Hydrotreated Light Petroleum Distillates
American Polywater Corporation Type HP™ Cleaner/ Degreaser	Medium Aliphatic Petroleum Solvent Monocyclic Terpene
Malco Fuel Injector Air Intake Cleaner (Aerosol)	Xylene; Toluene; Propane; Isobutane; Acetone

Tire

One tire cleaning formulation, Bio Chem Systems Bio T General Purpose Foam, contained 2-propanol and was therefore a lower priority for assessment.

The remaining four products were selected for assessment. These products are Armor All Tire Foam (Aerosol), Armor All STP® Son of a Gun® One Step Tire Care, AMREP Inc, Misty Detailing & Dressing Spray and Mirachem 500 Foaming Aerosol.

Table 5.3.3 E: Tire Cleaning Aerosol Alternatives and Classifications

Tire Cleaning Aerosol Alternatives Evaluated	Classifications
Armor All Tire Foam (Aerosol)	Silicone Emulsion; Dimethyl Ether; Propylene glycol; Propane and Isobutane
Armor All STP® Son of a Gun® One Step Tire Care	Diethylene Glycol Monoethyl Ether; Alkyloxy polyethylene oxyethanol; Isobutane; Poly dimethylsiloxane; Water
Misty Detailing & Dressing Spray	Hexane; Poly Dimethylsiloxane; Petroleum Distillates; Isobutane- Propane propellant
Mirachem 500 Foaming Aerosol	Aqueous with propane-isobutane propellants

5.3.4 Summary of Alternatives Prioritization

Almost all of the alternative chemical formulations for the high priority uses selected for PCE passed the initial screening criteria of the TUR More Hazardous List, EPA or IARC carcinogen, and PBT limit values. Products were then selected for full assessment based on preferable screening results, professional recommendations and representation from different classes of formulations.

5.4 PCE Alternatives Assessment

5.4.1 Alternatives Assessment for Dry Cleaning

Technical Assessment

Dry cleaning practices must meet certain industry expectations for various operating parameters. These conditions include operating times, amount of clothes cleaned, quality of cleaning, compatibility with a wide range of clothing materials, pre-spotting requirements, and post cleaning handling (pressing, etc.).

The overall cleaning ability of a process depends on soil chemistry, textile fabric type, transport medium (aqueous vs. non-aqueous), chemistry of the additives (detergents, surfactants), the use of spotting agents, and process considerations (California Air Resources Board 2005).

Additional solvent properties to consider include evaporation rate and ease of purification through distillation. The solvent should not cause fabric to unnecessarily fade, shrink, weaken, or bleed color and should be compatible with detergents (California Air Resources Board 2005).

Each alternative is summarized briefly below. For more detailed descriptions of the different technologies, see Wolf and Morris, 2005.

Summary of Alternatives

The alternative processes and chemistries to be assessed are listed in Table 5.4.1A.

Table 5.4.1 A: Dry Cleaning Alternatives

Alternatives	Classification	General Name
DF 2000	Isoparaffin Hydrocarbon	HC
GreenEarth	Volatlile methyl siloxane	VMS
Rynex	Substituted aliphatic glycol ethers	SGE
Wet Cleaning - traditional	Aqueous based	Wet Cleaning
Wet Cleaning -Icy Water	Aqueous based	Icy Water
Wet Cleaning -Green Jet	Aqueous based	Green Jet
Carbon Dioxide	Liquid carbon dioxide	CO_2

Hydrocarbon (HC – DF 2000)

Hydrocarbon technology is the most widely used alternative to PCE Dry cleaning. The industry has a long history of using petroleum solvents as the industry relied on them for cleaning garments and other items prior to switching to the nonflammable PCE. The new version of the HC cleaning materials are most often isoparaffins, synthetic hydrotreated aliphatic hydrocarbons. DF-2000 is a combustible liquid (flashpoint >38° C and <93° C) with a flashpoint of 64° C.

The equipment for use with the new HC solvents is different from the equipment used with PCE because of HC's low flash point. Some of the machines are equipped with a refrigerated condenser (for vapor recovery) while others are not. Distillation of the HC is done in a vacuum to adjust for the higher boiling points. Initial cycle times of HC machines were longer than they were for PCE; however manufacturers have been working on reducing the process times to match those for PCE.

One issue with the HC solvent is that the use can support bacteria growth. Systems using the HC should remain free of water. The control of water can be accomplished by using an absorbent material such as Tonsil®. This additive may also eliminate the need to distill and may reduce the need to add detergents during cleaning (Wolf, Morris 2005).

Volatile Methyl Siloxanes (VMS - GreenEarth)

GreenEarth is a volatile cyclic methyl siloxane (VMS) and is a combustible liquid with a flash point of 76.7°C. As was the case for HC, VMS based solvents need to be used with equipment that is designed to handle combustible solvents. Newer equipment has been designed with larger and increased extraction speeds that work to reduce the cycle time. Due to VMS physical characteristics, the separation of the solvent and water can be difficult and separators for use with the technology have been designed to address this challenge (Wolf, Morris 2005).

Substituted Aliphatic Glycol Ethers (SGE - Rynex)

The substituted glycol ethers have a flash point of >93° C and is not considered a combustible solvent. However, equipment must be designed to handle solvents with a flash point. Cleaning does not require additional detergents as the glycol ethers are capable of removing oil-based and water-soluble soils.

Distillation is difficult for this solvent due to the interaction with water. The solvent is miscible in water and has a similar specific gravity making separation more challenging. The traditional combustible solvent equipment must be modified to route the water to one chamber and the glycol ether to another based on their boiling point differences. The separation process is slow. However, manufacturers have claimed that the equipment problem has been solved (Wolf, Morris 2005).

Aqueous Based Wet Cleaning (Traditional – PowerBrite)

Professional wet cleaning has been available to dry cleaners for more than a decade. It relies on water, conditioners, degreasers and detergent for cleaning the garments. Despite the wide use of this type of cleaning, only a few cleaners have adopted the technology as an exclusive cleaning method.

Equipment generally consists of a computer controlled washer and dryer and specialized finishing units called tensioning equipment. To prevent dimensional change and to make finishing easier, many garments are not completely dried leaving a residual of moisture. The tensioning equipment is then used to help to form garments and restore constructed garments to their final or original shape during finishing and helps to prevent them from shrinking. Disadvantages of wet cleaning are that cleaners must learn entirely new processing methods (Wolf, Morris 2005).

Aqueous Based Wet Cleaning (Icy Water- DWX 44)

This technology is similar to traditional wet cleaning but has been designed to control shrinkage and minimize tensioning. Like traditional wet cleaning, the icy water technology relies on water, detergent, conditioners and degreasers to accomplish cleaning. The process operates at a temperature of 38^{o} F and is dried with cold air. In addition, the garments are agitated at one revolution per minute in the washer and only 60 revolutions per minute in the dryer, much slower than in the traditional aqueous process.

Aqueous Based Wet Cleaning (Green Jet – DWX 44)

This aqueous process involves the use of chemical cleaning and drying in one machine. Cleaning takes place using a mist of water and detergent. The garments are not immersed in liquid. The machine cycle is shorter than the cycle for PCE but can only be used for garments that are lightly soiled. The detergent used for this process, as well as Icy Water is predominantly DWX 44 (Wolf, Morris 2005).

Carbon Dioxide (CO_2)

This process relies on liquid carbon dioxide under a pressure of 700 lb/in^2 to clean garments. Because of the pressure used the equipment is expensive and costly to maintain; it is made of stainless steel and must be capable of withstanding significant pressure. During cleaning, the system is pressurized prior to the cleaning cycle and depressurized after the cleaning cycle. The equipment may include filters for removing particulate contaminants and a distillation unit for separating the soluble contaminants. The detergent used in the carbon dioxide process is relatively expensive and is described by some cleaners who use the technology as not aggressive enough.

The carbon dioxide used in the process can be stored in a bulk tank onsite or a service can be used which regularly changes out the empty tanks when more carbon dioxide is needed. The most common equipment requires a large amount of space yet there are some machines that are about the same size as a traditional PCE machine (Wolf, Morris 2005).

While CO_2 is known to be a green house gas, the CO_2 used for dry cleaning is captured as a byproduct of industrial production. There is no overall net increase in CO_2 emitted to the atmosphere and therefore does not contribute to global warming overall (California Air Resources Board 2004).

Emerging Technologies

Household dry cleaning, air-cleaning and textile alternatives are emerging technologies. While sufficient information to conduct an alternatives assessment was not available, a brief description is provided at the end of this section.

Performance Criteria

Performance information was drawn largely from two sources. One source was the *Evaluation of New and Emerging Technologies for Textile Cleaning* conducted by the Institute for Research and Technical Assistance (IRTA) that was prepared for the California Air Resources Board and the U.S. Environmental Protection Agency in 2005(Wolf, Morris 2005). In order to relate the California study to Massachusetts Dry cleaning companies and to collect additional information, site visits and interviews were used to gather information from local businesses using either PCE or an alternative. The Korean Dry Cleaners Association expressed interest in providing information to support the assessment, and a project assistant fluent in Korean made many site visits to their member's facilities. The Northeast Fabricare Association also expressed a willingness to share information and several site visits were made to their members as well.

Two types of site visits were conducted. Initial site visits set out to determine the profile of the industry in regard to the use of PCE and the alternatives. Over thirty facilities completed questionnaires regarding current dry cleaning practices. A summary table of these visits is listed in Table 5.4.1 B. In addition a copy of the questionnaire filled out by the dry cleaners can be found in Appendix E.1 along with a short summary of the drycleaner's comments.

Table 5.4.1 B: Dry Cleaning Preliminary Data Collection

Location	Years in Operation	# of Employees	Machine Generation	Solvent Use	Past PCE Use	Gallons/ year	Spotting Chemical
Leominster	3	Full: 2 Part:1	4th	PCE		30	No PCE
Leominster	9	Full: 2 Part:0	5th	PCE		40	No PCE
Westborough	2	Full: 2 Part:2	3rd	PCE		70	No PCE
Methuen	18	Full: 3 Part:2	4th	PCE		60	No PCE
Canton	1.5	Full: 5 Part:1	4th	PCE		150	No PCE

Table 5.4.1 B: Dry Cleaning Preliminary Data Collection							
Location	**Years in Operation**	**# of Employees**	**Machine Generation**	**Solvent Use**	**Past PCE Use**	**Gallons/ year**	**Spotting Chemical**
Salem	13	Full: 2 Part:3	3rd	PCE		100-140	No PCE
Newton	10	Full: 2 Part:1	4th	PCE		100	No PCE
North Attleborough	5	Full: 2 Part:0		Hydrocarbon (DF2000)	Never	450-500	No PCE
Beverly	10	Full: 3 Part:3	4th	PCE		60	No PCE
Dracut	15	Full: 2 Part:2	2nd	PCE		65-70	No PCE
Stoneham	2	Full: 2 Part:2	4th	PCE		40	No PCE
Stoneham	18	Full: 6 Part:1	5th	PCE		140	No PCE
Arlington	15	Full: 1 Part:3	3rd	PCE		100	No PCE
Townsend	9	Full: 2 Part:1		PCE		30	No PCE
Newburyport	9	Full: 4 Part:0	3rd	PCE		70	No PCE
Waltham	1	Full: 1 Part:2		Hydrocarbon (DF2000)	7 years ago	150	No PCE
Haverhill	18	Full: 2 Part:1		Rynex	Before Jan, '05	35	No PCE
Northborough	7	Full: 3 Part:3	4th	PCE		25	No PCE
West Concord	6	Full: 3 Part:0	5th	PCE		60	No PCE
Concord	2	Full: Part:		Siloxane (Green Earth D5)	2 years ago		No PCE
Westborough	12	Full: 2 Part:2		Hydrocarbon	4 years ago	20-25	No PCE
Shrewsbury	3	Full: 4 Part:2	3rd	PCE		70-80	No PCE
Ruxbury	10	Full: 2 Part:1	4th	PCE		10	No PCE
West Boylston	2	Full: 4 Part:2		Hydrocarbon (DF2000)	2 years ago	20	No PCE
Leominster	1	Full: 2 Part:	4th	PCE		40	No PCE

Table 5.4.1 B: Dry Cleaning Preliminary Data Collection							
Location	**Years in Operation**	**# of Employees**	**Machine Generation**	**Solvent Use**	**Past PCE Use**	**Gallons/ year**	**Spotting Chemical**
		3					
Wilmington	9	Full: 3 Part: 0	4th	PCE		65	No PCE
Acton	8	Full: Part:		PCE		75	No PCE
Chelmsford	6	Full: Part:	4th	PCE			No PCE
Woburn	7	Full: Part:		Siloxane (Green Earth D5)	7 years ago	60	No PCE
Stoughton	16	Full:1 Part: 3		PCE		80	No PCE

The second type of site visit was designed to gather information from companies that had made the switch to one of the alternatives being reviewed in the assessment. During these visits, information on past and present cleaning practices and benefits and drawbacks to the alternatives was collected. Six alternative evaluation site visits were conducted. Location and dry cleaning solvents used are listed in Table 5.4.1C.

