California Environmental Protection Agency
AIR RESOURCES BOARD

California Dry Cleaning Industry Technical Assessment Report

Stationary Source Division
Emissions Assessment Branch

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I. INTRODUCTION

A. Background

An assessment of dry cleaning technologies was performed as part of the technical evaluation of the Airborne Toxic Control Measure for Emissions of Perchloroethylene from Dry Cleaning Operations (Dry Cleaning ATCM). The purpose of the assessment was to compare perchloroethylene (Perc) dry cleaning to the available alternatives and determine whether the Dry Cleaning ATCM, which was originally adopted in 1993, continues to be adequately protective of public health. The last technology assessment was conducted from 1991 to 1993 as part of the Air Resources Board's development of the Dry Cleaning ATCM. This report details the dry cleaning technology assessment and compares some of the results to the earlier assessment.

Information regarding the California dry cleaning industry was obtained from several surveys of the dry cleaning industry. This includes the types of machines being used, the types of machines that are available, and the amount of Perc being sold. The Dry Cleaning Facility Survey was developed by the California Air Resources Board (ARB), in cooperation with the California Cleaners Association, the Korean Dry Cleaners-Laundry Association, other industry representatives, and the local air districts. The purpose of the survey was to collect information from the dry cleaning facilities. The Machine Manufacturer's Survey was used to collect information about cost and other machine information. The Perc Distributor's Survey was used to collect information on the percentage of Perc that is used by the dry cleaning industry and to confirm Perc usage obtained from the dry cleaning facilities survey. Additionally, a solvent manufacturer's survey was used to obtain formulation information which was shared with the Office of Environmental Health Hazard Assessment (OEHHA). OEHHA used this information to provide input to the ARB regarding the health effects and toxicity of the solvents that are discussed in this report.

ARB staff conducted site visits of dry cleaning facilities and conducted emissions testing to enhance our understanding of the California dry cleaning industry and the dry cleaning process. Staff visited over 100 facilities around the state collecting relevant information (e.g. distance to receptors, ventilation practices, and solvent usage). Our testing included collecting and testing sludge from Perc and DF-2000™ Fluid (DF-2000) dry cleaning facilities, evaluating the effectiveness of Perc detectors, and measuring Perc concentrations around Perc dry cleaning machines and other locations in the facilities.

B. Industry Characteristics

California dry cleaners are typically small businesses employing less than five employees, with over half of them employing two or less full time employees. They are usually independently owned and are often operated by the owner and/or their spouse. Over 50 percent of a facility's income is from the dry cleaning of garments. Other

common sources of income include laundry and alteration. The industry is highly competitive; even though about half of the dry cleaners have been in operation for 10 years or more, around 30 percent have been in the business for five years or less. Most facilities are open for business from Monday through Saturday

There are about 5040 dry cleaning facilities in the state. Over 95 percent of these facilities operate a single dry cleaning machine and over 82 percent of the dry cleaning machines use Perc as the solvent. There are three types of Perc dry cleaning machines in use: machines converted from vented to closed-loop (converted), closed-loop machines with primary control (primary), and closed-loop machines with both primary and secondary control (secondary). Over half of the machines in operation are primary machines and about a third of the machines are secondary machines. The percentage of converted machines is small.

Based on extrapolation of the facility survey data, estimates of the Perc dry cleaning operations can be made. Table I-1 compares these estimates with those made in the early 1990's during the ATCM rule development process.

Table I-1. Statewide Estimates of Perc Dry Cleaning Operations

Statewide Estimates	1992 Survey	2003 Survey
Number of Perc dry cleaning machines[1]	5310	4670
Pounds of materials dry cleaned annually[2]	258 million	256 million
Pounds of materials dry cleaned using Perc annually[2]	247 million	214 million
Gallons of Perc used[3]	1,100,000	378,000
Gallons of Perc emitted[3]	742,000	222,000

1. Values are rounded off to the nearest ten.
2. Values are rounded off to the nearest million.
3. Values are rounded off to the nearest thousand.

As shown on Table I-1, there are about 4670 Perc machines currently in operation statewide. This is an estimated 12 percent decrease from 1992. In addition, the amount of clothes cleaned by Perc machines has correspondingly decreased by approximately 13 percent. An interesting observation is that the amount of clothes dry cleaned annually has remained about the same. We believe this indicates an increase in the use of alternative dry cleaning processes. For statewide Perc emissions, the amount of Perc emitted is estimated to have decreased by about 70 percent after implementation of the Dry Cleaning ATCM.

The types of alternative solvents used in 1992 included: Stoddard Solvent (Stoddard), CFC-113, and 1,1,1,-Trichloroethane. And, as shown on Table I-1, about 96 percent of the clothes dry cleaned used Perc. Currently, about 84 percent of the clothes dry cleaned use Perc; the second solvent of choice is DF-2000, a high flash point synthetic hydrocarbon solvent manufactured by ExxonMobil. Other alternative cleaning processes and cleaning solvents include: carbon dioxide (CO_2) cleaning, water-based cleaning systems such as professional wet cleaning (wet cleaning) and

Green Jet® (Green Jet), PureDry® (PureDry), GreenEarth® (GreenEarth), Rynex® (Rynex), Stoddard, as well as other high flash point hydrocarbon solvents such as EcoSolv® (EcoSolv) and Shell SOL 140 HT (Shell 140). Table I-2 summarizes the current technologies used by California dry cleaners. An analysis of these technologies, as well as other available technologies is presented in Chapter II.

Table I-2. Statewide Estimates - California Dry Cleaning Industry[1]

Statewide Estimates	Number[2]	Percent (%)[3]
Dry cleaning facilities	5040	n/a
Perc dry cleaning facilities	4290	85
Mixed facilities (Perc + Alternative)	190	4
Non-Perc facilities	550	11
DF-2000	400	8
GreenEarth	90	2
Others (wet cleaning, Green Jet, PureDry, Rynex, Stoddard, and other high flash point hydrocarbon solvent)	60	1

1. Source: 2003 survey.
2. Values are rounded to the nearest 10.
3. Values are rounded to the nearest integer.

Wet cleaning and Stoddard facilities usually employ a transfer process that requires moving the material being cleaned from a washer to a dryer. The facilities that use DF-2000 and other available alternatives normally operate with a single closed-loop machine. Except for the machines that operate with Tonsil® (a bleaching clay made of natural calcium bentonite material that is acid activated) and CO_2 machines, most of these closed-loop machines operate with primary control and usually with a water separator and vacuum still. It is reported that the machines that operate with Tonsil® (Tonsil) can operate without a still (Kelleher, 2004). Tonsil has been in use for the last few years and cleaners typically use it in a 50 percent tonsil/ 50 percent diatomaceous earth blend (IRTA, 2005). Cost of alternative machines, with the exception of wet cleaning and Green Jet machines, are typically higher than Perc machines. However, other operational costs can be lower with non-Perc processes (see Chapter VII).

II. DRY CLEANING TECHNOLOGIES

This chapter provides some background and technical information regarding the dry cleaning technologies used in California. The economic details of these technologies are presented in Chapter VIII. This chapter also briefly discusses some emerging dry cleaning technologies which are not fully commercially developed in California.

A. Perchloroethylene Cleaning

Perchloroethylene (Perc) is the most widely used dry cleaning solvent in California. Perc is also used in other industry sectors including degreasing operations, paints and coatings, and industrial and consumer products. The Airborne Toxic Control Measure for Emissions of Perchloroethylene from Dry Cleaning Operations (Dry Cleaning ATCM) currently permits the use of closed-loop, dry-to-dry machines when Perc is the solvent of choice. The vast majority of California dry cleaners are familiar with the operation of this technology. Vented and transfer machines have been phased out and no Perc dry cleaners should be using these systems at this time.

Closed-loop, dry-to-dry machines are equipped either with primary controls (primary control machines) or with both primary and secondary controls (secondary control machines). Primary control machines feature a refrigerated condenser which cools the hot air exhaust from the drum to at least 45 degrees Fahrenheit (°F). This allows for the recovery of at least 50 percent more Perc than in older generation machines. The cooled exhaust stream is then reheated and returned back to the drum. The reheated exhaust helps to remove residual Perc from the clothes during the drying cycle. A secondary control machine typically features one or more carbon adsorber beds in addition to the refrigerated condenser. The carbon adsorber operates during the cool-down phase and can reduce the Perc concentration to less than 300 parts per million by volume (ppmv). During regeneration of the carbon beds (usually a fixed interval based on number of loads or manufacturer's recommendation), recovered Perc is returned to the machine's Perc storage tank.

Many machines also feature an inductive door fan. This device, which draws air through the loading door and drum when the door is opened, is used to minimize the release of residual solvent vapor during unloading (after cool-down). Door locks, which prevent the door from being opened when the drum concentration exceeds a set point (normally 300 ppmv), may also be installed.

B. Hydrocarbon Solvent Cleaning

All hydrocarbon solvents used in dry cleaning consist of aliphatic hydrocarbons, meaning they are straight-chained, branched or cyclic as opposed to aromatics, which contains stable carbon-ring structures called benzene rings. Hydrocarbon solvents are combustible. Inherent properties of petroleum-based solvents include high flammability

(more detailed discussion of flammability is presented in Chapter VI), volatility, odor, and toxicity. Toxicity varies by compound; however, none of the petroleum-based solvents have been evaluated by the California Air Resources Board (ARB) for their potential to be toxic air contaminants (toxicity of various solvents is discussed in Chapter V). All of the solvents are volatile organic compounds (VOCs). The machines predominately used for petroleum solvents mentioned below are closed-loop machines equipped with primary control.

1. DF-2000™ Fluid

DF-2000 ™ Fluid (DF-2000) was introduced in 1994 by ExxonMobil as an alternative solvent to Stoddard and Perc. Currently, it is the most popular alternative to Perc. Consisting of C_{11} to C_{13} aliphatic hydrocarbons, it is a synthetic mix of isoparaffins and cycloparaffins (naphthenes) that boils between 185 and 211 degrees Centigrade (OEHHA, 2003). Machines designed for DF-2000 and other hydrocarbon solvents offer closed-loop, dry-to-dry operation. Most include a primary control device (refrigerated condenser) and offer computerized control.

2. PureDry®

PureDry® (PureDry) was developed as a replacement for Perc. It is a blend of isoparaffinic hydrocarbon and a chemical additive produced by 3M. The mixture contains about 95 percent odorless mineral spirits. The odorless mineral spirits are a mixture of aliphatic hydrocarbons (C_9 to C_{12}). Mineral spirits can cause neurotoxicity, and eye and respiratory irritation at high concentrations. It also contains HFE-7200 (a mixture of ethyl perfluoroisobutyl ether and ethyl perfluorobutyl ether), FC-43 (perfluoro compounds of primarily 12 carbons), PF-5070 (perfluoro compounds of primary seven carbons), and PF-5060 (perfluoro compounds of primarily six carbons) (OEHHA, 2003). The flash point of PureDry is 350°F with a boiling point temperature of 298°F. The flash point of a solvent is the temperature at which vapor given off will ignite when an external flame is applied under specified test conditions. A flash point is defined to minimize fire risk during normal storage and handling. Flash points for all dry cleaning solvents range from 110°F to 350°F.

3. EcoSolv®

Chevron Phillips Chemical Company manufactures EcoSolv® (EcoSolv). This dry cleaning fluid is 100 percent isoparaffin with carbon numbers ranging from C_9 through C_{13}. The manufacturer formulated this product by adding butylated hydroxytoluene at 10 parts per million (ppm) to act as an oxygen stabilizer. The isoparaffin is a branched hydrocarbon that is also used for food processing, cosmetic and personal care formulations, and as a solvent for a number of industrial products. EcoSolv has a flash point between140°F and 200°F, and is classified as Class IIIA solvent. (ARB, 2004h)

4. Shell Sol 140 HT

Shell Sol 140 HT (Shell 140) is a high flash point hydrocarbon solvent. Shell 140's flash point is 145°F. This solvent works well in closed-loop machines. However, it is listed as a hazardous material by Occupational Safety and Health Administration (OSHA) standards because it is a combustible liquid and the flash point is above 140°F. (ARB, 1996)

5. Stoddard Solvent

Stoddard Solvent (Stoddard), a class of petroleum solvents, consists of a blend of C_8 to C_{12} hydrocarbons and is similar to kerosene. It is classified as hazardous because its flash point is below 110°F. Stoddard contains small amounts of chemicals known to be carcinogenic but are not classified as toxic. Stoddard also contains benzene, which has been identified as a toxic air contaminant. It also gives off an irritating odor.

Volatile Methyl Siloxane Cleaning

Decamethylcyclopentasiloxane (D_5) or volatile methyl siloxane is an odorless, colorless liquid that has many consumer and industrial applications. D_5 is used as an ingredient in a number of personal health and beauty products, including deodorants, antiperspirants, cosmetics, shampoos, and body lotions. It is also used as a dry cleaning solvent.

D_5 is present in the GreenEarth® (GreenEarth) dry cleaning solvent. GreenEarth solvent is mostly being used in hydrocarbon machines. Although, GreenEarth is used in some converted Perc machines, the manufacturer does not recommend this option. In order for Perc machines to be converted, the following assemblies must be installed by manufacturer: filtration system; temperature control sensors; pre-water separator filter; water separator; and electrical control panel. GreenEarth Cleaning, who distributes the solvent, recommends the purchase of new GreenEarth machines from their approved machine list.

D. Rynex® (Propylene Glycol Ether) Cleaning

Rynex® (Rynex) is an organic and biodegradable solvent with low volatility and a high flash point (>200°F) and is classified as a Class IIIB solvent. Rynex is lighter than water and, therefore, floats on water after separation. It is a mixture of substituted aliphatic glycol ethers. It is considered to be hazardous under OSHA Hazardous Communication Standards because it is a combustible liquid. It is also considered a VOC.

Rynex can be used in most hydrocarbon machines without modifications. Converting Perc machines to use Rynex is not recommended by the solvent

manufacterer. It is not an economically prudent exercise due to the differences in physical properties of Perc and Rynex.

E. Carbon Dioxide (CO_2) Cleaning

Carbon dioxide cleaning (CO_2) is a process that has been developed for use by commercial and retail dry cleaners. CO_2 is a non-flammable, non-toxic, colorless, tasteless, odorless naturally-occurring gas that, when subjected to pressure, becomes a liquid solvent. The liquid CO_2 cleaning machines have a configuration which is similar to a solvent or Perc machine. The system is closed loop and comes equipped with a cleaning chamber, storage unit, filtration, distillation, and lint trap. Washing, vapor recovery, and drying are all performed in the cleaning chamber.

The CO_2 machines pressurize the gas in a drum to between 700 and 800 pounds per square inch (psi). For comparison purposes, a fire extinguisher is at 800 psi and a home oxygen tank is at 2,400 psi. Liquid CO_2 and detergent is circulated through the clothes via jets inside the chamber. The jets are placed such that fluid impact upon the clothes results in rotation. Next, the CO_2 is pulled out to prevent the dirt from being re-deposited on the clothing. At the end of the cycle (35-40 minutes), the pressure is released and the CO_2 returns to a gaseous state, with dirt and substances removed from the clothing (the dirt and debris end up in the bottom of the tank). Cooling and drying of the clothes occurs as the liquid CO_2 evaporates.

The CO_2 used in this process is an industrial by-product from existing operations, primarily anhydrous ammonia (fertilizer) production. There is no net increase in the amount of CO_2 emitted; therefore, this process does not contribute to global warming. CO_2 is naturally occurring and is also used in other applications such as carbonating soft drinks. There are three manufacturers of CO_2 equipment in the United States (U.S.).

F. Professional Wet Cleaning

Professional Wet Cleaning (wet cleaning), an alternative to dry cleaning that was first introduced in 1991, is different than commercial laundering in several aspects. Wet cleaning uses computer-controlled washers and dryers with detergents that have been specially formulated for the process. Specialized equipment is used because ordinary washers and dryers lack the necessary control needed to ensure that garments are processed properly. Finishing equipment includes pressing and tensioning units. The tensioning units are used in dry cleaning industry to touch-up, stretch, reform, and finish the garments.

Due to the high agitation during the wash and spin cycles, an ordinary washer can damage garments. However, the washers used in wet cleaning use a frequency-controlled motor to control the rotation of the wash drum. As a result, a gentle wash action is produced and smoother acceleration and deceleration can be

created. The wash program software can determine the appropriate combination of time, water level, water temperature, extraction, and drum rotation when manual operation is not desired. Washers are also designed to mix water with cleaning agents prior to entering the drum.

Wet cleaned garments must be carefully dried in preparation for finishing. Wet cleaning generally takes about 45 minutes from wash through drying, not including the finishing time. As with high drum agitation, prolonged tumbling in a dryer, or otherwise over drying clothes, can cause shrinkage. Ordinary dryers control the drying process based on time and temperature. The dryers used in wet cleaning are based on humidity and are able to end the cycle when the desired humidity level in the garments has been achieved.

Wet cleaning systems use non-toxic, biodegradable detergents, which are approved for disposal into the sewer system. The detergents are designed to be pH neutral and incorporate agents which prevent the interlocking of fibers. Many stains, such as salts, sugars, and foods and drinks, are readily removed by the wet cleaning process. Wet cleaning can also clean oil-based stains with the use pre-spotting chemicals that are specifically designed for water-based cleaning. Wet cleaning systems may also be gentler on buttons and ornamental pieces on clothing.

G. Green Jet®

The Green Jet® (Green Jet) machine cleans and dries garments in a single computer-controlled unit. The machine is designed to receive a full 45 pound load of garments. It then dehydrates the garments to remove humidity and reduce surface tension, which allows mechanical action and pulsating air jets to dislodge and remove non-soluble soil from the garments. This soil is then collected in a lint chamber. Next, a pre-determined amount of water-based cleaning solution is injected through air jet nozzles to re-hydrate the fabric. After about a pint of solution has been injected, heavy felt pads attached to the ribs and the cylinder absorb the soluble soil. After the cleaning process, the unit goes into a conventional dry cycle and then a cool-down cycle.