Table 5.4.1 C: Dry Cleaning Alternative Evaluation Site Visits

Solvent Used	Location
PERC	Nashua, NH
Hydrocarbon	Quincy, MA
Hydrocarbon2	Waltham, MA
Green Earth	Charleston, MA
Rynex	Haverhill, MA
Wet Cleaning	Arlington, MA

Operating Time

The operating time for dry cleaning includes time to run the machine for cleaning and drying (designated as cleaning time). It does not include loading, unloading, pre- and post spotting. In order to compare each process to a PCE system, the average cleaning time for each system was divided by the time for PCE cleaning. Any process that took longer than PCE would have a normalized time greater than one. Of the alternative processes reviewed only two had shorter cleaning times. These were Green Jet and CO_2 cleaning, both of which require little to no drying times. The most popular alternative, HC cleaning, requires about one third more time for the cleaning process.

The IRTA study measured operating times for each of the alternatives. The Institute supplemented the IRTA data with information from Massachusetts facilities. The Massachusetts site visits documented times for cleaning that were slightly longer than those found in the IRTA Study. The only Massachusetts based process that had an improved operating time was the drycleaner using the HC process. They switched from a "hard mount" system, taking over an hour to clean, to a "soft mount" method reducing their cleaning time to under an hour. The soft mount allowed for a faster drum rotation during the drying portion. The VMS process was used at two visited locations. One of those no longer uses the process as they were unsatisfied with performance and times. Their cleaning time was over 2.5 times longer than with their PCE system. A qualitative comparison of the various methods from both the IRTA study and the Massachusetts site visits are in Table 5.4.1D.

Table 5.4.1 D: Operating Time Qualitative Comparison

Process	Time (min) California Facilities	Normalized Rate		Time (min) Massachusetts Facilities	Normalized Rate	
PCE	45	1		45	1	
HC	60	1.33	-	55	1.22	-
VMS	62	1.38	-	73	1.62	-
				120	2.67	-
SGE	63	1.40	-	66	1.47	-
Wet Cleaning	65	1.44	-	60	1.33	-
Icy Water	long drying					
Green Jet	30	0.67	+			
Carbon Dioxide	30	0.67	+			

Comparison Key + Better = Similar - Worse ? Unknown

Load Capacity

Most of the manufacturers of the dry cleaning equipment, including the alternative processes, offer equipment with various load capacities. Based on supplied literature, the data from the IRTA Study, and Massachusetts site visits, the available load capacity ranges were used in this study to determine an average load in pounds. Some members of the Korean Dry Cleaning Association noted that they run their machines based on the quantity of clothing cleaned and were less concerned about operating times. They went on to say that they use most of their machines at approximately 80% capacity to ensure proper cleaning and that no damage will be done to the machines due to overloading. Therefore these calculations were made in an attempt to determine the number of loads that could be run as compared to typical or past PCE systems.

The average value for PCE was used to normalize the alternatives to the PCE load capacity. In this situation, processes with values greater than one would have a larger cleaning capability and likewise, those with a normalized capacity less than one would have a lower load capacity. The IRTA Study revealed that on average, three alternative dry cleaning systems would have an equal or greater capacity, with all of the processes comparable to PCE systems, ranging from 0.86 to 1.12.

From the Massachusetts site visits a separate load capacity average was found for PCE based on the actual capacities used at the locations. The HC facility reported an average load capacity that was

33% greater than their previous PCE system, and 50% greater than the average PCE system for all facilities. The VMS system being used at the Massachusetts site had a capacity of 50 lb but the system was only operating at 40 lb at a time to ensure proper cleaning. The normalized capacity at 40 lb was three-quarters of the average PCE system. This load capacity was similar to that being used in the SGE system. A qualitative comparison of the load capacities of the various processes from both the IRTA Study and the Massachusetts site visits are in the following Table 5.4.1E.

Table 5.4.1 E: Load Capacity Qualitative Comparison

Process	California Facilities	Average Load			Massachusetts Facilities	Average Load		
	pounds	pounds	Normalized Load		pounds	pounds	Normalized Load	
PCE	35-65	50	1		45-60	53	1	
HC	35-50	43	0.86	-	80	80	1.51	+
VMS	46-66	56	1.12	+	40	40	0.75	-
SGE	35-50	43	0.86	-	40	40	0.75	-
Wet Cleaning	30-70	50	1	=	12		0.27	-
Icy Water	55	55	1.1	+				
Green Jet	45	45	0.9	-				
Carbon Dioxide	45	45	0.9	-				

Comparison Key + Better = Similar - Worse ? Unknown

Cleaning Quality

The cleaning quality comparison revealed that many of the alternative processes were not as aggressive as PCE. In general, this results in a reduced efficiency in cleaning. The HC system operators visited in Massachusetts indicated that they had problems with water soluble soils and water contamination from spotting chemicals and detergents. The VMS facility operators stated that they had to sacrifice some of their cleaning capabilities when using the alternative to PCE. Comparison of the various methods from both the IRTA Study and the Massachusetts site visits are given in Table 5.4.1F for soil removal.

Table 5.4.1 F: Soil Removal Comparison		
Process	**Soil Types California Facilities**	**Massachusetts Facilities**
PCE	Relatively aggressive cleaner for oil based soils	
HC	Not as aggressive as PCE for grease and oil contaminants	Issues with water soluble soils
VMS	Less aggressive for oil based contaminants than PCE	Lost some cleaning performance
SGE	Aggressive solvents for oil based contaminants; They can remove water soluble soils very effectively	
Wet Cleaning	Aggressive cleaning method; effective on both oil based and water soluble soils	
Icy Water	Same advantages as the traditional wet cleaning technology	
Green Jet	Effective for lightly soiled fabrics	
Carbon Dioxide	Many oil based contaminants are soluble - similar to HC	

Garment Compatibility

The information gathered from the IRTA Study was for the most part consistent with what was found during the Massachusetts site visits. PCE is capable of cleaning a wide range of materials, although it sometimes has trouble with leather, suede, beaded materials and many delicate garments. The Massachusetts HC facility operators stated that they had trouble with maintaining silk sheen whereas the IRTA Study implied that the HC process would be able to clean silks well. This Massachusetts company also found they needed to do more lint removal prior to cleaning. However, this effort was offset with having to do less lint removal after cleaning.

The VMS facility operator stated that they were able to clean just about any fabric; what they could not do with the VMS they also could not previously do with PCE. The user of the SGE process found that they were now able to do beaded materials when their PCE system could not. Both processes (PCE and SGE) had trouble with leather and suede. Comparison of the various methods from both the IRTA Study and the Massachusetts site visits are presented in Table 5.4.1G for clothing compatibility.

Table 5.4.1 G: Clothing Compatibility		
Process	**Clothing types California Facilities**	**Massachusetts Facilities**
PCE	Compatible with numerous textiles	Trouble with leather, beads, suede
HC	Delicate garments like silks, wedding gowns, drapes, suede and leathers and beaded garments	Had trouble with silk sheen. More lint control up front but less afterward
VMS	Delicate items can be cleaned	Can do just about any fabric including suede & leather trim. What it can not do, (rain coats) neither could PCE
SGE	Wide range of fabrics; safe for most beads, sequins, buttons, trimmings, vinyl	Can do beads that PCE could not. Can not do leather and suede
Wet Cleaning	Delicate items like wedding gowns and suede and leather garments	Limitation of garment materials that could be cleaned; trouble cleaning leather, suede, rayon and some types of wool
Icy Water	More forgiving than traditional wet cleaning; Wools, Silks, Spandex, Leather, Suede, Real/Fake Fur, Gowns with decorative beads and trim -	
Green Jet	Clean garments that are currently sent out or that can't be cleaned with other solvents	
Carbon Dioxide	Gentle cleaner; Some materials, like vinyl, rubber or beads, swell during the cleaning process; Some acetate materials cannot be cleaned; fur and leather can be cleaned	

Spotting and Post Handling

In most forms of dry cleaning spotting agents are usually used to remove the spots before dry cleaning takes place in the machine. PCE is an aggressive solvent, it is easy to use and it is very forgiving. Even when a cleaner is not especially good at spotting, the PCE machine will remove many stains. After the cycle is completed, the garments, which are fully dry, are removed from the machine and finished with standard equipment (Wolf, Morris 2005).

The IRTA study reported that PCE and TCE were found in the effluents of some of the wet cleaning facilities used in the study. The origin of the contamination, sometimes in concentrations high enough to classify the waste as hazardous, was surmised to be either cross contamination with the PCE dry cleaning machines or the spotting agents being used on the clothing. From the data gathered from over two dozen site visits in Massachusetts, the facilities reported that no TCE or PCE based spotting agents were used. In the past this was not the case, according to Peter Blake of Northeast Fabricare Association. He stated that there had been efforts made to guide dry cleaners away from spot cleaners containing PCE and TCE. The dry cleaning industry responded by creating alternatives to replace spotting agents containing these chlorinated solvents. These spotting chemicals are typically tailored for a specific soil type eliminating the need for a universal spotting agent (traditionally PCE based).

The IRTA Study data for spotting and post handling were adjusted for this study so that the times were all based on a uniform amount of clothes cleaned per hour. As with the cleaning times and load capacities, these qualitative rates were normalized based on a PCE system. For these performance criteria, systems requiring less time would have a normalized value less than one and systems requiring more time would have a normalized value greater than one.

According to the data from the IRTA Study, three of the processes required about twice as much pre-spotting time. The SGE system claimed to need only a fraction of the time that PCE required for cleaning. For post cleaning only VMS and carbon dioxide required more effort than PCE. When comparing the overall pre and post handling times, SGE, wet cleaning and carbon dioxide all resulted in time savings.

The qualitative comparison of the various methods for spotting and post handling from both California and Massachusetts site visits is given in Table 5.4.1 H. The numbers in the table are times relative to that for PCE.

Table 5.4.1 H: Pre-Spotting and Post Handling Qualitative Comparison

Process	Pre Spotting California Facilities		Post Cleaning Finishing California Facilities		Combined pre/post California Facilities		Massachusetts Facilities	
PCE	1		1		1			
HC	1.81	-	0.63		1.22	-	>1	-
VMS	2.39	-	1.24	-	1.81	-	>1	-
SGE	0.08	+	0.01	+	0.04	+	1.20	-
Wet Cleaning	0.72	+	0.88	+	0.80	+		
Icy Water								
Green Jet	2.03	-	0.86	+	1.44	-		
Carbon Dioxide	0.56	+	1.17	-	0.87	+		

Comparison Key + Better = Similar - Worse ? Unknown

The Massachusetts site visits yielded more qualitative information about the individual processes. The HC facility found that they needed more effort on spotting for grease-based soils. They had to retrain their workers to address the spotting issues that arose with this system. Furthermore, the facility had to add a second spotting station. They continued to use the same spotting agents that they were using for PCE.

The workers interviewed at the VMS facility found spotting to be more difficult, since they had to utilize specially formulated spotting agents that were compatible with the VMS solvent and supplied to them by the solvent manufacturer. They found that these new spotting agents were not as effective as those used with PCE cleaning.

In the SGE plant the spotting process was taking two minutes longer than the PCE system, an increase of 20% in labor time. This increase is significant as labor costs can be upwards of thirty percent of the overall cost of dry cleaning and is by far the most expensive component of the total process.

Many of the issues for spot cleaning were similar to what was found for the various processes in the collected technical information from the IRTA report, the various manufactures' literature and Massachusetts site visits as shown in Table 5.4.1 I.

Table 5.4.1 I: Massachusetts Site Visit Pre-Spotting and Post Handling Qualitative Comparison

Process	Technical Information Review	Massachusetts Facilities
PCE		
HC	"Hand" or the feel of the garments cleaned with HC is better than the hand of garments cleaned with PCE.	More spotting effort, grease spots - retrain workers, same spotting agents
VMS	More spotting is likely to be required, very good hand better than HC	Spotting difficult; Spotters less aggressive, not as good, more effort, different spotting agents
SGE	Finishing of the garments which may contain high concentrations of water could be more difficult	20% more spotting time, use less spotting agents, less post spotting
Wet Cleaning	Prevent dimensional change; wet garments are hung and later finished using tensioning equipment	50% more time for spotting
Icy Water	Minimize or eliminate garment shrinkage; tensioning equipment but does not need to use it for finishing the garment	
Green Jet	Spotting is more difficult, finishing is much easier than for other technologies	
Carbon Dioxide	More spotting is required; post spotting instead; similar to finishing requirements with PCE	

Recycling

The recycling process for the HC facility was found to require less maintenance than the previously used PCE process. The distillation unit was easier to clean as it had less oily residue baked onto the unit. The PCE process required workers to chip away at the hardened material whereas the HC process required no chipping or hard labor to remove the solid waste. The bulk could be picked up and the residual removed with a rag.

The VMS operator stated that the distillation process was inefficient and time consuming. They have plans to lease new machines that come without a distillation system. Instead of distilling, the company plans to institute a new process using filter material called Tonsil®.

Tonsil® filter powder is produced from bentonite then enhanced by an acid process producing very fine clay with highly adsorbent properties. Typically, Tonsil® is used in combination with diatomaceous earth. Both compounds are placed on a typical nylon spin disk filter. The additive can adsorb dyes, water soluble soils, solvent soluble soil, moisture and fatty acids from the solvent. Tonsil® also exhibits an inhibiting property for reducing or eliminating corrosion and bacteriological growth (Childers 2004). This process would require the filters to be cleaned each day and reportedly could eliminate the need to distill the cleaning solvent.

The SGE facility does no distillation of their cleaning solvent and disposes of the solvent as a hazardous waste. Comparison of the various methods from both the IRTA Study and the Massachusetts site visits are presented in Table 5.4.1J.