H. Emerging Technologies

There are four emerging technologies which are expected to be readily available to the dry cleaning industry within the next few years. These technologies are: 1) Cold Water Cleaning Systems; 2) the Resolve™ Dry Cleaning System; 3) the Impress™ Solvent, and 4) Hydroclene Fluids.

1. Cold Water Cleaning Systems

Cold water cleaning systems (washer and dryer) can wash and dry all fabrics, including fine fabrics. Suntech Company, Ltd. manufactures cold water cleaning systems. The product literature states that the system uses 100 percent water and biodegradable detergents to clean garments. Garments are washed in chilled water

which ranges in temperature from 36°F to 39°F. The use of chilled water is expected to minimize shrinking and may leave the use of tensioning equipment at the discretion of the dry cleaners. (ARB, 2004i)

2. Resolve™ Dry Cleaning System

Resolve™ (Resolve) is a new dry cleaning technology that uses dipropylene glycol normal butyl ether (DPNB). DPNB is a solvent which has been commonly used for more than 20 years in consumer products. R. R. Street, who is developing this technology, claims that extensive exposure studies have shown no known adverse health effects. According to the product literature, the Resolve system is able to take advantage of the low volatility of DPNB and uses liquid CO_2 in the same equipment to extract the DPNB from garments without the use of heat. The garments can then dried by depressurizing the system to a gaseous state. Resolve is considered a VOC. (ARB, 2004j)

3. Impress™ Solvent

Impress™ (Impress) dry cleaning solvent is a new propylene glycol-ether-based solution created by Lyondell Chemical Company. This solvent is readily biodegradable and compatible with hydrocarbon machines. According to manufacturer, the solvent is gentle on fabrics. Impress has a flash point of 190°F and is classified as a Class IIIA solvent. As with any hydrocarbon or glycol ether, Impress is considered a VOC. According to Lyondell Chemical Company, Impress dry cleaning solvent is of low acute toxicity by oral and dermal (skin) exposure. Currently, further toxicity and tests assessments are underway. (ARB, 2005f)

4. Hydroclene Fluids

Hydroclene is a mixture of normal-, iso-, and cyclo-paraffins. It is a complex solvent with the ability to dissolve a broad range of strains. It is a clear liquid with a boiling point 368°F and flash point of 145°F. Hydroclene is owned by Caled Chemical but the product is manufactured by Shell Chemical.

I. Flammability and Safety

Dry cleaners should be aware of the flammability and safety issue of all the technologies described above, especially for converted machines. Dry cleaners are recommended to consult with machine manufacturers to determine if a converted machine is able to operate safely with the solvent of choice. The flammability details and the summary of flash points and classification for various commonly used solvents are presented in Chapter VI, Table VI-1. Detailed information on products, technical data, as well as material safety data sheet (MSDS) are available by contacting the manufacturers. Appendix I lists the alternative solvents manufacturers contact information.

III. EMISSION CONTROL AND VENTILATION TECHNOLOGIES

This chapter briefly describes emission control and ventilation technologies. In dry cleaning operations, the majority of solvent is lost either through emissions to the atmosphere or via waste products. Furthermore, with perchloroethylene (Perc), a very small amount is also retained in clothes (relative to the total Perc emitted from dry cleaning operations). Some of the fugitive emissions can be controlled by using proper emission control and ventilation technologies to further reduce or capture emissions.

A. Emission Control Technologies

Over the past several years, the use of Perc recovery devices has become common in the dry cleaning industry because of economic considerations, environmental concerns, worker exposure concerns, and regulatory actions. Emission reduction from the dry cleaning industry can be attained through the use of proper operating practices and control equipment. These greatly increase the amount of solvent being recycled while at the same time minimize the solvent loss to the atmosphere. Housekeeping measures include promptly repairing any worn or cracked gaskets, covering all solvent and waste containers, identifying and repairing any leaking equipment, and removing any lint build-up from the steam or water coils. Available control devices such as carbon adsorbers, refrigerated or chilled water condensers, and distillation units have proven to be very effective for reducing emissions and recovering the solvent for reuse.

1. Primary Controls

Primary control systems operate during the heating and cool-down phases of the drying cycle. They are designed such that they neither exhaust to the atmosphere or workroom nor generate additional solvent-contaminated waste water (where applicable). Today, the most commonly used primary control device is the refrigerated condenser. In the past, carbon adsorbers and polymeric vapor adsorbers (a largely unproven technology) were also considered but could not compete with the overall efficiency of the refrigerated condenser.

Refrigerated condensers operate throughout the drying cycle, in which solvent-laden air is continually recirculated through the condenser. The condenser recovers both the solvent and water vapors from the air stream, sending a liquid solvent and water mixture to a water separator. The solvent recovered by the water separator then goes to the solvent storage tank. During the drying cycle, the air stream circulates past the refrigerated condenser, is reheated by the heating coils, circulates through the drum evaporating more solvent from the materials, and then flows through the condenser again where the solvent is recovered. (ARB, 1996)

In some hydrocarbon systems, the refrigeration unit is divided into separate segments for simplified maintenance and reduced downtime. The compressor,

refrigeration coil, and heat-exchange coil can be individually serviced without removing the entire system. Sealed coils plus quick disconnects prevent Freon® gas discharge. The refrigerated condenser keeps the temperature low during the drying cycle.

2. Secondary Controls

A significant source of solvent emissions from closed-loop machines is from opening the drum at the end of the drying cycle to remove materials. For example, the concentration of Perc in the drum at the end of the drying cycle can be as high as 8600 parts per million by volume (ppmv) (ARB, 1993). The operation of a secondary control device (typically a carbon adsorber - activated carbon bed contained in a housing), which operates in series with a refrigerated condenser, can further reduce solvent vapor concentrations in the drum and, therefore, reduce fugitive emissions and solvent consumption. Secondary control devices are activated at the end of the cool down step before the machine door is opened. These devices route solvent vapors from the drum and button and lint traps through a vapor adsorber, which strips solvent vapors from the air. In order to keep operating efficiently, the carbon must be periodically regenerated. The regeneration process typically uses heat to strip and recover the adsorbed solvent. This desorption process usually occurs after a specific number of loads or according to the manufacturer's recommended schedule. (ARB, 1996)

The Airborne Toxic Control Measure for Emissions of Perchloroethylene from Dry Cleaning Operations (Dry Cleaning ATCM) requires that closed-loop machines with secondary control systems reduce the concentration of Perc in the drum to less than 300 ppmv at the end of the drying cycle. Based on source test results submitted to the California Air Resources Board (ARB) for the approval of the secondary control systems, some systems can reduce the Perc concentration to below 100 ppmv. There are no similar statewide requirements for other solvents.

3. Other Control Technologies

Inductive door fans may be installed to further reduce fugitive emissions. This device, which draws air through the loading door and drum when the loading door is opened, is also beneficial in protecting the machine operator from residual solvent vapor during unloading. The inductive door fan may also be paired with a regenerative carbon canister.

B. Ventilation Technologies

Ventilation at dry cleaning facilities is implemented in several different ways. Ventilation is important as it affects the dispersion of solvent vapors and other airborne compounds in the facility which in turns impacts the potential health risk to nearby residences and businesses. In many cases, the type of ventilation system found at a facility is a function of its construction. The facility owner most likely had little or no input into the design and construction of the ventilation system. Newer facilities tend to

have more aggressive (or “active”) systems compared to the relatively passive implementations in older facilities.

1. Natural Ventilation

Many facilities do not have active ventilation systems. This means that solvent vapors, such as Perc, are emitted from doors, windows, roof vents, and other openings throughout the facility. Natural ventilation depends upon wind and convective forces to move air and is typically considered the least effective.

2. Window Fans

Window fans or wall fans are high flow rate propeller type fans that are installed vertically in a wall (window-type-opening). The air is exhausted horizontally, typically near ground level. These also provide an improvement to a facility with only natural ventilation.

3. General Ventilation

General ventilation systems typically have one or more large capacity fans on the roof of the facility. Capture efficiency depends on the air exchange rate inside the facility and is a function of the fan air flow rate and the size of the facility. General ventilation is considered an upgrade from natural ventilation.

4. Local Ventilation

Local ventilation is a phrase used to describe a ventilation system with a high capacity fan, exhaust stack, and physical apparatus/structure (fume hoods, shrouds, flexible walls, vertical plastic strips) near the dry cleaning machine. This system is designed to capture fugitive emissions. Emissions are then exhausted through a stack on the roof of the facility. Fume hoods typically have plastic curtains on the sides (or a combination of walls and curtains) to minimize cross-flow drafts and provide better capture of fugitive emissions.