Table 5.4.1 J: Dry Cleaning Solvent Recycling Comparison

Process	From Literature Review	Massachusetts Facilities
PCE	PCE, which is heavier than water, is physically separated from the water.	Re-deposition issues (likely related to particular distillation process)
HC	Distillation of the HC must be performed in a vacuum. Tonsil® filters may make distillation unnecessary	Distillation maintenance was easier than PCE as it created less build up on the distillation unit
VMS	Separation of the solvent and water is more difficult	Distillation changed the cleaning chemical; Expect to eliminate the need to distill by using Tonsil® filtering process.
SGE	Problems for the water separation process	Not distilling
Wet Cleaning		Not applicable
Icy Water		Not applicable
Green Jet		Not applicable
Carbon Dioxide		Not applicable

Wastewater

Wet Cleaning operators in Massachusetts must adhere to the state's Title V regulations that prohibit commercial discharge to septic systems. A commercial wet cleaner, drycleaner, or laundry may not discharge gray water to a septic system. In addition, these industries can only discharge to the ground with a groundwater discharge permit.

Financial Assessment

Data were collected during the site visits on costs associated with dry cleaning. When looking at machine costs, the alternative solvent process machines were found to be 40 to 50% more expensive than PCE machines. The wet cleaning facility reported a lower purchase price for their equipment when compared to PCE.

Likewise the alternative solvent cost was also greater than PCE, ranging from 25% greater to twice the cost; the wet cleaning process used more detergents and water, but no solvents. One HC facility was paying more for their detergent but another HC facility was paying about the same. The SGE facility was using no additional detergents and only had the solvent to purchase. From the VMS process, costs for solvent and detergents were about the same as what they were spending when they used PCE.

Despite the fact that nearly all of the alternative facilities were paying about the same price for spotting agents (SGE was 67% less), spotting labor costs were all greater than when using a PCE based system. Spotting expenses with VMS were found to be sixty percent more.

Maintenance requirements were higher in both the HC plants resulting in an increase in operating costs. This increase would likely also apply to a CO_2 facility due to the specialized maintenance required for equipment. The wet cleaning facility reported a 60% decrease in maintenance needs and expenses. The SGE location had yet to spend any money or time on maintenance on its relatively new machine (14 months). VMS maintenance resulted in an increase in costs.

Utility expenditures were roughly equal to the PCE based dry cleaning process. For some alternatives there were minor to moderate increases of 25-35%. Some of the facilities stated that their utility costs were the same.

Most of the companies spent the same or less time on regulations and paperwork. The SGE process resulted in a 60% decrease in the amount of hazardous wastes generated. Wet cleaning created no hazardous waste. The other processes generated about the same amount of hazardous waste as the PCE process. All companies that had to dispose of hazardous waste were paying the same rate per drum with the same waste handler as they had been for PCE removal.

The costs comparisons for the various Massachusetts locations surveyed are included in Table 5.4.1 K. Additional information on the economic comparisons can be found in Appendix E.1.

Table 5.4.1 K: Costs Comparisons for Massachusetts Facilities

Location	**U[7] Cleaners**	**C Cleaners**	**D Cleaners**	**L Cleaner**	**T Cleaners**
Process	Wet Cleaning	HC	HC	SGE	VMS
Machine cost	Less	More	40% more	50% more	45% more
Solvent Cost	None	35% less	27% less	100% more	Same
Cost of detergent	100% more	100% more	Same	None	Same
Spotting agent cost	Same	Same	Same	67% less	Same
Spotting labor cost	50% more	30% more	60% more	20% more	60% more
Maintenance of equipment	60% less	40% more	60% more	None	Same
Overall cost of maintenance	60% less	40% more	60% more	None	Same
Water	Same	25% more	Same	None	Same
Gas	30% more	25% more	Same	Same	Same
Electricity	35% more	25% more	Same	Same	Same
Paperwork required per week		None		50% less	Less
Regulation-Compliance Costs	Same	None	None	Same	
Licenses			None		$3,250

[7] Facility names will be included pending approval from facilities.

Table 5.4.1 K: Costs Comparisons for Massachusetts Facilities

Location	U[7] Cleaners	C Cleaners	D Cleaners	L Cleaner	T Cleaners
Hazardous Waste Disposal	None	Same	Same	67% less	Same
Hazardous Waste Costs	Same	Same	Same	Same	Same

None - potential for savings, Same - equal costs, Less - cost savings, More - greater costs

Despite the increases in operating costs for many of the alternative processes, the price the consumer was charged for cleaning the garment remained the same.

Environmental Assessment

Several key factors, including persistence, bioaccumulation and toxicity potential, were reviewed to determine the environmental profile of dry cleaning solvents. Further information on environmental parameters and levels of concern are included in Appendix A; detailed data for dry cleaning alternative chemistries are included in Appendix D.3.

The persistence and bioaccumulation potentials were estimated using the EPA PBT profiler. The aqueous based detergent did not have a specific list of constituents that could be assessed. The persistence of the solvents in water was low, less than 60 days. Persistence in soil for the alternatives was found to be high except for carbon dioxide. VMS, SGE and PCE were all in the persistent range. The HC solvents were found to be at the borderline of being very persistent, with a value of 180 days. For sediment persistence, the alternatives had shorter residence times than PCE, although the VMS and SGE were still very persistent. There was no value determined for the HC solvent due to the limitations of the tool. None of the alternatives had persistence in air exceeding PCE's 93 days except carbon dioxide.

The modeled bioaccumulation factors for most of the alternatives and PCE were below the EPA listed criteria for bioaccumulative. A log K_{ow} value was estimated for the HC solvent (6.6-7.0 using the EPI program (SRC, EPA, EPI (Estimation Programs Interface) Suite http://www.epa.gov/opptintr/exposure/docs/episuite.htm) for hexane (C6H12). The estimated log K_{ow} was 6.6 to 7.0, which indicates a higher affinity for lipids (fat cells) than for water, and potential for bioaccumulation.

According to the MSDS for PCE, the solvent is considered to be toxic to fish. None of the alternatives exceeded the threshold for aquatic toxicity.

If the solvents are incinerated at their end of life, combustion by-products may be produced. Combustion byproducts of PCE may include hydrogen chloride and phosgene. Many of the alternatives break down into carbon dioxide, carbon monoxide and oxygen.

PCE is a NESHAP, whereas none of the alternatives are. None of the assessed products, including PCE, were listed by the EPA as ozone depleting chemicals. Carbon dioxide was the only greenhouse gas, but as previously stated CO_2 is generally not created especially for use as a dry cleaning solvent and therefore does not add to net greenhouse gas emissions.

Human Health Assessment

Acute Effects

PCE has a PEL of 100 ppm. The only other alternative that had a listed PEL was carbon dioxide with a value of 5000 ppm. Two of the other alternatives have an REL listed. The HC's REL was 171 ppm and VMS was 10 ppm. There is no PEL or REL for SGE.

According to the NIOSH Pocket Guide to Chemical Hazards PCE can irritate the skin, the eyes and the respiratory track. Similarly, according to MSDS for the water based product and SGE, these two alternatives can cause the same types of irritation. From the MSDS for VMS and carbon dioxide, neither will result in irritation to the skin, the eyes and the respiratory track. In sufficient concentrations, carbon dioxide is an asphyxiant. The HC solvent MSDS states that the solvent may produce eye irritation including watering and redness as well as mild skin irritation. Respiratory irritation is not expected to occur

Chronic Effects

Long term hazards examined include mutagenicity, carcinogenicity and reproductive and developmental toxicity. The EPA has classified PCE as reasonably anticipated to be a human carcinogen and IARC lists the solvent as category 2A, probably carcinogenic to humans. PCE is also listed for cancer on California's Prop 645. In contrast, the alternatives are not classified by EPA or IARC with regard to carcinogenicity.

In June of 2005 the Silicones Environmental, Health and Safety Council of North America (SEHC), the European Silicone Industry (CES) and the Silicones Industry Association of Japan (SIAJ) released a White Paper on Health Research Findings of Decamethylcyclopentasiloxane (D5), the Dry cleaning solvent used in the VMS system. Two consistent reported adverse effects of D5 exposure in rats have been increased liver weights in male and female rats and also an increase of uterine endometrial adenocarcinoma tumors in female rats at the highest concentration (160 ppm for 24 months), while no adverse effects were observed in male rats (Silicones Environmental, Health and Safety Council of North America (SEHC); European Silicone Industry (CES); Silicones Industry Association of Japan (SIAJ) 2005). The authors hypothesize that the liver weight increase is due to an increase in liver enzyme production in order to process and eliminate D5 from the rat's body and is reversible, and do not expect to see the same effect in humans. To date there has been no known peer review or outside scientific analysis of the findings.

PCE can damage the eyes, skin, respiratory system, liver, kidneys and the central nervous system. SGE affects the eyes, skin and central nervous system. High concentrations of carbon dioxide can affect the respiratory system, cardiovascular system, lungs, skin and central nervous system.

Other Hazards

Flammability and Flash Point

PCE is considered to be non-flammable and has no flash point. Based on the National Fire Protection Association (NFPA) rating system PCE has a zero fire hazard, whereas both the HC solvent and VMS have a rating of 2. The HC has a flash point of 64^{o} C and VMS's flash point is 76.7^{o} C. SGE has a NFRP fire rating of one with a flash point greater than 93^{o} C. Like PCE, carbon dioxide and the various water based detergents have a fire rating of zero and no flash points.

In the context of worker health and safety, PCE and the water based cleaners pose no auto-ignition and fire hazard in the work place while the HC, VMS and SGE solvents all possess flashpoints under 93° C and are considered combustible and carry with them a possibility of fire near an ignition source of a spark or open flame. A fire hazard may also be a factor if the machinery possesses a leak and solvent vapors accumulate to a dangerous level and could ignite.

Reactivity

All of the dry cleaning solvents had a NFPA reactivity rating of zero which would signify that the products are stable when exposed to heat pressure or water.

Corrosivity

Corrosiveness was measured using pH values. Products with a pH less than 2 and greater than 12 would be considered to be corrosive. Products with no pH, (PCE, HC and VMS), would not applicable to this measurement of corrosivity. SGE had a pH of 7. The Aqueous based product had a pH of 8.5 at a 1% concentration. All solvents fall within a range that is safe for workers in the case of an accidental spill

Summary of Dry Cleaning Alternatives

As demand increases for alternatives to PCE in dry cleaning, manufacturers of the alternative cleaning equipment and chemistries have been working to address many of the issues that still exist, such as longer cleaning cycles, limited soil removal and garment compatibility.

Table 5.4.1 M summarizes the technical, economic, environmental persistence, human health and other hazards that are associated with the alternative processes and compares them to the current practice of using PCE for dry cleaning.

In the table a "+" sign denotes a benefit associated with the alternative process. A "-" symbol implies that the alternative had a characteristic that was not as desirable as PCE. When the alternative process was comparable to the traditional solvent an "=" was used. In some cases when multiple facilities provided information on a process, observations were made that were not the same at both facilities. In these instances, two symbols could appear in the comparison table. For any criteria that was not found or unknown, a "?" was used.

Based on the gathered data from the alternative site visits, most of the alternative processes took longer for the cleaning process, and may not be as universally applicable to different soils and garment materials as PCE. In addition, VMS, substituted glycol ether and carbon dioxide had slightly higher costs than a PCE system, whereas HC and wet cleaning were equivalent to PCE.

The data in Table 5.4.1 M shows that overall, the alternative solvents were less persistent in the environment than PCE. From a human health perspective, most of the alternatives are preferable or equivalent to PCE. It should also be noted that there is a lack of toxicological data on some of the alternatives.

The major concern that existed for many of the alternatives was flammability. Only water cleaning and carbon dioxide were equal to PCE with no fire hazard. The other alternatives all possessed flashpoints and were rated as combustible, thus requiring specialized equipment to protect against fire or explosion.

Table 5.4.1 L: Assessment Summary for Dry Cleaning Alternatives

Assessment Criteria		PCE reference	HC	VMS	SGE	Wet Cleaning	Carbon Dioxide
Technical Criteria	Time	45 min	-	-	-	-	+
	Load capacity	60 lbs	-	+	-	+/-	=
	# of Soils		-	-	=	-/=	=
	Clothing types		+	=	+	-	-
	Spotting requirements		-	-	=/-	-	+
Financial Criteria	Equipment		-	-	-	+	-
	Solvent		+	?	-	+	?
	Labor		-	?	=	-	?
	Operating		=	?	=	=	?
	Regulatory		+	=	+	+	+
Environmental Criteria	Water	60 days	+	+	+	+	+
	Soil	120 days	-	+	+	+	+
	Sediment	540 days	+	+	+	+	+
	Air	98 days	+	+	+	+	-
	BCF	83	-	+	+	+	+
Human Health Criteria	Exposure limits	100 ppm; 25 TLV	+	-	?	+	+
	Dermal/Oral/Respiratory	Irritant	?	+	=	=	+
	Mutagenicity	No	=	=	=	=	=
	Carcinogenicity	2A	+	+	+	+	+
	Repro/Develop Tox	No/?	=	=	=	=	=

Table 5.4.1 L: Assessment Summary for Dry Cleaning Alternatives

Assessment Criteria		PCE reference	HC	VMS	SGE	Wet Cleaning	Carbon Dioxide
Safety Criteria	Flammability	Nonflammable	-	-	-	=	=
	Reactivity	Non reactive	=	=	=	=	=
	Corrosivity	Non corrosive	=	=	=	=	=

Comparison Key + Better = Similar - Worse ? Unknown

Emerging Dry Cleaning Alternatives

Household Dry Cleaning

These in-home products provide a convenient system that delivers fresh clothes in about 30 minutes. The products are reported to remove stains and odors and help minimize wrinkles. Most garments are purportedly ready to wear with little or no ironing. These do-it-yourself kits include a pre-spotting stain remover with blotting pads to absorb the stain. Odors are removed by a gentle steaming caused by the moist dryer sheet and the heat of the dryer. Manufacturers claim that they can be used on items such as sweaters, blouses, blazers, dresses, slacks and vests. They can be used on fabrics that include wool, rayon, silk, linen, acetate and blends of these fabrics. One of these alternatives, Dryel, states that it is safe for brass buttons, shoulder pads or sequins but should not be used on leather, suede, velvet, or fur, or with large items that do not have room to tumble freely.