5. Partial Vapor Rooms

A Partial Vapor Room (PVR) encloses the back of a dry cleaning machine in a small room with the front panel and loading door exposed for convenient loading and unloading. As a result, PVRs are able to more effectively capture fugitive emissions from leaks and maintenance activities when compared to local or general ventilation systems. Maintenance doors are normally closed and can be equipped with a self-closing device or alarm. Additionally, any windows are typically constructed of Plexiglas or tempered glass (for safety reasons). PVRs are typically used in co-located situations such as multi-story commercial buildings, mixed-use (residential/commercial) buildings, and shopping centers.

6. Vapor Barrier Rooms

Improving on partial vapor rooms, vapor barrier rooms (VBR) are the most efficient vapor capture systems. A VBR is able to restrict the diffusion and transport of solvent vapors that escape from a dry cleaning machine because a ventilation fan collects virtually all the vapors and exhausts them through a stack above the building. The door(s) to vapor barrier rooms are normally equipped with a self-closing device. Design features may vary, but normally include a “swinging” design that opens both ways or a sliding door. Additionally, any windows are typically constructed of Plexiglas or tempered glass (for safety reasons). VBRs are currently required for co-residential dry cleaning facilities in the San Francisco Bay Area and for all dry cleaners in mixed-use buildings in the State of New York.

IV. CURRENT DRY CLEANING STATUS

Current dry cleaning status was assessed based on several surveys, site visits of dry cleaning facilities, and emission testing. This chapter discusses the procedures used, and the results of the surveys, site visits, and emission testing.

A. Dry Cleaning Facility Survey Results

The Dry Cleaning Facility Survey (Facility Survey) was designed to collect information from the dry cleaning facilities. Many questions were asked on the Facility Survey to gather information concerning: operating information, facility information, potential future machine purchase/replacement, machine(s) type, solvent usage, waste produced, and maintenance information. Because of the large percentage of Korean dry cleaners, the Facility Survey and the cover letter were also translated into Korean. The Facility Survey and the cover letter are shown in Appendix A.

1. Facility Survey Response and Analysis

A mailing list of dry cleaning facilities was compiled based on listings from Dun and Bradstreet and the local air districts. The lists were combined and duplicate addresses were deleted. With the help of Antelope Valley Air Pollution Control District (APCD), Mojave Desert Air Quality Management District (AQMD), and Ventura County APCD, over 6300 Facility Surveys were sent in September 2003. The returned Facility Surveys were checked for address accuracy via yellow pages on the Internet. When needed, the facilities were called to verify address and/or if they were a dry cleaner. Where incorrect addresses were found, it was corrected and the Facility Surveys were mailed out again. Where the address did not exist, or there was currently not a dry cleaner at the address, that address was deleted from our database.

In all, around 5800 Facility Surveys were delivered and the response rate was 32 percent. There were 265 drop off or agency shop returns. The number of Facility Surveys returned from dry cleaning facilities with dry cleaning machine(s) on-site was 1634. Assuming the 14 percent proportion of drop off shops to dry cleaning plants is the same for those that did not return the Facility Survey, there are about 5040 dry cleaning plants and 816 drop off shops in the State.

During early 2004, the completed Facility Surveys were reviewed to see if they were from drop off shops or if they were from dry cleaners that operate machine(s) on-site (dry cleaning plants). The drop off shop returns were compiled and accounted for while the Facility Surveys from dry cleaning plants were reviewed for completeness. The facility operators or owners were contacted as necessary to obtain missing data, or to clarify the information submitted. Information obtained from the dry cleaning plants was then entered into a database. Each database entry was compared with the original Facility Surveys for accuracy. During survey analysis, the Facility Survey results were compared with site visit results. In most cases, the site visit results were reasonably similar to the Survey results.

2. Business Information

Dry cleaners in California are mostly small businesses employing less than five employees. After equating 40 part-time hours worked by part-time employees to one equivalent full time employee, it is estimated that over half of the dry cleaners employ two or less equivalent full time employees. Dry cleaners are usually independently owned and often are operated by the owner and/or the spouse. Approximately 40 percent of the dry cleaners gross less than 100,000 dollars annually, and, in general, income from dry cleaning constitutes 50 percent or more of their income. Other common sources of income include laundry and alteration. The industry is highly competitive; even though almost half of the facilities have been in operation for ten years or more, about a third have been in business for less than five years. Those who are in business for less than five years include both newly opened facilities and new owners of existing facilities. A summary of the discussed business information is shown in Table IV-1.

Table IV-1. Business Information

Years Owned Facility	**Percent[1]**
< 1	7
≥1 and < 5	25
≥ 5 and <10	19
≥10 and < 20	37
≥20	12
Business Status	**Percent[1]**
Independently Owned	98
Chain Operation	1
Franchise	2
Annual Receipts From Total Operation	**Percent[1]**
Less than $100,000	40
$100,000-$500,000	55
$500,000 – above	5
Percent Annual Receipts From Dry Cleaning Only	**Percent[1]**
Less than 25%	7
25-50%	18
50-75%	48
More than 75%	27
Number of Equivalent Employees[2]	**Percent[1]**
≤2	57
> 2 and ≤ 3	14
> 3 and ≤ 4	8
> 4 and ≤ 5	5
> 5	16

1. Values are rounded off to the nearest integer and may not add up to 100.
2. Equivalent Employees include both full-time and part-time workers.

During discussions at a workgroup meeting, it was noted that practically all dry cleaning facilities are open from Monday through Friday (ARB, 2003a). Our Facility Survey results showed the same information. Most of the facilities open at 7:00 AM in the morning and close between 6:00 PM and 7:00 PM in the evening from Monday through Friday. Our Facility Survey also showed that most (96 percent) of the facilities are open for business on Saturdays, but closed on Sundays. The business hours are summarized in Table IV-2 below.

Table IV-2. Summary of Business Hours

Business Hours	Percent[1]
Monday through Friday - Open	100
Saturdays – Open	96
Saturdays – Closed	4
Sundays – Open	4
Sundays – Closed	96

1. Values are rounded off to the nearest integer.

Most dry cleaning facilities are plants where the material that is dry cleaned include clothing, curtains, sleeping bags, blankets, comforters, and leather goods (ARB, 1993a). Other business types make up less than five percent of the total and include: industrial dry cleaners, nonprofit organizations, and hotels/motels. This is similar to the findings of the survey the California Air Resources Board (ARB) conducted in 1992 (1992 Survey). A comparison of the business types obtained from the 1992 Survey and the current, 2003 Dry Cleaning Facility Survey, is shown in Table IV-3.

Table IV-3. Comparison of Business Type

Business Type	2003 Dry Cleaning Facility Survey (Percent)[1]	1992 Survey (Percent)[1]
Plant/Retail	96	96
Industrial	<1	1
Government	<0.5	1
Nonprofit	<0.5	<0.5
Hotel/Motel	<0.5	1
Other	3	0

1. Values are rounded off to the nearest integer unless they are less than 1 and may not add up to 100.

3. Operating Information

The majority of the dry cleaning facilities operate a single dry cleaning machine. When considering the number of facilities that have more than one machine, the ratio is 1.091 machines per facility. Therefore, there are about 5500 dry cleaning machines in California. Most of these dry cleaning machines use Perchloroethylene (Perc) as the solvent.

Besides Perc, the second solvent of choice is DF-2000™ Fluid (DF-2000), a high flashpoint, synthetic hydrocarbon solvent manufactured by ExxonMobil. Other alternative solvent/processes include: PureDry®(PureDry), GreenEarth® (GreenEarth), Rynex® (Rynex), carbon dioxide (CO_2) cleaning, water-based cleaning systems, such as Professional Wet Cleaning (wet cleaning) and Green Jet® (Green Jet), Stoddard, as well as other high flashpoint hydrocarbon solvents, such as EcoSolv® (EcoSolv) and Shell Sol 140 HT (Shell 140). Wet cleaning and Stoddard usually employ a transfer process, while the facilities that use DF-2000 and other available alternatives normally operate with a closed-loop machine. Except for CO_2 machines and machines that operate with Tonsil®, most of these closed-loop machines operate with a refrigerated condenser, a water separator and vacuum still. A summary of the operating information is listed in Table IV-4.

Table IV-4. Summary of Operating Information

Number of Dry Cleaning Machines	**Percent of Facilities[1]**
1	92
2	8
More than 2	< 1
Solvent Type	**Percent of Machines[1,2]**
Perc	85
DF-2000	8
Rynex	0
Stoddard	< 0.5
GreenEarth	2
Water (Professional Wet Cleaning)	3
Water (Green Jet)	< 0.5
PureDry	< 0.5
EcoSolv	0
Liquid CO2	< 0.5
Other	< 1
Separator Water Treatment Method	**Percent of Entry[1]**
Wastewater treatment Unit	63
Evaporator	48
Atomizer	7
Liquid Discharge	2
Collected by waste hauler	26
Discharge to sewer	< 1
Used in cooling tower	2
Used to generate steam	5

1. Values are rounded off to the nearest integer unless they are less than 1 and may not add up to 100.
2. Values added to over 100 because of multiple entries per facility.

As shown on Table IV-4, about three percent of the facilities use wet cleaning. This value was based on verification of the input on the Facility Survey. After calling 20 of the facilities that checked that they had wet cleaning on-site, it was found that a large percentage thought the term wet cleaning meant laundry and the Facility Survey result was adjusted accordingly. Currently, there are 37 dedicated wet cleaning

facilities and 43 facilities that use wet cleaning together with another type of dry cleaning process (mixed shops) in the South Coast AQMD (ARB 2005c). Facilities that use wet cleaning outside of the South Coast AQMD are mostly mixed shops.

In addition, as shown on Table IV-4, the Facility Survey indicated that two percent of facilities use GreenEarth. This equates to about 100 facilities and is lower than the 146 facilities as of January 2005 that was submitted to ARB by GreenEarth. Because the Facility Survey was sent out in 2003, the difference in number may reflect an increase in the number of GreenEarth facilities since the Survey was taken, or it could be due to uncertainties associated with the Facility Survey. Also, none of the facilities that responded to the Facility Survey use the solvents Rynex and EcoSolv. Currently, we know that Rynex is being used by one facility in California; however, we are not aware of a dry cleaning facility in California using EcoSolv.

Also shown on Table IV-4 is the method of separator water treatment being used by the facilities. Besides water-based cleaning systems and CO_2 cleaning, dry cleaning machines usually operate with a water separator, which generates wastewater. Because separator water from a Perc dry cleaning machine contains Perc, it must be handled properly. The two most popular methods of separator water treatment are the use of a waste water treatment unit and the hiring of a waste hauler.

Currently, there are three types of wastewater treatment units: evaporator, atomizer, and liquid discharge. The categories specify the method of waste effluent elimination, i.e. evaporators would eliminate the waste effluent via evaporation, atomizers via atomization, and liquid discharge via discharge as a liquid. According to the Facility Survey, a majority of the dry cleaning facilities (63 percent) have a wastewater treatment unit on-site, with a majority of these facilities using an evaporator. A significant portion (26 percent) of facilities have their wastewater collected by a waste hauler. There is also a small percentage of dry cleaners (less than one percent) who discharge their wastewater into the sewer, which is not allowed if they are using a Perc machine. On closer look of these dry cleaners, they are either new facility operators or operate one of the alternative dry cleaning processes.

4. Machine Information and Operating Schedule

A summary of machine information is shown on Table IV-5. There are four types of dry cleaning machines in use: transfer machines, machines converted from vented to closed-loop (converted), closed-loop machines with primary control (primary), and closed-loop machines with both primary and secondary controls (secondary). Transfer machines in use today are for wet cleaning or for cleaning with hydrocarbon solvent, mainly Stoddard. Wet cleaning machines may either be transfer or closed-loop. The percentage of converted machines, about 2 percent, is small.

As shown on Table IV-5, about 60 percent of the machines in operation are primary machines and about a third of the machines are secondary machines. The median capacity of the machines is 40 pounds (lbs). The average age of the machines surveyed is 8 years, and most of them were bought new.

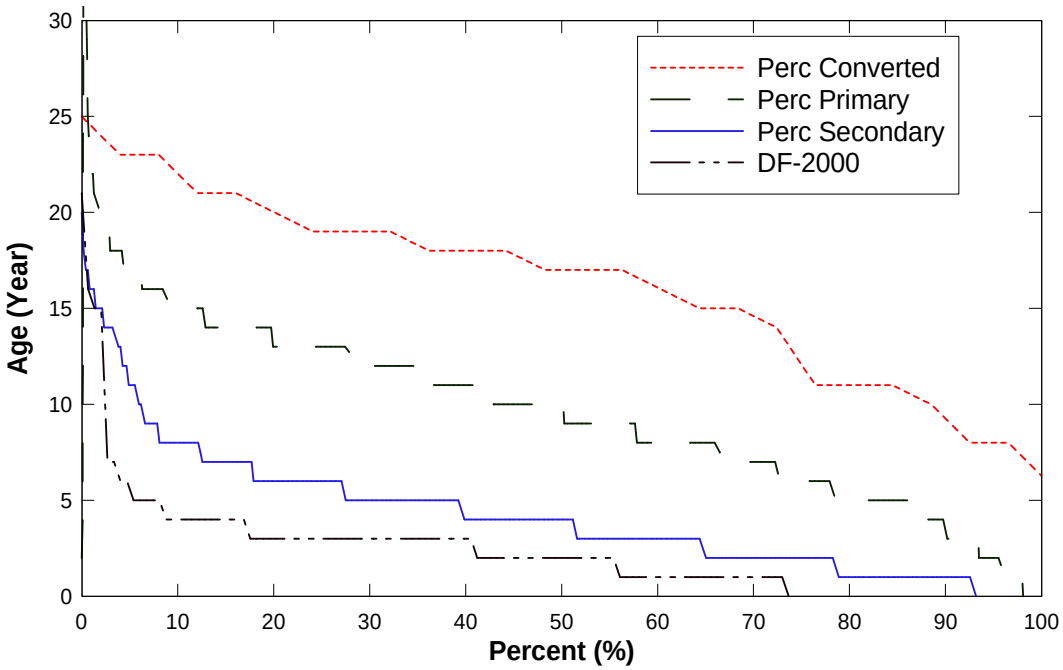
Table IV-5. Machine Information

Machine Information		
Average Age	(years)	8
Bought New	(percent)	89
Bought Used	(percent)	11
Median Rated Capacity	(lbs)	40
Machine Type		**Percent**[1]
Transfer		1
Primary Control		62
Secondary Control		28
Converted (vent to no-vent)		2
Wet Cleaning		2

1. Values are rounded off to the nearest integer unless they are less than 1 and may not add up to 100.

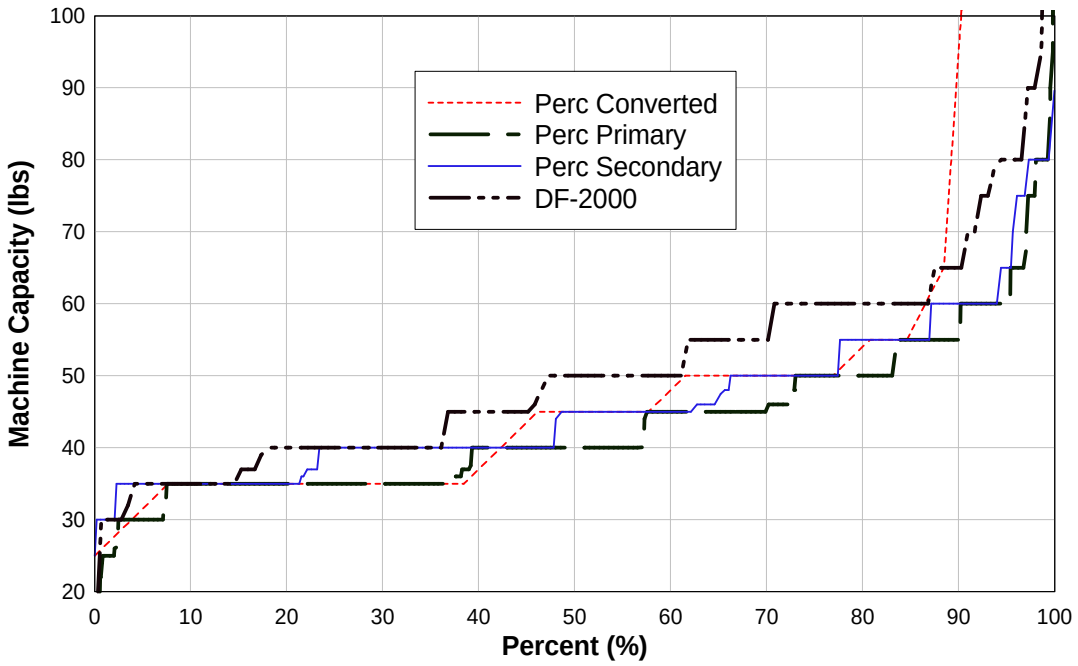
The machine age and capacity were grouped and compared by machine type as well as solvent types. When comparing machine age of the three types of Perc machines (converted, primary and secondary machines), there is a trend of lowering in age with the progression of machine types. The average age of Perc converted machines is 16 years, and it is six years older than that of Perc primary machines. The average age of Perc primary machines is 10 years and it is 6 years older than that of Perc secondary machines. In general, the machine age of the alternatives is lower than that of the Perc machines. The machine age comparison is shown in Figure IV-1 below. As shown in Figure IV-1, the age of DF-2000 machines, with an average of 2 years is 2 years newer than that of the Perc secondary machines.