More information on two existing home dry cleaning products can be found at Procter and Gamble Dryel - (http://www.dryel.com/using/index.html) and Clorox™ FreshCare™ Dry Clean and Gentle Fabric Cleaning - (http://www.cloroxfreshcare.com/dryclean.html).

The home dry cleaning kit does not offer a viable substitution for professional pressing. In addition, neither kit is as effective as traditional dry cleaning for removing more serious stains. The International Fabricare Institute (IFI), the leading association representing the cleaning industry, disputes some of Dryel's claims. Earlier this year, IFI published a report on Dryel, concluding that while the product does remove odors and is effective on water-soluble stains, it is not as effective as dry cleaning in stain removal (International Fabricare Institute (IFI)).

When subjected to the same parameters in the summary table, these products do not provide the same level of cleaning as dry cleaning but do cost less and take less time for certain applications. Sufficient information was not available from the products' Material Safety Data Sheets (MSDS) to provide an environmental, health and safety profile.

Air-cleaning

"Aircleaning" could join dry cleaning and wetcleaning as a possible option for garment cleaning. A "concept appliance" was designed by students in Singapore. This waterless washing process, called Airwash, won the Design Lab Award in a competition sponsored by Electrolux to develop appliances for the future based on satisfying consumers' needs and trends.

The Airwash prototype unit developed by the students uses negative ions, compressed air and deodorants to clean clothes. The device would eliminate detergents and water from the cleaning process. More information on the air cleaning process can be found at the National Clothesline Magazine, December 2005 issue.

Textile Alternatives

The need for dry cleaning originates with the textile and garment manufacturers. Using textiles that can be wet cleaned, or are compatible with alternative cleaning solvents, will reduce the need for solvent-based dry cleaning. Other emerging technologies for textiles include chemical treatments that reduce the ability of a stain or odor to penetrate the fabric, or that eliminate the need for pressing. It should be note, however, that these fabric treatments may contain formaldehyde, fluoropolymers, nanomaterials or other substances that warrant further investigation.

5.4.2 Alternatives Assessment for Vapor Degreasing

Many of the companies still using vapor degreasing are doing so because they believe that the aqueous-based alternative cleaning processes will not work for them, either for performance or equipment compatibility. There are also companies that may be willing to switch to an alternative less toxic cleaning process, including an aqueous system, but due to other barriers, such as managerial concerns, cost and resource constraints, process changes have not been pursued.

Solvents in the vapor form have shown to be successful in reaching hard-to-clean areas; these unique situations may still require the use of vapor degreasing cleaning processes. Site visits conducted by the Institute and the Office of Technical Assistance (OTA) over the last few years found very few companies using open top vapor degreasing equipment. Most facilities had invested resources into the use of closed-loop airless degreasers.

PCE is generally used in degreasing operations because of its high boiling point or chemical stability. Its high boiling point allows the solvent to remove soils and waxes that lower-boiling solvents may not. The stability of the chemical makes it particularly useful in airless degreasing systems where low emissions mean less virgin solvent and stabilizers being added.

Under an EPA grant awarded to the Institute and OTA, the TURI Laboratory compared the vapor degreasing alternatives listed in Table 5.4.2 A below, as well as many others, to the physical properties and cleaning performance of PCE and other chlorinated solvents.

Under the grant, site visits were conducted to determine what type of cleaning equipment was being used for vapor degreasing. For the companies that were using older open-top degreasing systems, the researchers were able to identify chemical alternatives that were as effective at cleaning as vapor degreasing and could be used with the existing equipment after minor modifications. One company changed from a vapor degreasing cleaning operation to cleaning with ultrasonic energy and a new chemistry by retrofitting the existing equipment

Other facilities were using more advanced, closed-loop systems recently purchased at high capital cost to the company. While these companies were open to the idea of substituting for PCE and other chlorinated solvents for cleaning, the sizable investment in existing equipment mandated its use. This required TURI's Lab to investigate other solvents with the required physical characteristics necessary for vapor degreasing solvents.

Table 5.4.2 A: Vapor Degreasing Alternatives

Vapor Degreasing Alternatives Evaluated	Chemical Type	Components	Code
Ensolv	n-propyl bromide (nPB)	n-Propyl bromide; Stabilizer package	nPB
DOW OS 10	Volatlile methyl siloxane	Hexa-methyldisiloxane	VMS
Flux Remover C	Hydrofluorcarbon	1,1,1,3,3-pentafluorobutane; 2,3-dihydrodecafluoropentane; trans-1,2-dichloroethylene Methanol	HFC1
DuPont Vertrel MCA	Hydrofluorcarbon	2,3-dihydrodecafluoropentane; trans-1,2-dichloroethylene	HFC2

Background on NPB, N-Propyl Bromide

N-propylbromide, or bromopropane is a non-flammable organic solvent with a strong odor. It is used to remove solder flux, wax, oil, and grease from electronics parts, metals, and other materials. In addition, nPB is used as a solvent in adhesive formulation. NPB has a low ozone depletion potential (ODP) of 0.013, and EPA is proposing to allow the use of nPB as a chemical alternative to other higher level ozone-depleting substances (ODS) under the SNAP program with certain conditions (USEPA) 2003).

NPB, has been reported to be a severe neurotoxin and NTP is currently conducting a two year inhalation study to test nPB for carcinogenicity potential. The chemical was added to California's Prop 65 list and the California Department of Health Services Hazard Evaluation System and Information Service (HESIS) issued a health alert for nPB in 2003 and 2004. HESIS issued the Hazard Alert because nPB "is being considered for widespread use and has not been regulated to protect workers, consumers, or the environment" (HESIS) 2003).

Background on VMS, Volatile Methyl Siloxanes

VMSs are mild combustible solvents, and possess a moderate level of toxicity with a manufacturer's recommended exposure level of 200 ppm. Because the cost is high, it is generally used for defluxing and/or degreasing high value parts and electronic components. It may be used for cold cleaning and wiping or in vapor degreasing equipment. Open top vapor degreasers are not suitable and would require retrofitting (Arthur D. Little Global Managment Consulting 1999). It should be noted that the VMS solvent used in vapor degreasing is not the same chemical that is used in Dry cleaning.

Background on HFC, Hydrofluorocarbon

Hydrofluorocarbons (HFCs) are compounds containing carbon, hydrogen, and fluorine. HFCs are often blended with trans-1,2-dichloroethylene (trans-DCE) to improve solvency. Because the HFCs contain no chlorine or bromine they do not directly affect stratospheric ozone. Although it is believed HFCs will not deplete ozone within the stratosphere, this class of compounds has other adverse environmental effects. Concern in particular over global warming impacts (according to the EPA, 2,3-dihydrodecafluoropentane has a GWP of 1610) may make it necessary to regulate production and use of these compounds at some point in the future. Such restrictions have been proposed in the Kyoto Protocol (Montzka 2004).

Technical Assessment for all Alternatives

Key physical properties for a vapor degreasing solvent include: low vapor pressure, low latent heat, low boiling point, low flash point, low surface tension and high solvency powers (typically Kb values are used as a representative of this characteristic – see discussion below). In addition, product alternative performance must be equal to or greater than the current vapor degreasing solvent. Physical properties for PCE and its alternatives are shown in Table 5.4.2.B, and discussed briefly below. Values were obtained from the material safety data sheets from the appropriate manufacturers.

Table 5.4.2 B: Physical Properties of PCE and Alternative Vapor Degreaser Solvents

Product	Vapor Pressure (mm Hg)	Latent Heat (cal/g)	Boiling Point (°C)	Flash Point (°C)	Surface tension (dyne/cm)	Kb value
PCE	15.8	50.1	121	none	32.3	90
nPB	139	58.8	70	none	25.9	129
VMS	42.2	293	100	-3	15.2	16.6
HFC 1	488	~45	36	none	18.1	75
HFC 2	464	43.3	39	none	15.2	35

Low vapor pressure will help to reduce potential air pollution due to solvent evaporation. All of the alternatives reviewed had higher vapor pressure than PCE.

Latent heat corresponds to the amount of energy required to cause a substance to change from one state to another (liquid to gas). The lower the value, the less energy needed to create a vapor for cleaning. Two products, HFC1 and HFC2, have lower latent heat values than PCE. Another product, nPB, had a slightly higher value than PCE. Only one product was significantly higher than PCE; the VMS product has a latent heat nearly six times that of PCE.

In addition to the latent heat, energy savings can be obtained by using a solvent with a low boiling point. PCE's boiling point was the highest of the evaluated solvents, boiling at 121° C. In contrast, the two HFC solvents boil at a temperature just less than 40° C.

PCE and three of the four alternatives did not have a flash point. The only product evaluated with a flash point was VMS, and its flash point was very low, -3° C. Concerns over flammability significantly limit the applicability of this particular VMS solvent.

For cleaning hard to reach areas, as is the case in most vapor degreasing applications, solvents should have low surface tension in order to clean any small spaces or unusual geometries of a part. The solvent would also be able to evaporate out of these tight spaces leaving no soil or residue behind. All of the alternatives had lower surface tensions than PCE and make them favorable for cleaning complex geometric parts.

Identifying effective alternatives can be a very challenging task. A quick check to see if an alternative might be acceptable is to use its Kb value. The Kauri-Butanol (Kb) value, an ASTM method, is used to compare the strength of organic solvents (used in paint and lacquer formulations). The higher the Kb value, the more effective the solvent should be. However, there is no guarantee that a high Kb value will result in success and a low Kb does not always indicate that the solvent will be ineffective. The nPB product has a higher Kb value than PCE. The other three alternatives have lower Kb values than PCE.

The values for the six physical properties discussed are summarized in Table 5.4.2 B, which includes PCE and the four alternative products. Values were obtained from the material safety data sheets from the appropriate manufacturers.

As mentioned previously, there is no easy way short of actual testing to determine if an alternative vapor degreasing product will work for a specific cleaning situation. By reviewing the above mentioned physical properties, however, the chances of finding a product that will work will be improved.

As part of the work conducted during the EPA funded study for replacing chlorinated solvents in cleaning applications the cleaning performances of several alternatives was measured for specific situations in Massachusetts companies. The tests utilized actual soils, consisting of various oils (soils 1-5, 8-11), a rust preventative coating (soil 6) and a paint/varnish mix (soil 7). In all situations, the soils were being removed from metal parts.

All of the alternatives worked very well on the four soils that were previously being cleaned in a PCE-based system. The solvents removed over 90% of the soils for all but one soil with one cleaner. The HFC1 removed 87% of soil 1.

In the other cleaning performance evaluations, the alternatives were again very effective for the various oils. Only one soil was not effectively cleaned by all of the alternatives. Soil 7, the paint/varnish mix was only removed by one alternative, nPB. The other products were less than 15% effective in removing this mix. Table 5.4.2 C contains the summary of the testing conducted on each alternative.

Table 5.4.2 C: Laboratory Performance of PCE and Alternative Solvents against 11 Soils

Product	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6	Soil 7	Soil 8	Soil 9	Soil 10	Soil 11
PCE	E	E	E	E	NT	NT	NT	NT	NT	NT	NT
nPB	99.98	99.88	99.43	99.98	100.0	100.2	98.60	100.0	100.1	100.0	99.70
VMS	99.95	99.33	100.06	91.43	98.90	99.10	10.60	97.40	99.90	99.60	99.70
HFC 1	87.04	99.50	100.01	98.97	99.90	100.8	-4.90	100.4	100.7	100.3	100.6
HFC 2	93.99	98.53	99.32	99.27	100.1	100.0	-5.10	100.1	99.80	100.2	100.0

E – Effective; NT – Not tested
Note: Results of table are in percents based on gravimetric analysis.
Note: Values greater than 100 are due to minor fluctuations in the balance.
Note: Values that are less than zero signify swelling of the contaminant due to the absorption of the solvent.

Financial Assessment

Purchase prices for all of the alternatives investigated for vapor degreasing applications were found to be greater than the purchase price of PCE. The cost of PCE is approximately four dollars per gallon. The n-propyl bromide products can cost up to three times as much as PCE. The other three alternatives are considerably more expensive, at 30 to 40 times as much as the PCE baseline. Many of the listed prices in Table 5.4.2 D are approximate costs. Depending on the volume of product be purchased the prices may go down; the prices may also go down in the future if overall demand and production increase.

Table 5.4.2 D: Cost Comparison of Alternatives

Product	$/gallon	Normalized
PCE	4.31	1
nPB	13	3
VMS	123	29
HFC1	150	35
HFC2	184	43

Although the current purchase costs are substantially higher, the alternative chemicals can be more competitive with PCE when other operating costs and environmental, health and safety benefits are considered. As mentioned in the PCE replacement study in Appendix E.1, operating a vapor degreaser with nPB created a savings in energy requirements as the alternative system operated at a lower temperature. In addition to energy savings, this company was also able to extend the life of the cleaning solvent by 66%, thus reducing the amount of virgin solvent they would need to purchase to operate their system. Little information exists on operating cost comparisons for VMS and HFCs as they are not yet widely used in closed loop vapor degreasing operations.

Environmental Assessment

Several key factors were reviewed to determine the potential environmental impact of vapor degreasing solvents. Further information on environmental parameters and levels of concern are included in Appendix A; detailed data for vapor degreasing alternative chemistries are included in Appendix D.3. Initially, all products including PCE were analyzed using the EPA PBT profiler to determine persistence and bioaccumulation potentials.

Both nPB and VMS had low persistence in water, with a half-life of 15 days. The other two alternatives, HFC1 and HFC2 were very persistent (180 days), both greater than PCE at 60 days. Again nPB and VMS had low persistence in soil, both with 30 day half-lives. HFC 1 and HFC 2 had long half-lives in soil, 360 days. PCE is very persistent in sediment, having a half-life of 540 days and would make the soil or ground water hazardous if PCE is spilled. NPB and VMS are considered persistent, with sediment half-lives of 140 days. Once more, the HFC 1 and HFC2 half-lives for sediment persistence were higher than PCE. All of the products investigated were considered to be persistent in air with nPB and VMS having the shorter half-lives, 14 and 12 days respectively.

Bioaccumulation factors for the alternatives and PCE were all below the EPA threshold for a substance to be considered bioaccumulative.

According to the MSDS for PCE, the solvent is considered to be toxic to fish. VMS had the lowest value (0.062 mg/L) and would therefore be of high concern for toxicity under EPA's PBT Profiler (<0.1). Both HFC1 and HFC2 had a value of 0.6 mg/L, which would be moderately toxic. Similarly nPB was moderately toxic with a ChV of 8.5 mg/L but was closer to the low toxicity range (>10 mg/l).

The various vapor degreasing solvents reviewed were not found on the EPA list of ozone depleting chemicals. Each of the alternatives and PCE are SNAP approved except nPB which is currently being considered for approval. However some of the products do have global warming potential. Three of the alternatives have low global warming potential (no specific value given but listed as "low"), while HFC2 had a global warming potential of 806 (CO_2 = 1).

Human Health Assessment

There is less acute and chronic health information available for the alternative solvents than for PCE. The following sections summarize the limited information that is available for these alternatives.

Acute Effects

PCE has an established PEL of 100 ppm. Two components of product HFC1, methanol and trans-1,2-dichloroethylene, have PELs of 200 ppm. Some products had an REL or TLV recommended by the manufacturers on the MSDS. NPB had a TLV of 10 ppm, lower than PCE's TLV of 25 ppm. VMS had a manufacturer exposure limit from Dow of 200 ppm. A third component of HFC1 had an REL of 200 ppm as did the second component of HFC2. In summary, Table 5.4.2 E presents PEL, REL and TLV values for PCE and each alternative, for either the component with the lower value or for the complete product.

Table 5.4.2 E: Exposure Limits

Product	PEL (ppm)	REL (ppm)	TLV (ppm)
PCE	100		25
nPB			10
VMS		200	
HFC1		200	
HFC2		200	200

All of the alternatives and PCE had similar effects on the skin, eyes and respiratory tract.

Chronic Effects

N-propyl bromide can cause eye and skin irritation and redness. Ingestion of a large amount can cause abdominal pain, nausea and vomiting. Elevated inhalation of nPB can cause respiratory tract irritation, CNS depression and anesthetic effects. Prolonged exposure may cause lung, liver and kidney damage. Extended skin exposure may lead to pain, cracking and dermatitis. There is no definitive information available regarding cancer or reproductive effects in humans but many studies have found evidence of carcinogenicity and reproductive effects in test animals. California added nPB to its Proposition 65 list in 2004 as a developmental toxin. NTP is currently conducting a two year inhalation study to test nPB for carcinogenicity potential.

In 2003, the Hazard Evaluation System & Information Service (HESIS) of the California Department of Health Services issued a health hazard alert for nPB (HESIS 2003). A recent study reported that five workers who glue foam cushions together with an nPB-based glue developed severe neurological symptoms, some of which may be permanent (Majersik 2004).

Volatile Methyl Siloxanes can cause adverse health effects when inhaled or ingested. These chemicals can also cause eye and skin irritation and redness. High levels of exposure can cause dizziness, disorientation and shortness of breath. Overexposure to skin can cause de-fatting and drying of skin leading to dermatitis. Repeated ingestion can cause internal injuries. There is insufficient information available on VMS cancer effects.

Hydrofluorocarbons can cause eye and skin irritation, pain, redness and swelling. HFC's may also cause blurred vision, shortness of breath, confusion, dizziness and weakness. High acute exposure can cause unconsciousness, cardiac irregularities and death. Prolonged inhalation exposure can cause liver and lung damage, may cause heart muscle damage, chemical pneumonia and pulmonary edema. This class of chemicals has not been listed as a carcinogen by IARC, NTP, NIOSH, OSHA or ACGIH.

Other Hazards

Flammability and Flash Point

PCE is considered to be non flammable and has no flash point. Based on the NFPA rating system PCE has a zero fire hazard. According to NIOSH, n-propyl bromide has an NFPA rating of three for fire, however, the manufacturer of nPB states that the product is not flammable and has no flash point. The VMS solvent being assessed has a very low flash point, less then -3° C and an NFPA rating of three for fire hazard. It would not be appropriate for open-top vapor degreasers. Both HFC1 and HFC2 have no flash points and have an NFPA fire hazard rating of zero.

Therefore, this VMS solvent would be used in only very specific cases for vapor degreasing, where other alternatives were not effective.

Reactivity

PCE, nPB and VMS all have an NFPA Reactivity rating of zero. The other two products would be considered unstable when heated and therefore have a reactivity rating of one based on the NFPA system.

Corrosivity

Corrosivity was measured using pH values. Products with a pH less than 2 and greater than 12 would be considered corrosive. Products with no pH, such as PCE, would not applicable to this measurement of corrosivity. NPB and HFC1 both have a neutral pH. The pH values for VMS and HFC2 have not been determined.

Summary of Vapor Degreasing Alternatives

Vapor Degreasing Alternatives

The alternative vapor degreasing alternatives were found to have comparable technical features to PCE. Cleaning effectiveness was similar to PCE for removing various manufacturing soils.

Two alternatives, nPB and VMS, had lower persistence in the environment. However, the two HFCs had longer residence times. Only nPB had a lower bioaccumulation factor than PCE. The two HFC's also have potential to cause global warming.

Little human health data were found for the alternatives. Each alternative has the same irritant potential as PCE for the skin, eyes and respiratory tract. One product, VMS, had a higher PEL than PCE. The two HFCs did not have an established PEL but did have a better profile when looking at the mutagenicity, carcinogenicity and reproductive-developmental toxicity. In contrast, the nPB and VMS products had no such data that could be compared to PCE. As previously stated nPB was added to the Prop 65 list in California December of 2005 as a reproductive toxicant. NPB is currently being investigated as a carcinogen and for reproductive toxicity and mutagenicity by the NTP. A proposal by EPA is pending to list nPB under the EPA SNAP program.

These products currently cost more to purchase than PCE, creating an initial barrier for companies looking to switch to an alternative vapor degreaser. Operating conditions may help to offset this higher purchase price. Many of the alternatives would require lower operating temperatures than PCE to achieve the same level of cleaning performance.

Table 5.4.2 F contains the data for major areas of performance, costs, environmental persistence and human exposure. Both HFC 1 and HFC 2 are more persistent than PCE, but are not carcinogens. Because VMS and nPB are relatively new alternatives with no significant body of toxicological research they are listed as unknowns for most of the human health categories. Further toxicological research is necessary in order to determine whether they are safer alternatives.

Table 5.4.2 F: Assessment Summary for Vapor Degreasing Drop-In Alternatives

Assessment Criteria		PCE reference	NPB	VMS [1]	HFC1	HFC2
Technical Criteria	Vapor Pressure	15.8 mm Hg	-	-	-	-
	Latent Heat	50.1 cal/g	-	-	+	+
	Boiling Point	121 °C	+	+	+	+
	Flash Point	None	=	-	=	=
	Surface tension	32.3 dyne/cm	+	+	+	+
	KB value	90	+	+	-	-
	Performance	Effective	=	=	=	=
Financial Criteria	Purchase	$4.31/gallon	-	-	-	-
	Energy [2]		+	=	+	+
Environmental Criteria	Water	60 days	+	+	-	-
	Soil	120 days	+	+	-	-
	Sediment	540 days	+	+	-	-

Assessment Criteria		PCE reference	NPB	VMS [1]	HFC1	HFC2
	Air	98 days	+	+	-	-
	BCF	83	+	-	-	-
Human Health Criteria	Exposure limits	100 ppm PEL; 25 ppm TLV	-	+	?	?
	Dermal/Oral/Respiratory	Irritant	=	=	=	=
	Mutagenicity	No	?	?	=	=
	Carcinogenicity	2A	?	?	+	+
	Rep/Develop	No	?	?	=	=
Safety Criteria	Flammability	Nonflammable	-/=	-	=	=
	Reactivity	Non reactive	=	=	-	-
	Corrosivity	Non corrosive	=	=	=	?

Comparison Key + Better = Similar - Worse ? Unknown

1 Not for open top vapor degreasing
2 Energy Savings based on latent heat requirements and boiling point.

<u>Non-Vapor Degreasing Alternatives</u>

The safest alternatives are likely to be: seeking an alternative cleaning process such as aqueous or semi-aqueous, working within the supply chain to change the contaminant on the part that is requiring the cleaning or investigate a materials change to prevent contamination and cleaning altogether. These options would likely be preferable to using PCE or any of the solvent drop-in alternatives. The case studies in Appendix E are examples of successful transitions to aqueous cleaning systems.

5.4.3 Alternatives Assessment for Automotive Aerosols

Automotive shops have utilized PCE aerosols in several end uses. One area has been in cleaning applications. The main categories reviewed in this study for PCE aerosol cleaning are tire cleaning, brake cleaning and engine cleaning. The last group was broken down further to look at products used for general external cleaning and for more sensitive cleaning of internal engine parts (carburetors, etc.). As mentioned in the alternatives prioritization section, the assessment was limited to formulations using aerosol delivery systems.

According to one manufacturer of aerosol cleaning products, the major use in the automotive industry for PCE-based aerosols is for brake cleaning. Their perspective is that tire and engine cleaning are no longer a significant use of PCE-based aerosols. While cleaners for each use were identified in the Household Products Database that included PCE as an ingredient, research and expert input have indicated that currently available brake and parts/engine cleaners are much more likely to contain PCE than tire cleaners.

Technical Assessment

Brake Cleaning

The characteristics of an effective aerosol brake cleaner involve several areas: performance, drying, and residue. Aerosol brake cleaners are used with a "spray and go" approach. As part of the cleaning process, road dirt, grease and oils must be cleaned off. Also, fibers from brake pads need to be wetted and removed safely. The end user is trying to complete the job as fast as possible. The aerosol cleaners need to clean well and evaporate quickly while leaving no residue behind. Approximately one-half to one full can is required per job (two sets of brakes).

The following four aerosol brake cleaners, listed in Table 5.4.3 A, were assessed as alternatives to PCE-based products. Products in the table will be referred to by the first or main component and the investigated use (see "Text Identification" column in table).

Table 5.4.3 A: List of Alternative Brake Cleaners

Brake Cleaning	Sample Product	Constituents	Text Identification
	AMREP Inc, Misty Brake and Parts Cleaner EF	Heptane-Acetone mix with Carbon Dioxide propellant	Heptane-Brake
	Bio Chem Systems BioBrake	C9-C12 hydrocarbons; Propanol ,2-methoxymethylethoxy; Acetone;	Hydrocarbon-Brake
	CRC Industries Brakleen Brake Parts Cleaner-Non-Chlorinated	Toluene; Methanol; Acetone; Xylene; Heptane; n-hexane; with Carbon Dioxide propellant	Toluene-Brake
	Mirachem 500 Foaming Aerosol	Aqueous based with propane-isobutane propellants	Aqueous 1

Information was gathered from product technical datasheets and labels to determine performance characteristics. The data collected were not based on technical performance testing as this was not available in the literature and was not within the scope of this study. Information was gathered from MSDS's, technical data sheets, industry experts and previously published reports on automotive aerosols. TURI does however recognize that testing in the lab as well as in the field is a further research need in this area in order to identify effective, less toxic alternatives.

The technical performance criteria included soil removal (oil, grease, and dirt), the control of fibers, drying times, and the lack of any residue. Each desired criteria was considered to be met if the literature for the product explicitly listed it as an attribute of the product. If it was not listed, performance was inferred from other information on the sheet. For example, the fiber control was not met by Heptane-Brake because the literature described the delivery as a powerful blasting spray. This could result in the fibers becoming airborne, increasing the inhalation exposure potential. For Aqueous 1 drying time and residue it was assumed that the foam would be designed to remain on the surface for an extended period of time.