Figure IV-1. Machine Age



The machine capacity is shown in Figure IV-2. The median machine capacity for each of the machine type plotted can be obtained from Figure IV-2 by looking at the capacity of that machine type that corresponds to 50 percent on the x-axis. The distribution of capacity for the converted machines roughly follows that of the Perc primary machines at below 40 percent and then of the Perc secondary machines up to about 85 percent. There is a slight increase in capacity when comparing Perc secondary machines to Perc primary machines; the median capacity for Perc secondary machines is 45 pounds while that for the Perc primary machines is 40 pounds. When comparing DF-2000 machines, they are generally slightly larger than the Perc secondary machines. The DF-2000 machines have a median capacity of 50 pounds.

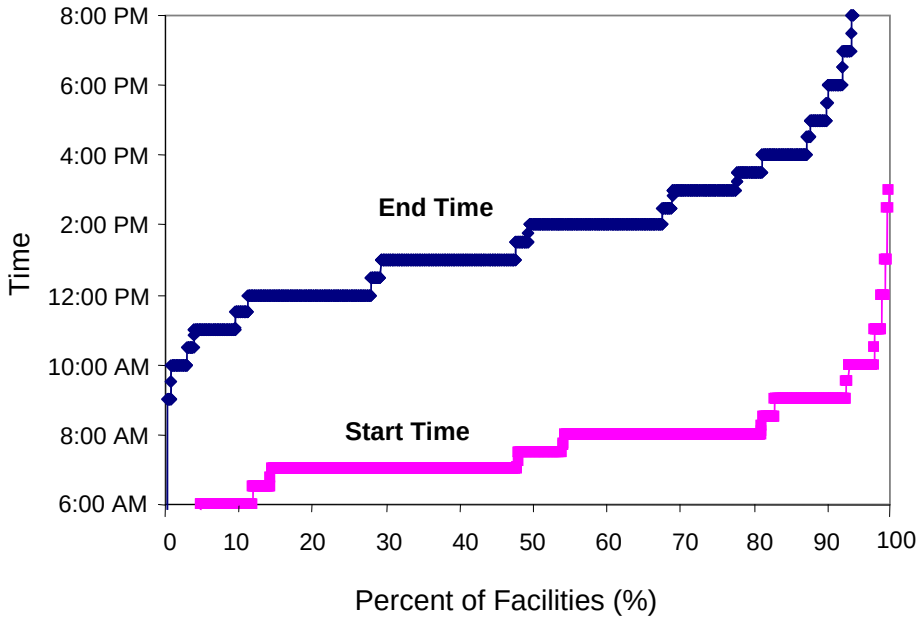
Figure IV-2. Machine Capacity



Based on time of machine operation, the operation duration is about six hours each day for five or six days of the week. The machine operation start and end times are shown on Figure IV-3. As shown on Figure IV-3, although machine start time varies, around 80 percent of the facilities start machine operation by 8:00 AM; therefore, about 20 percent of the facilities start machine operation after 8:00 AM. Correspondingly, around 80 percent of the facilities stop machine operation at or before 3:00 PM.

The machine operation hours discussed above reflect a majority of the dry cleaning business. Usually, processing of the garments immediately follows machine operation during the early part of the day because it involves steam presses which generate heat. One noted exception is wet cleaning. Because clothing from the wet cleaning process may not be processed right after it comes out of the machine, the machine operating time may be varied to allow for morning processing of the garments.

Figure IV-3. Time of Machine Operation



The number of days of machine operation in a week is shown on Table IV-6. As shown on the table, the majority of the facilities operate their machine(s) either five or six days per week. There is 55 percent (over half) of the facilities that operate their machines for five days during the week and 39 percent of the facilities that operate their machines for six days. The remaining facilities, about six percent, operate either seven days or less than five days.

Table IV-6. Days of Machine Operation

Number of days per week	Percent[1]
5 days	55
6 days	39
Others	6

1. Values are rounded off to the nearest integer unless they are less than 1.

5. Facility Size

One of the tools that are used to estimate potential health impacts at dry cleaning facilities is air dispersion modeling. Information needed for dispersion modeling includes physical dimensions of the facilities, as well as emission estimates and emission release parameters. Information on facility area and height were obtained from the Facility Survey.

The average area of the facilities is 1900 square feet (sq. ft.), and the average height is 14 feet (ft.). The median facility area is 1600 sq. ft., and the median facility height is 12 ft. Plots of the distributions of facility area and facility height are shown in Figures IV-4 and IV-5 below. As shown on Figure IV-4, about 10 percent of the dry

cleaning facilities have facility areas that are under 1100 square feet; therefore, about 90 percent of the dry cleaning facilities have facility areas that are over 1100 square feet. Also, as shown on Figure IV-5, about 50 percent of the dry cleaning facilities have heights that are lower than 12 feet; therefore, about 50 percent of the dry cleaning facilities have facility heights that are higher than 12 feet.

Figure IV-4. Distribution of Facility Area

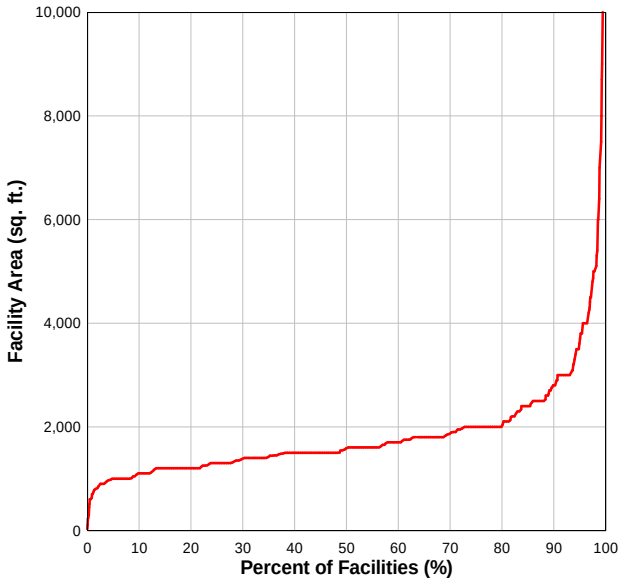
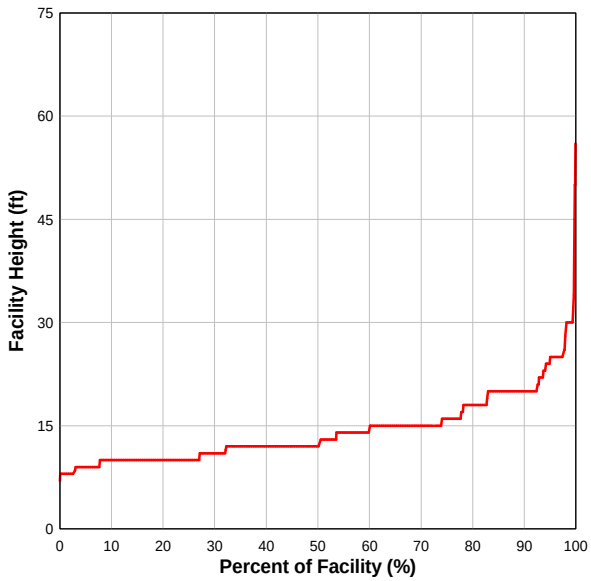


Figure IV-5. Distribution of Facility Height



6. Receptor Distance

Information on whether there are people living above or next to a dry cleaning facility (co-location information) and receptor distances to facilities were obtained from the Facility Survey. The type of receptors included businesses, residences, schools, day care facilities, hospitals, and senior communities. This information helps to characterize the location of the facilities and will be considered during risk assessment. A summary of receptor distances is shown on Table IV-7.

As shown on Table IV-7, about two percent of the facilities are co-located, with about one percent having people living next to and one percent having people living above the dry cleaning facilities. Also, over half of the facilities are within 20 feet of the nearest business indicating that many facilities are most likely located in strip malls. In contrast, about four percent of the facilities are within 20 feet of the nearest resident, and about 85 percent of the facilities are over 50 feet from the nearest resident. The number of facilities that are less than 100 feet away from schools, day care facilities, hospitals, and senior communities is two percent or less.

Table IV-7. Summary of Receptor Distances[1]

Information on Co-location	Percent of All Facilities
People live in building (above and next)	2
Above building	1
Next to building/facility	1
Distance of Nearest Business	**Cumulative Percent**
≤ 20 feet	56
≤ 50 feet	70
≤ 100 feet	77
≤ 500 feet	83
Distance of Nearest Residence	**Cumulative Percent**
≤ 20 feet	4
≤ 50 feet	15
≤ 100 feet	28
≤ 500 feet	63
Distance of Nearest School	**Cumulative Percent**
≤ 50 feet	<1
≤ 100 feet	3
≤ 500 feet	7
Distance of Nearest Day Care	**Cumulative Percent**
≤ 100 feet	2
≤ 500 feet	5
Distance of Nearest Hospital	**Cumulative Percent**
≤ 100 feet	<0.5
≤ 500 feet	3
Distance of Nearest Senior Community	**Cumulative Percent**
≤ 100 feet	<1
≤ 500 feet	3

1. Values are rounded off to the nearest integer unless they are less than 1.

7. Ventilation Type

Ventilation type is used to identify emission release parameters that are needed for air dispersion modeling. On the Facility Survey, we assessed facility ventilation type by asking whether the facility has open doors, open windows, window fans, powered ceiling fans, non-powered ceiling fans, a local ventilation system (fume/exhaust hood or shroud over machine), a partial vapor barrier room, or a vapor barrier room. Based on information from the local air districts and information gained through site visits, we categorized the ventilation information obtained into all six ventilation types. These six ventilation types are: natural ventilation, wall fan, general ventilation, local ventilation system (LOC), partial vapor barrier room (PBR), and vapor barrier room (VBR).