All of the products claimed to meet the most crucial criteria of removing oil, grease and dirt. However, only one product specifically mentioned the ability to control fibers from becoming airborne during the cleaning process. It is possible that many of the alternatives could wet the fibers enough to be able control the release into the surrounding air. Collected information on each product is presented in the Table 5.4.3 B.

Table 5.4.3 B: Brake Cleaning Performance Comparison

Product	Oil, grease, dirt	Fiber control	Drying time	Residue
Heptane-Brake	Y	N - Powerful blasting spray		
Hydrocarbon-Brake	Y		Y	Y
Toluene-Brake	Y			Y
Aqueous 1	Y		N	N - Creates foam- need rinsing

Y = Yes, according to manufacturer's claims

N = No, unlikely to meet performance criteria

Blank = no information available from literature

Engine Cleaner

The use of PCE in engine cleaning applications has traditionally not been a high volume application. This limited use was due to the differing requirements for cleaning engine parts. In contrast to the brake cleaning, engine cleaners can remain on surfaces, and so don't have to evaporate quickly. The ability to cling to a surface was another desirable attribute of this cleaning process that differed from brake cleaning.

According to an industry expert, even though water-based products have been shown to work in many instances for general external engine cleaning, water based products are still not well accepted because they frequently need additional mechanical agitation (*i.e.,* scrubbing) to achieve adequate cleaning performance. In addition the water-based aerosol products tend to require rinsing after cleaning is complete.

For internal engine cleaning applications, the chemicals used must be registered as a fuel additive. Traditionally, these products have been based on methylene chloride. Some of the other products that are commonly used for engine cleaning include kerosene and Stoddard solvents. For both internal and external uses, products need to have a high flash point.

Products selected for comparison are listed in the Table 5.4.3 C. Products in the table will be referred to by the first or main component and the investigated use.

Table 5.4.3 C: List of Alternative Engine Cleaners

	Sample Product	**Constituents**	**Text Identification**
Engine Cleaning External	Misty Heavy Duty Butyl Degreaser	Aromatic Petroleum Distillates; 2-Butoxyethanol; with an Isobutane-Propane propellant blend	Petroleum 1-Engine
	Citrus Engine Brite Engine Cleaner & Detailer	2- Butoxyethanol; Methyl Esters of C16–C18 and C18; Unsaturated Fatty Acids; Petroleum Sulfonate; Kerosene; Orange Peel Oil Sweet Cold Pressed; Nonyl Phenol Ethoxylate; Carbon Dioxide	Butoxyethanol-Engine
	3M Citrus Base Cleaner (Aerosol)	D-Limonene with propane propellant	Terpene 1-Engine
	Misty Solvent Cleaner & Degreaser	Monocyclic Terpene Methyl Esters Of Soybean Oil	Terpene 1-Engine
	Misty Coil Cleaning Foam	Aqueous with propane-isobutane propellants	Aqueous 2
	Mirachem 500 Foaming Aerosol	Aqueous with propane-isobutane propellants	Aqueous 1
	Berryman Products Inc New Engine Degreaser	Nitrogen Propellant	Aqueous 3
Engine Cleaning Internal	ZEP Manufacturing Company ZEP Carb X (Aerosol)	Toluene; Methanol; Xylene; Hydrotreated Light Petroleum Distillates	Toluene-Engine
	American Polywater Corporation Type HP™ Cleaner/ Degreaser	Medium Aliphatic Petroleum Solvent Monocyclic Terpene	Petroleum 2-Engine
	Malco Fuel Injector Air Intake Cleaner (Aerosol)	Xylene; Toluene; Propane; Isobutane; Acetone	Xylene-Engine

Each product selected was found to meet the needs for the specific soils that were associated with engine cleaning. Only three of the products stated that they were designed to cling to vertical surfaces. One of the products was designed to leave behind a residue that would create a protective layer. This film was intended to make subsequent cleaning easier as it would prevent build up from occurring. Another product, even though it was a foam-based cleaner, was made to be free rinsing using only condensate from the air to remove the foam from the surface. The comparison of selected products for the designated performance criteria is listed in Table 5.4.3 D.

Table 5.4.3 D: External Engine Performance Comparison

Product	Oil, grease, dirt	Cling to Surface	Residue
Petroleum 1-Engine	Y	Y - Light foam	
Butoxyethanol-Engine	Y		Y - Leaves protective layer
Terpene 1-Engine	Y		
Terpene 1-Engine	Y		
Aqueous 2	Y	Y - Foam	Y - Self rinsing
Aqueous 1	Y	Y - Foam	N -Must rinse
Aqueous 3	Y		

Y = Yes, meets criteria according to manufacturer's claims

N = No, not expected to meet criteria

Blank = no information available from literature

PCE has been a minor use for carburetor, fuel injector and air intake cleaning with methylene chloride as the cleaning solvent of choice. Technical requirements include the ability to remove the appropriate soils and there are requirements that the cleaner be registered as a fuel additive. The performance criteria for internal aerosol engine cleaning products are listed in Table 5.4.3 E.

Table 5.4.3 E: Internal Engine Performance Comparison

Product	Oil, grease, dirt	Fuel Additive Registered
Toluene-Engine	Y	Y
Petroleum 2-Engine	Y	
Xylene-Engine	Y	

Y = Yes, meets criteria according to manufacturer's claims

N = No, not expected to meet criteria

Blank = no information available from literature

Tire Cleaner

Tire cleaners are used for aesthetic cleaning of rims to remove dirt and brake dust build up. PCE was found as an ingredient in some consumer based tire cleaning products in the Household Products Database, although the use of such formulations does not appear to be wide spread in businesses. One industry representative stated that PCE-based aerosol products were not used for tire cleaning by most of the businesses he supplied to. More often, the major component of tire cleaning has been ammonium bifluoride which aids in the removal of brake dust from the tire rims.

Ideally, industry experts state, tire cleaning formulations should not be corrosive; avoiding high or low pH values. In addition, cleaners should leave tires with a shine and require minimal effort for cleaning.

Products to be assessed are listed in the Table 5.4.3 F. Products in the table will be referred to by the first or main component and the investigated use except for the aqueous based product.

Table 5.4.3 F: List of Alternative Tire Cleaners

Tire Cleaning	Sample Product	Constituents	Text Identification
	Armor All Tire Foam (Aerosol)	Silicone Emulsion; Dimethyl Ether; Propylene glycol; Propane and Isobutane	Silicone-Tire
	Armor All STP® Son of a Gun® One Step Tire Care	Diethylene Glycol Monoethyl Ether; Alkyloxy polyethylene oxyethanol; Isobutane; Poly dimethylsiloxane; Water	Gycol Ether - Tire
	Misty Detailing & Dressing Spray	Hexane; Poly Dimethylsiloxane; Petroleum Distillates; Isobutane- Propane propellant	Hexane- Tire
	Mirachem 500 Foaming Aerosol	Aqueous with propane-isobutane propellants	Aqueous 1

Each product formulation claimed to meet the necessary requirement for the particular soil removal. Additionally, all the products were found to be non-corrosive with pH values ranging from 7.3 to 10. Three of the products provided one-step cleaning that resulted in a shiny tire. The last product did not specify if the process was a one-step process or if the tire would be shiny. The results for the performance comparison gathered from vendor information are listed in the Table 5.4.3 G.

Table 5.4.3 G: Tire Cleaning Performance Comparison

Product	Oil, grease, dirt	Shine	One Step	Non-corrosive -pH
Glycol Ether - Tire	Y	Y	Y	Y - 9-10
Hexane- Tire	Y	Y	Y	Y - 9.4-9.8
Glycol Ether - Tire	Y	Y	Y	Y - 7.3-8.3
Aqueous 1	Y			Y

Y = Yes, meets criteria according to manufacturer's claims

N = No, not expected to meet criteria

Blank = no information available from literature

Financial Assessment

A comparison on the purchase cost for alternative aerosol cleaners was conducted using data collected from various distributors of the aerosol products. Whenever possible, the price for one case of product was used. Normalizing the volume of the case was necessary as many of the products were available in different volumes. If more detailed information on performance were available, costs could also be normalized for amount of product required to do one job.

Brake Cleaning

The Heptane-Brake and the Aqueous 1 products had comparable costs. The Toluene-Brake product had the highest cost per ounce. This upfront purchase cost does not address usage rates. Some products may work more efficiently than others, requiring less material to clean the desired parts. This would bring the overall operating costs down. Typical costs for a PCE-based cleaning product are approximately $4/can or about $0.25/oz. Three of the four products were comparable to this purchase price and are listed in the Table 5.4.3 H.

Table 5.4.3 H: Cost Comparison for Brake Cleaners

Product	Purchase Price ($/oz)
Heptane-Brake	0.15
Hydrocarbon-Brake	0.28
Toluene-Brake	0.57
Aqueous 1-Brake	0.18

Engine Cleaner-External

Many of the alternative aerosol engine/parts cleaners had purchase costs that exceeded that for PCE-based products. Only two products had equal or lower prices. However, only two products were considerably higher than the PCE price. Depending upon efficacy of the alternatives, the higher costs could be offset by using less of a product per task. Purchase costs for engine cleaners are listed by product in Table 5.4.3 I.

Table 5.4.3 I: Cost Comparison for Engine Cleaner-External

Product	Purchase Price ($/oz)
Petroleum 1-Engine	No Data
Butoxyethanol-Engine	0.36
Terpene 1-Engine	0.43
Terpene 1-Engine	0.63
Aqueous 2	0.25
Aqueous 1	0.18
Aqueous 3	0.33

Engine Cleaner-Internal

Due to the cleaning requirements for carburetor and air intake cleaning, the purchase cost for the alternatives are much higher than the PCE based products. The prices are more than twice the cost of the $0.25/oz average for PCE aerosol cleaners. The costs for two of the three alternatives are listed in the Table 5.4.3 J.

Table 5.4.3 J: Cost Comparison for Engine Cleaner Internal

Product	Purchase Price ($/oz)
Toluene-Engine	No Data
Petroleum 2-Engine	0.59
Xylene-Engine	0.53

Tire Cleaner

Alternatives for tire cleaners were found to be similar to the cost of PCE ($0.25/oz). For the three products that data were available for, all three were equal to or less expensive than PCE (assuming 100% PCE in the reference product). Many of these products are foaming products. Table 5.4.3 K lists the costs.

Table 5.4.3 K: Cost Comparison for Tire Cleaners

Product	Purchase Price ($/oz)
Silicone-Tire	0.25
Glycol Ether-Tire	No Data
Hexane-Tire	0.20
Aqueous 1	0.18

Environmental Assessment

Several key parameters were reviewed to determine the potential impact of aerosol cleaning solvents in the environment. Human health effects will be discussed separately in the following section. Further information on environmental and health parameters and levels of concern are included in Appendix A; detailed data for automotive aerosol alternative chemistries are included in Appendix D.3. Initially, all products and their ingredients, including the current solvent, were analyzed using the EPA PBT profiler to determine persistence and bioaccumulation potentials.

Brake Cleaning

The constituents for each brake cleaner were not persistent in water. Each constituent had a half-life less than that for PCE (60 days). Soil half-lives were also lower than the PCE level for all components except one. The Hydrocarbon-Brake cleaner had one component, C9-C12 hydrocarbon, with a soil half-life listed as less than 180 days which persistence in soil. PCE had a soil half-life of 120 days, also in the considered persistent.

For sediment persistence, each component was lower then the PCE half-life of 540 days. All values for the alternatives were less than the 180 day limit for very persistent. Most of the listed alternatives had half-lives of approximately 140 days, indicating that they are persistent. There were some components for which a half-life could not be established.

Air persistence resulted in the most concern for half-life values. Only two components of one product, Hydrocarbon-Brake cleaner, were below the persistence level of 2 days. All other components and PCE were above this value. The air persistence is of concern as many of the components will end up in this medium due to the aerosol delivery system.

According to the MSDS for PCE, the solvent is considered to be toxic to fish. The only constituent in the alternatives that was of moderate concern for chronic fish toxicity was the heptane in the Heptane-Brake; its value was also close to the 0.1 mg/l limit for high level of concern.

PCE, toluene and methanol were all hazardous air pollutants on the NESHAP list. However, neither PCE nor any of the alternative products contained any chemical listed as ozone depleting or a greenhouse gas.

Engine Cleaner

Several of the constituents of the engine cleaners could not be assessed using the PBT Profiler because they are mixtures of chemicals within a particular chemical classification. This was the case for some petroleum distillates and soy-based products. For the remaining chemicals, the water and soil half-lives were low. The sediment half-life values were in the persistent range with most products having a 140 day half-life. Air half lives were mixed with some chemicals having low residence time in air, less than two days and others having longer times. Most formulations had at least one chemical with half-life greater than two days, indicating persistence in air.

Only d-limonene, found in Terpene 1-Engine and Terpene 2-Engine, was considered bioaccumulative. D-limonene had a BCF of 4770, which is close to the EPA threshold of 5000 for very bioaccumulative.