Natural ventilation is the category for facilities that do not have any type of ventilation beyond open doors, open windows, non-powered ceiling fans, and/or passive roof vents. Wall fan (or window fan) is the category for facilities that have, in addition to natural ventilation, a high capacity wall fan. General ventilation stands for facilities that have one or more high capacity powered ceiling fans but no additional ventilation enhancement over/around the machine. LOC is for the facilities that have a fume/exhaust hood or a shroud over the dry cleaning machine. PBR is for the facilities that have enclosed part of the machine to capture fugitive emission. And, VBR is for the facilities that have a room enclosure for their dry cleaning machine(s). A summary of the ventilation information results from the Facility Survey is listed on Table IV-8.

Table IV-8. Ventilation Information

Type of Ventilation	Percent[1]
Natural Ventilation	8
Wall Fan	8
General Ventilation	48
Local Ventilation System (LOC)	27
Partial Vapor Barrier Room (PBR)	4
Vapor Barrier Room (VBR)	5

1. Values are rounded off to the nearest integer unless they are less than 1 and may not add up to 100.

As shown on Table IV-8, about half of the facilities have general ventilation and general ventilation is the most common ventilation type in the industry. This information was compared with site-visit results. The Facility Survey result for local ventilation systems is about 27 percent; this is significantly higher than site visit results. In addition, the eight percent obtained for those that have natural ventilation is lower than site visit results. Further verification indicated that many owner/operators misunderstood the terminology used for types of ventilation in the Facility Survey. The ventilation information was modified based on the verification and is detailed discussion in Section B.

8. Maintenance Information

Maintenance practices were obtained from the Facility Survey. Facility operators were asked how often they inspect the machine(s), what type of leak detector is used during inspection, how many certified operator(s) are on-site, and how often they regenerate the carbon in the secondary control machines. Because the Airborne Toxic Control Measure for Emissions of Perchloroethylene from Dry Cleaning Operations (the Dry Cleaning ATCM) contains statewide requirements for inspection and certified operator(s) for facilities that use Perc, the results indicate how well the industry is complying with the Dry Cleaning ATCM.

The Facility Survey showed that the majority of the Perc facility operators inspect their machine on a weekly or daily basis. About five percent of the facilities responded inspecting their machine less frequently (note: the Dry Cleaning ATCM requires leak checks on at least a weekly basis). Based on the Facility Survey, leak checks are performed using a halogen leak detector (TIF detector) by a majority of the facilities.

The TIF detectors that are used in the industry can start detecting Perc at around 8 parts per million (ARB, 2004f). See Section G for more detailed discussion on Perc detectors.

About 16 percent of the facilities have more than one certified operator with about 84 percent having only one certified operator. Although the alternative dry cleaning facilities are not required by the Dry Cleaning ATCM to have a certified operator on site, all responded that they have at least one certified operator on-site. The reason may be that many of the alternative dry cleaning facilities formerly used Perc.

The Facility Survey also showed that about 65 percent of the facilities that have a secondary control machine would regenerate carbon according to machine manufacturer's specification, while about 30 percent responded that the carbon is regenerated automatically. There is about three percent that reported not regenerating the carbon at all. If the carbon in the secondary control system is not properly regenerated, it might become over saturated and would not be efficient in adsorbing Perc. The summary of the maintenance information is tabulated on Table IV-9 below.

Table IV-9. Summary of Maintenance Information

	All Users	Perc Users Only
Frequency of inspecting machine	**Percent[1]**	**Percent[1]**
Daily	44	42
Weekly	50	53
Monthly	3	3
Bi-monthly	<1	<1
Quarterly	<1	<1
Twice a year	<0.5	<0.5
Yearly	<0.5	<0.5
Never	<0.1	0[2]
Number of certified operators on-site	**Percent[1]**	**Percent[1]**
One	84	84
Two	14	14
More than 2	2	2
Frequency of regenerating carbon	**Percent[1]**	Percent[1]
According to machine manufacturer's specification	N/A	65
Machine regenerates carbon automatically	N/A	30
Never	N/A	3
Other	N/A	2

1. Values are rounded off to the nearest integer unless they are less than 1 and may not add up to 100.
2. None reported.

9. Future Machine Purchase

The facility operators were asked whether they would buy a new or used machine if they had to replace their current machine or purchase a new machine. They

were further asked what type of solvent that machine would use. As shown in Table IV-10, most facility owners would opt to purchase a new machine instead of a used one. Staff also observed this trend during site visits, where only a few mentioned that they might purchase a used machine due to price difference. Many commented that they do not intend to replace their machine in the near future. And even though less than 50 percent said they would use Perc in their new machine, it is still the solvent of choice compared to the alternatives. The second solvent of choice is DF-2000.

Table IV-10. Summary of Future Machine Purchase

Type of Machine	**Percent[1]**
New	96
Used	4
Type of Solvent	**Percent[1,2]**
Perc	44
DF-2000	24
Rynex	2
Stoddard	3
GreenEarth	15
Liquid CO_2	10
EcoSolv	1
PureDry	4
Water (wet cleaning)	13
Other	8

1. Values are rounded off to the nearest integer.
2. Values added to over 100 because of multiple entries per facility.

Other information obtained from the Facility Survey is discussed in Section H. This information includes the amount of Perc purchased, the amount of clothes dry cleaned, and the amount and type of waste generated.