Two components, d-limonene, found in Terpene 1-Engine and Terpene 2-Engine, and nonyl phenol ethoxylate, found in the Butoxyethanol-Engine, had ChV values that would classify these chemicals as having chronic fish toxicity. D-limonene had value of 0.045mg/l, about half the established level of 0.1 mg/L. NPE had about one fifth of the 0.1mg/L level

No external alternative engine cleaning products contained chemicals that were hazardous air pollutants on the NESHAP list. However, the internal alternative cleaning products had some components that were hazardous air pollutants. These chemicals were xylene, toluene and methanol. No alternatives contained chemicals that would be classified as ozone depleting chemicals or greenhouse gases.

Tire Cleaner

Both water and soil persistence for the alternative constituents are below the 60 day half-life signifying that they are not persistent. Sediment persistence values were all lower than the 180 day limit for very persistent but were greater than the 60 day half-life. Air persistence resulted in the greatest number of constituents exceeding the persistent levels.

PCE is not considered to be bioaccumulative. Alternatives contain constituents that are both higher and lower than PCE, none of which exceed the EPA criteria for bioaccumulative.

Only Hexane-Tire contained a chemical, a petroleum distillate, with high concern for chronic fish toxicity with a ChV value of 0.056 mg/L. Several constituents had values greater than the 0.1mg/L but less than 10, indicating moderate concern for chronic fish toxicity.

PCE and hexane (in Hexane-Tire) were the only two products to be listed as hazardous air pollutants under NESHAP. No products contained ozone depleting chemicals or greenhouse gases.

Human Health Assessment

Acute Effects

Brake Cleaning

The assessed alternative brake cleaners did not contain any component that had a PEL lower than PCE. PEL's for constituents in alternatives ranged from 100 to 5000 ppm.

According to the NIOSH Pocket Guide to Chemical Hazards PCE can irritate the skin, the eyes and the respiratory tract. When possible, the alternative's potential to cause irritation was based on the product as a whole. Three of the four brake cleaners were found to irritate the skin, the eyes and the respiratory tract. The one alternative that was considered to be non-irritating was the Aqueous 1 product.

The use of n-hexane in brake cleaners reportedly can result in incidences of numbness of fingers and arms among users (HESIS 2001; CDC 2001). The HESIS Health Advisory Alert on n-hexane (CAS# 110-54-3) further states the chemical can enter the body when spray in the air is breathed in or comes in contact with skin. Exposure of long durations (months) can cause damage to nerves of the extremities called peripheral neuropathy. Symptoms of this condition can be numbness or tingling in the feet, legs and hands, a reduced sense of touch, pain, vibration or temperature and muscles may weaken in the legs, feet and hands. Symptoms have been seen to gradually improve when exposure ceases, but may last for months or be permanent. Short term exposures of n-hexane may produce headaches, dizziness, and loss of appetite or drowsiness but seem to improve a few hours after exposure ceases.

The HESIS Health Alert further states that workers exposed to air concentrations slightly over the workplace PEL of 50 ppm can suffer nerve damage.

Engine Cleaner

There was a wide range of PELs for the different constituents of the alternative aerosol engine cleaners. Therefore, for each engine cleaning product the constituent with the lowest PEL, REL or TLV was selected for comparison to PCE. Two external products (Petroleum 1-Engine and Butoxyethanol-Engine) each contained the component, 2-butoxyethanol, that had a PEL and TLV lower than those for PCE. The vapor pressure of 2-butoxyethanol is lower than PCE, so it is less likely to evaporate into the air than PCE. Depending on the percent of PCE and 2-butoxyethanol in the respective products, and their efficiency (how much product you need to clean effectively), this could result in lower exposures to 2-butoxyethanol. The internal engine alternatives had a PEL equal to PCE and a TLV that was greater than that for PCE. Table 5.4.3L lists the lowest values for each alternative aerosol product.

Table 5.4.3 L: Exposure Limits

	PEL (ppm)	REL (ppm)	TLV (ppm)
PCE	100		25
External			
Petroleum 1-Engine	50	5	20
Butoxyethanol-Engine	50	5	20
Terpene 1-Engine	1000	1000	
Terpene 1-Engine			
Internal			
Toluene-Engine	100	100	50
Petroleum 2-Engine			
Xylene-Engine	100	100	50

Most of the alternative products posed the same hazards as PCE for the skin, the eyes and the respiratory tract.

Tire Cleaner

Many of the alternative tire aerosol cleaning formulations did not have PELs for their constituents. For the chemicals with PEL's, only one was lower than the 100 ppm currently established for PCE. This component diethylene glycol monoethyl ether, (Glycol Ether-Tire) had a PEL of 50 ppm. When comparing the TLV's for the alternatives, all of the listed values were safer than the 25 ppm value set for PCE.

Each product contained at least one component that would either cause irritation to the skin, eyes and the respiratory tract. When looking at each product as a whole, the only alternative considered to be non-irritating was Aqueous 1.

Chronic Effects

Long term hazards include mutagenicity, carcinogenicity and reproductive and developmental toxicity. The EPA has classified PCE as reasonably anticipated to be a human carcinogen and IARC lists the solvent as a 2A probable. PCE can affect the eyes, skin, respiratory system, liver, kidneys and the central nervous system.

Brake Cleaner

Toluene was the only alternative constituent with listed chronic effects. This chemical was found in the Toluene-Brake. Toluene is listed as a developmental toxin under California's Proposition 65 and adversely affects the central nervous system.

The alternatives contain at least one chemical constituent that can affect the skin, respiratory system and central nervous system. Three of the products contain components that also affect the eyes. Aqueous 1 was the only product that did not contain such an eye hazard. Toluene-Brake also could affect the lungs, liver, kidney and the gastrointestinal tract.

Engine Cleaner

Toluene used in engine cleaners have adverse chronic effects (see discussion for brake cleaners above). Several studies also have shown reproductive effects from glycol ether exposure.

Each of the alternatives contains at least one chemical that can affect the skin, respiratory tract and the kidneys. In additional all but Terpene 1-Engine contained a component that can affect the eyes. Petroleum 2-Engine and Terpene 2-Engine do not contain chemicals that would affect the central nervous system.

Tire Cleaner

No constituents of the aerosol tire cleaners were recorded as being mutagens or carcinogens. One component, poly dimethylsiloxane, found in two products (Glycol Ether-Tire and Hexane-Tire) has been shown in studies to cause reproductive or developmental effects. In addition, one product formulation, Glycol Ether-Tire, had reproduction or development effects listed on the MSDS.

Other Hazards: Flammability and Flash Point

PCE is considered to be non flammable and has no flash point. Based on the NFPA rating system PCE has a zero fire hazard.

Brake Cleaning

Aqueous 1 was the only alternative brake cleaner with a flash point greater than 100°C and an NFPA rating of one for fire. The other products (Heptane-Brake, Hydrocarbon-Brake, Toluene-Brake) had an NFPA fire rating of three and flash points less than 0° C. These products are considered flammable.

Engine Cleaner

The Butoxyethanol-Engine product had an NFPA rating of 2 and flashpoint of 64° C. Likewise, Petroleum 2-Engine had an NFPA rating of 2 and a flashpoint of 60° C. The Terpene 1-Engine based cleaner had an NFPA rating of 4 and flashpoint of -10° C. Similarly, Xylene-Engine cleaner had an NFPA rating of 4 and a flash point of -97° C. Although the Toluene-Engine did not have an NFPA rating for the product as a whole, three of the four components had NFPA ratings of three for fire. The flashpoints for these three components were less than 30° C. One alternative, Petroleum 1-Engine, did not have enough information to characterize the flashpoint.

Tire Cleaner

Two products, Silicone-Tire and Aqueous 1, had flash points greater than 93.3° C and NFPA ratings of one for flammability. Glycol Ether-Tire did not list a flash point for the complete formulation and had an NFPA rating of two for fire. The remaining product, Hexane-Tire, did not have either a flash point or NFPA rating listed for the complete product.

Other Hazards: Reactivity

Brake Cleaning

All of the aerosol brake cleaning solvents had an NFPA Reactivity rating of zero and would be considered to not cause a worker risk in this category.

<u>Engine Cleaner</u>

The Terpene 1-Engine based cleaner and the Petroleum 2-Engine product both had an NFPA rating of one for reactivity which would result in the product becoming unstable if heated.

<u>Tire Cleaner</u>

Only one constituent, Dimethyl Ether in the Glycol Ether-Tire product had an NFPA rating of one for reactivity. All other components in this formulation had an NFPA rating of zero.

Other Hazards: Corrosivity

Corrosivity was measured using pH values. Products with a pH less than 2 and greater than 12 would be considered to be corrosive. Products with no pH, such as PCE, would not be applicable to this measurement of corrosivity.

None of the alternative products for the three automotive aerosol applications were considered to be corrosive.

Summary of Automotive Aerosol Alternatives

Effectiveness of the alternatives and information regarding constituents was based on information supplied by manufacturers. No independent testing has been conducted to verify and compare the performance of these alternatives to PCE based products.

<u>Brake Cleaning</u>

More information is needed on the control of fibrous particles as a criterion. One product claims to limit the fibers from becoming airborne, for the others it was inferred or unknown. Depending on the nature of the airborne fibers, they could pose a serious health risk to the worker due to the body's difficulty in clearing these particles from the lung.

The alternatives are comparable in purchase price. Only one product (Toluene-Brake) had higher cost than the current cost for PCE-based products.

The assessed alternatives had lower environmental persistence. Neither PCE nor the alternatives exceed the EPA limit for being considered bioaccumulative. The worker exposure review showed that the alternatives may be safer for the user than PCE based cleaners. The alternatives also had the same reactivity and corrosivity levels as the traditional cleaner. The Heptane Brake and the Hydrocarbon Brake have flammability concerns. Only one product, Toluene-Brake had similar mutagenicity and reproductive or developmental toxicity levels as PCE.

The summary for brake cleaning alternatives is found in Table 5.4.3 M. For most indicators, the alternatives appear to offer an improved environmental, health and safety profile over PCE. All except the Aqueous 1 product are flammable, however, and introduce a new hazard to the work environment.

Table 5.4.3 M: Assessment Summary for Brake Cleaning Alternatives

Assessment Criteria		PCE reference	Heptane-Brake	Hydrocarbon-Brake	Toluene-Brake	Aqueous 1
Technical Criteria	Cleaning	Effective	=	=	=	=
	Fiber control	Unknown	-	?	?	?
	Drying	Quick	?	=	?	-
	Residue	None	?	=	=	-
	Flammable	Non	-	-	=	=
Financial Criteria	Purchase	$0.25/oz	+	=	-	+
Environmental Criteria	Water	60 days	+	+	+	+
	Soil	120 days	+	=	+	+
	Sediment	540 days	+	+	+	+
	Air	98 days	=	+	=	+
	BCF	83	-	-	+	+
Human Health Criteria	Exposure limits	100 ppm; 25 TLV	+	+	+	+
	Dermal/Occular/Respiratory	Irritant	+	=	=	+
	Mutagenicity	No	=	=	-	=
	Carcinogenicity	2A	+	+	+	+
	Reproductive or Developmental Toxicity	No	=	=	-	=
Safety Criteria	Flammability	Nonflammable	-	-	-	+
	Reactivity	Non reactive	=	=	=	=
	Corrosivity	Non corrosive	=	=	=	=

Comparison Key + Better = Similar - Worse ? Unknown

Engine Cleaning – External

One important criterion for engine cleaning was the ability of the cleaner to cling to a vertical surface. Half of the evaluated products appeared to meet this criterion. Most of the products had comparable flash points to PCE. Only two products could be confirmed to leave no residue behind after cleaning was completed and only one product had a similar non-VOC status to PCE.

Four of the alternatives cost more than PCE-based products. The two aerosol aqueous based alternatives were approximately the same or less expensive than PCE was. An industry expert also stated that for whole engine cleaning and degreasing a non aerosolized aqueous parts and engine cleaning system can work as well as an aerosolized solvent cleaner and may prove less expensive due to the amount of cleaner needed to clean an entire engine.

Nearly all of the evaluated products had improved environmental persistence profiles. One product had higher air persistence and two had higher BCF levels. The aqueous based products could not be assessed for the worker exposure profile as there was not enough constituent information. The only listed components were for the propellants. However, typically this class of products would have a better profile than solvent based products for worker health and safety. In all other cases, the alternatives had fewer hazards for the worker than PCE-based products.

It should be noted again that PCE-based cleaners have not been widely used for general engine cleaning due to the higher evaporation rate of the PCE cleaners but that they have been used for cleaning parts of the engine that need to be removed and repaired. The summary table for engine (external) cleaning alternatives is found in Table 5.4.3 N and shows that the alternatives appear to be less toxic to the environment and be less persistent and bioaccumulative. For human health effects the alternatives seem to be of less concern for chronic health hazards of carcinogenicity, mutenagenicity and reproductive and developmental hazards. The two products that contain 2-butoxyethanol are a concern for worker exposure. The exposure limits for that constituent are lower than for straight PCE.

It should also be noted that the possible synergistic effect of chemical mixtures has not been evaluated in this assessment.

Table 5.4.3 N: Assessment Summary for Alternatives Engine Cleaning (External) Aerosols

Assessment Criteria		PCE reference	Petroleum 1-Engine	Butoxyethanol-Engine	Terpene 1-Engine	Terpene 2-Engine	Aqueous 2	Aqueous 1
Technical Criteria	Cleaning	Effective	=	=	=	=	=	=
	Cling to surface	Unknown	+	?	?	?	+	+
	Residue	None	?	+	?	?	+	-
	Flash Point	None	=	=	-	=	=	=
Financial Criteria	Purchase	$0.25/oz	-	-	-	-	=	+
Environmental Criteria	Water	60 days	+	+	+	+	+	+
	Soil	120 days	+	+	+	+	+	+
	Sediment	540 days	+	+	+	+	+	+
	Air	98 days	+	-	+	+	+	+
	BCF	83	+	+	-	-	+	+
Human Health Criteria	Exposure limits	100 ppm; 25 TLV	-	-	+	?	?	+
	D/O/R	Irritant	=	=	=	=	?	+
	Mutagenicity	No	=	+	+	+	?	+
	Carcinogenicity	2A	+	+	+	+	?	+
	Rep/Develop	No	+	+	+	+	?	+
Safety Criteria	Flammability	Nonflammable	-	-	-	=	?	+
	Reactivity	Non reactive	=	=	=	=	?	=
	Corrosivity	Non corrosive	=	=	=	=	?	=

Comparison Key + Better = Similar - Worse ? Unknown

Engine Cleaning - Internal

Only one product, Toluene-Engine, was assumed to meet the fuel additive requirement as this product was specifically designed to clean carburetors. The other two alternatives were more generalized cleaners and the same assumption could not be made for them.

Costs were again higher for two of the products reviewed (Petroleum 2-Engine and Xylene-Engine) and unknown for the third (Toluene-Engine).

From an environmental standpoint, the alternatives had lower environmental persistence. Only one of the formulations had a BCF that was worse than the PCE value. The alternatives were comparable or better than PCE for most human health effects. Each of the alternatives had some level of concern regarding flammability whereas PCE is non flammable. The summary table for engine (internal) cleaning alternatives is found in Table 5.4.3 O and the same issues seen for external engine cleaners and the other automotive aerosols should be considered for this use as well.

Table 5.4.3 O: Assessment Summary for Alternative Automotive Engine Cleaning (Internal) Aerosols

Assessment Criteria		PCE reference	Toluene-Engine	Petroleum 2-Engine	Xylene - Engine
Technical Criteria	Cleaning	Effective	=	=	=
	Fuel Additive	Unknown	+	?	?
Financial Criteria	Purchase	$0.25/oz	?	-	-
Environmental Criteria	Water	60 days	+	+	+
	Soil	120 days	+	+	+
	Sediment	540 days	+	+	+
	Air	98 days	+	+	+
	BCF	83	+	-	+
Human Health Criteria	Exposure limits	100 ppm; 25 TLV	=	?	=
	D/O/R	Irritant	=	=	=
	Mutagenicity	No	+	+	+
	Carcinogenicity	2A	+	+	+
	Rep/Develop	No	+	+	+
Safety Criteria	Flammability	Nonflammable	-	-	-
	Reactivity	Non reactive	=	=	=
	Corrosivity	Non corrosive	=	=	=

Comparison Key + Better = Similar - Worse ? Unknown

Tire Cleaning

Most of the alternatives met the desired criteria for a tire cleaner. Only one product (Aqueous 1) did not specify whether it created a shine on the tire or whether it was a one-step process. This product was more of a general cleaning product that may be effective for tire cleaning. The identified alternatives cost approximately the same (Silicone-Tire or less Hexane-Tire and Aqueous 1) as PCE-based products. Only one product (Glycol Ether-Tire) did not have cost information.

Environmental persistence for each alternative was lower for water, soil, sediment and air. The BCF for two products (Glycol Ether-Tire and Hexane-Tire) was greater than PCE. Only one product (Glycol Ether-Tire) had a higher PEL. All other worker exposure data were equal to or better than a

PCE based product. Flammability concerns were found for three of the four alternatives. The summary table for tire cleaning alternatives is found in the Table 5.4.3 P.

Table 5.4.3 P: Assessment Summary for Alternatives for Automotive Tire Cleaning Aerosols

Assessment Criteria		PCE reference	Silicone-Tire	Glycol Ether-Tire	Hexane-Tire	Aqueous 1
Technical Criteria	Cleaning	Effective	=	=	=	=
	Shine	Yes	+	+	+	?
	One Step	Yes	+	+	+	?
	Non-corrosive	Yes	=	=	=	=
Financial Criteria	Purchase	$0.25/oz	=	?	+	+
Environmental Criteria	Water	60 days	+	+	+	+
	Soil	120 days	+	+	+	+
	Sediment	540 days	+	+	+	+
	Air	98 days	+	+	+	+
	BCF	83	+	-	-	+
Human Health Criteria	Exposure limits	100 ppm; 25 TLV	+	-	+	+
	D/O/R	Irritant	=	=	=	+
	Mutagenicity	No	=	=	=	=
	Carcinogenicity	2A	+	+	+	+
	Rep/Develop	No	-	=	=	=
Safety Criteria	Flammability	Nonflammable	-	-	-	+
	Reactivity	Non reactive	-	=	=	=
	Corrosivity	Non corrosive	=	=	=	=

Comparison Key + Better = Similar - Worse ? Unknown

Emerging Aerosol Cleaning Alternatives

Recently a study was conducted by Institute for Research and Technical Assistance (IRTA) for California's Department of Health Services Hazard Evaluation System & Information Service (HESIS) to identify and test alternative safer water-based aerosol cleaning products. The focus was on developing and testing alternative aerosol cleaners for four categories of automotive cleaning (HESIS 2004). In addition to the water based products, the project including developing, testing and demonstrating low-VOC, low toxicity soy/acetone based cleaners as potential alternatives.

From field testing conducted by various end users, the alternatives performed adequately and, in some cases, very well. The VOC content of the alternative cleaners ranged from zero to 10% using hydrocarbons as the propellant. If carbon dioxide could be used as a propellant for the water-based cleaners, the VOC content of the alternative products would be near-zero. The alternative products developed and tested during this project are lower in toxicity than most products currently used in aerosol automotive cleaning applications (HESIS 2004).

Despite the success of many of the products, IRTA determined from their testing that the water based formulations foamed when they were packaged into an aerosol delivery. As described previously, foaming is considered a benefit for some uses but can cause problems in processes that require fast drying such as brake cleaning.

Although it was not originally part of the project plan, IRTA included an evaluation of alternative propellants in an attempt to find one that would not contribute to smog formation. The most common propellants in automotive aerosols are hydrocarbon-based. The hydrocarbons are VOCs that lead to the creation of smog. Additionally, during the testing process, IRTA found that the alternative propellants could improve the overall performance of the alternative products. When the soy/acetone products for carburetor and fuel injection system cleaning were packaged with both hydrocarbon and carbon dioxide propellants the IRTA found that the carbon dioxide propelled products had a better delivery and cleaning efficiency (HESIS 2004).

The two delivery mechanisms included carbon dioxide and nitrogen. As mentioned, the carbon dioxide propellant improved delivery and efficiency with certain formulations. However, a major disadvantage of carbon dioxide arises when it is used with highly alkaline water-based cleaners. It can react with the alkaline components forming carbonic acid which can lead to corrosion of the can.

Nitrogen was considered as a propellant because it is not classified as a VOC and it has a very low cost. Two problems have been observed with nitrogen propellants. First, some packagers claim it loses pressure as the product is expelled from the aerosol. Second, other packagers claim that it has lower pressure on a continuous basis as the product is expelled.

One possible solution to the loss of pressure during usage would be to utilize a rechargeable system. EnviroCaddie LLC has a unit designed for spraying brake cleaners, penetrants and choke cleaners. The device is designed to be refillable & rechargeable, thus eliminating this drawback. The reusability of the container would eliminate the need for aerosol can disposal. According to the manufacturer, any product that can be sprayed from an aerosol container also could be sprayed from the EnviroCaddie equipment.

The company offers an array of cleaning products that from recognized manufacturers (Dynatex; CRC; Castle) which can be used effectively in the EnviroCaddie II. They will also consider other products and formulations on an individual basis (ENVIROCaddie LLC).

5.5 Summary and Conclusions

Perchloroethylene, or PCE, is a non-flammable, man-made chlorinated hydrocarbon with the chemical formula C_2Cl_4. It is used primarily as a solvent in dry cleaning, industrial degreasing and as a chemical intermediate.

Exposure to PCE can be as a result of environmental contamination, presence in consumer products or occupational sources. PCE levels in the environment tend to be higher in urban and industrial areas. The most prevalent route of exposure to PCE is by inhalation and it is readily absorbed into blood through the lungs. Other exposure routes of concern are oral via drinking water or contaminated food. Dermal exposure is generally considered a minor route of exposure but direct skin exposure to PCE in the liquid form can result in irritation and blistering.

Target organs for PCE are the central nervous system, kidneys and the liver. Some studies suggest that frequent over exposure to some organic solvents over months or years may cause lasting and possibly permanent central nervous system effects. IARC lists PCE as Group 2A, "probably carcinogenic to humans".

The three PCE uses assessed in this study are dry cleaning, vapor degreasing and automotive aerosol cleaners. These uses were chosen because of their importance to Massachusetts and their potential for worker and consumer exposure.

5.5.1 Dry Cleaning

Complete alternatives assessments were performed for five alternatives to PCE, *i.e*, hydrocarbons (HC), volatile methyl siloxanes (VMS), substituted aliphatic glycol ethers (SGE), wet cleaning, and liquid carbon dioxide (CO_2). A specific formulation was selected from each of the first four categories for detailed analysis; these assessments should be considered to be representative of each category. The first four alternatives are commercially available in Massachusetts, and interviews with users find that, in general, technical and economic performance approaches that of PCE. No commercial CO_2 facilities were identified in Massachusetts, although there are facilities in other states.

In general, the EH&S impacts of the solvent-based alternatives are less well-understood than those of PCE, with an absence of in-depth toxicological studies in the peer-reviewed literature; overall, however, they appear to represent an improvement over PCE. There is one major exception - the three solvent-based cleaners, HC, VMS and SGE, are combustible where PCE is not. Importantly, none of the alternatives are suspected or confirmed human carcinogens, although this may be due to the lack of any studies being performed as reflected in the absence of published studies in the peer-reviewed literature.

5.5.2 Vapor Degreasing

The alternatives assessment was limited to drop-in replacements to PCE; aqueous cleaning systems were not included since the TURI SSL has already documented the advantages and disadvantages of this approach. A product based on n-propyl bromide (nPB), a product based on VMS, and two hydrochlorofluorocarbons (HCFCs) were selected for the alternatives assessment.

Soil removal testing performed at the TURI SSL as part of another study found that all four alternatives were as effective as PCE in removing oil-based soils. The alternative cleaners had higher vapor pressures than PCE, which will contribute to product loss through evaporation. On the other hand, the alternatives all had lower surface tensions than PCE, which should enhance their ability to clean complex parts.

The financial assessment found that all of the alternatives were considerably more expensive to purchase than PCE, although other operating costs such as energy use, waste solvent handling costs, and solvent lifetime would tend to reduce the overall cost differential. On the other hand, all of the alternative solvents are more volatile than PCE, which could increase costs due to greater evaporative losses.

All of the alternatives have potentially significant environmental and occupational health and safety impacts. The HCFC products have significant adverse environmental impacts, including persistence and global warming potential, but should be somewhat less toxic than PCE. There are significant concerns about the toxicity of nPB; it is a neurotoxin, and its carcinogenicity is now under study. The ACGIH TLV for nPB is 10 ppm, well below the PCE TLV of 25 ppm. VMSs can cause dizziness, disorientation, and shortness of breath, but at relatively high exposure levels; the manufacturer's recommended exposure limit is 200 ppm.

All of the alternatives have higher vapor pressures than PCE, which will lead to greater evaporation and the potential for more vapors to escape from the degreaser; this will increase the potential for worker exposure, and may cause greater fugitive emissions than with PCE. A significant safety hazard is presented by the particular VMS studied, which is highly flammable with a very low flash point. Its use in a vapor degreaser would present a significant fire and explosion hazard.

5.5.3 Aerosol Automotive Cleaning

Many alternative automotive cleaning products are available commercially, so a large number of alternatives were evaluated. Full alternatives assessments were performed on four brake cleaning alternatives, seven external engine cleaning alternatives, three internal engine cleaning alternatives, and four tire cleaning alternatives.

It is difficult to assess the likely technical performance of any of the alternatives, since actual test data are not available. Experts indicated that the alternative solvent-based cleaners are likely to perform as well as PCE-based cleaners, but that aerosol-type aqueous-based cleaners may require more mechanical agitation (*i.e.,* hand-scrubbing) to achieve equivalent results. Cost information is also difficult to assess. Some alternative products were more expensive per ounce than their equivalent PCE product, and some were less expensive per ounce. The actual cost *per use* may be quite different, however, since more or less of the different products may be required to obtain equivalent cleaning ability.

Many of the alternative cleaners had the potential for significant environmental impact upon release; the medium of most concern is air, since these products are used as aerosol sprays. Most of the alternative products had ingredients with atmospheric half-lives exceeding two days, which is also the case for PCE; this puts them in the persistent category.

With regard to human toxicity, the products containing n-hexane, toluene, and two glycol ethers, 2-butoxyethanol and diethylene glycol monomethyl ether (DGME), will be of equal or more concern to those products containing PCE. The aqueous-based products will have lower human health concerns than any of the solvent-based products.

Flammability is an issue for many of the alternatives. Most of the solvent-based cleaners are highly flammable, and great care must be taken in their use – especially around hot engines. PCE is nonflammable, as are the aqueous-based cleaners, so these alternatives are preferable with regard to fire potential.

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