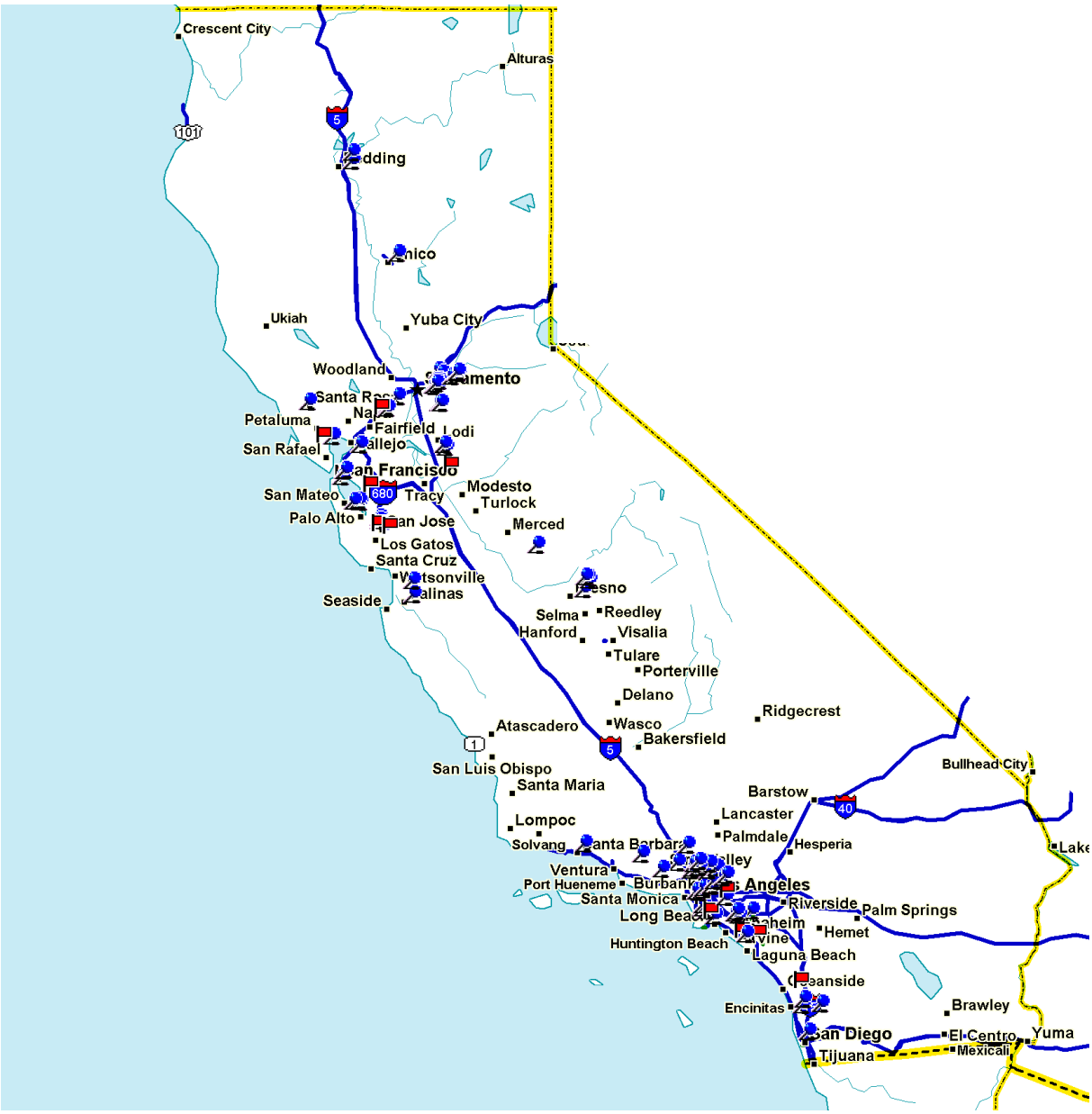
B. Site Visit Results

At the beginning of the evaluation process, staff visited facilities around Sacramento to get feedback on the Facility Survey. After the Facility Survey was mailed in September 2003, staff visited over 100 facilities around the State to get more detailed data. The facilities were located in 66 cities and covered nine air districts. The local air districts visited include: Bay Area AQMD, Butte County AQMD, San Diego County APCD, Sacramento Metro AQMD, San Joaquin Valley Unified APCD, Shasta County AQMD, South Coast AQMD, Ventura County APCD, and Yolo/Solano AQMD. In addition, staff requested facility data from Monterey Bay Unified APCD and Santa Barbara County APCD. In all, 11 local air districts, encompassing about 97 percent of the facilities statewide, are represented in the site visit analysis.

Most of the facilities were selected randomly. Some facilities were selected because they gave us the opportunity to learn more about ventilation practices and alternative technologies. During the site visits, staff measured receptor distances, gathered information regarding ventilation types, and gathered general information from

the machine operator, owner, and/or worker. A copy of the Site Visit Survey is shown in Appendix B. A map of the facilities visited is shown in Figure IV-6.

Figure IV-6. Map of Site-Visit Facility Locations



The site visit facility information was compared with the Facility Survey results. The comparison of the amount of co-located facilities and the facility area and height is shown in Table IV-11.

Table IV-11. Comparison of Amount of Co-location and Facility Size

	Facility Survey Results	Site Visit Information
Information on Co-location		
People live in bldg (above and next), (percent)[1]	2	4
Facility size		
Average area (sq ft)[2]	1900	1900
Average height (ft)[1]	14	13

1. Values are rounded off to the nearest integer.
2. Values are rounded off to the nearest hundred.

As shown on Table IV-11, the Facility Survey results compare well with the site visit information. The reason for the higher value of site visit co-location facilities may be due to the effort made to visit facilities with vapor barrier rooms and that the Bay Area AQMD requires vapor barrier rooms for certain co-located facilities. A comparison of distance to receptors is shown on Table IV-12.

Table IV-12. Comparison of Distance to Receptors[1]

	Facility Survey Results	Site Visit Information
Distance to Nearest Business	**Cumulative Percent**	**Cumulative Percent**
20 ft or less	56	55
50 ft or less	70	93
100 ft or less	77	98
500 ft or less	83	98
Distance to Nearest Residence	**Cumulative Percent**	**Cumulative Percent**
20 ft or less	4	9
50 ft or less	15	16
100 ft or less	28	36
500 ft or less	63	79
Distance to Other Receptors[2]	**Cumulative Percent**	**Cumulative Percent**
50 ft or less	3	1
200 ft or less	10	10
500 ft or less	19	21

1. Values are rounded off to the nearest integer.
2. Other receptors include: schools, day care, park, senior community, and hospital.

As shown on Table IV-12, there is reasonably good agreement between the Facility Survey and the site visit results on receptor distances. Table IV-13 shows a

comparison of Facility Survey and site visit results on facility ventilation type.

Table IV-13. Comparison of Facility Ventilation[1]

	Facility Survey Results	Site Visit Information	Bay Area AQMD
Type of Facility Ventilation	**Percent**	**Percent**	**Percent**
Natural ventilation	8	22	16
Wall Fan	8	9	8
General ventilation	48	60	55
Local Ventilation System (LOC)	27	1	6
Partial Vapor Barrier Room (PVR)	4	1	8
Vapor Barrier Room (VBR)	5	8	8

1. Values are rounded off to the nearest integer unless they are less than 1 and may not add up to 100.

As shown on Table IV-13, there are significant differences between the Facility Survey and site visit results on some of the facility ventilation data, with the LOC values having the greatest contrast. Because of the difference between these results, staff compared them to those of the Bay Area AQMD (also shown on Table IV-13). The Bay Area AQMD is the only local air district that requires enhanced ventilation when the potential cancer risk exceeds a certain level, historically 100 in a million. About 200 dry cleaning facilities in that district had installed some form of ventilation to achieve the 100 in a million risk level. In addition, Bay Area AQMD required all facilities co-located with residences to install a vapor barrier room, and recent amendment to the Bay Area AQMD's Toxics New Source Review policy require all new facilities to have a total risk of less than 10 in a million. Existing facilities that replace their Perc machine(s) will be treated as new sources.

As shown on Table IV-13, the Bay Area AQMD values agree better with the site visit results. To better understand this difference, staff conducted site visits to four Sacramento facilities that reported having LOC on the Facility Survey. During the site visits, all four owner/operators explained that they did not understand fully what was meant by LOC and checked it by mistake. Therefore, staff concluded that many of the dry cleaning owner/operators must have a different interpretation of the terms used. Unfortunately, this potential for misinterpretation did not arise during our field testing of the Facility Survey. Because the LOC impacts the percentages on the other categories of facility ventilation, our assessment of facility ventilation type is based on site visit and Bay Area AQMD information.

C. Machine Manufacturers Survey Results

A Machine Manufacturers Survey was developed to assess list price of the dry cleaning machines. Other information requested included: recommended maintenance schedule, maintenance cost, and machine brochures. The Machine Manufacturers Survey (shown in Appendix C) provided staff with current information on machine and maintenance costs, recommended maintenance schedule/practices, and latest technologies available on the machines.

When compared to the cost of a secondary Perc machine, the cost of the commercially available water-based cleaning system is either similar or less. In contrast, all other closed-loop machines used for the alternative solvents are generally higher in cost. The most costly machine type is the one used for liquid CO_2. Detailed cost information/discussion is presented in Chapter VII.

General maintenance practices for the closed-loop machines using Perc and other alternative solvents (except water) include: cleaning of button and lint traps, cleaning of the still, draining and cleaning of the separator, and cleaning and/or changing of filters. Other maintenance practices may include proper lubrication of machine parts, checking the pressure level, and changing the carbon for certain carbon filters and for secondary control machines. Therefore, the time and effort spent on maintenance procedures are similar. For special cases where a still is not needed for some alternative solvents, there might be some decrease in maintenance time. Also, although the maintenance practices are similar, the frequency recommended for maintenance varies with the manufacturer.

Several features of the current technology on Perc machines minimize fugitive Perc emissions. These include the use of spin disk filters, automatic cleaning of the still, and secondary control devices. Spin disk filters, when compared to cartridge filters, do not need to be replaced regularly and therefore significantly reduce fugitive emissions associated with filter replacement. Spin disk filters also allow for the recovery of the Perc that is normally embedded in the used cartridge filters. Automatic cleaning of the still eliminates the need to open it, which can expose the operator to Perc fumes and increase fugitive emissions. Secondary control devices reduce the Perc content within the machine drum to below 300 parts per million (ppm) before the clothes are removed and therefore reduce fugitive emissions.

D. Dry Cleaning Solvent Manufacturers Survey

To ensure that our health and environmental impact assessment are based on the correct chemical(s), a Dry Cleaning Solvent Manufacturers Survey was sent to some of the alternative dry cleaning solvent manufacturers. This survey was primarily a request for solvent formulation and therefore we did not send out surveys to those solvent manufacturers where we already had information on solvent formulation. After the survey, staff obtained adequate formulation information associated with petroleum solvent cleaning (DF-2000™, PureDry®, EcoSolv®, Shell Sol 140 HT, Stoddard), volatile methyl siloxane cleaning (GreenEarth®), glycol ether cleaning (Rynex®), CO_2 cleaning, and water-based cleaning systems. Several manufacturers also provided health and environmental impact data. Information gathered is used in our health/environmental impact evaluation.

E. Perc Solvent Distributors Survey Results

A Perc Solvent Distributors Survey (Distributors Survey) was developed to assess the amount of Perc that is sold to the California dry cleaning industry. Information for years 2001, 2002, and 2003 were gathered from the distributors. A summary of the total amount of Perc bought and sold by the distributors for those

three years are shown in Table IV-14. Based on Table IV-14, the majority of the Perc that was purchased was sold to the dry cleaning industry. In general, there is a continuing decrease in usage. This is most likely due to regulations that are in place and improved processes.

For comparison purposes, the amount of Perc purchased by the dry cleaning industry was calculated based on the Facility Survey. Since the estimated total number of machines around the state is about 5500 (based on 5040 facilities and 1.091 machines per facility), and the percent of Perc machines about 85, the usage can be estimated from facility survey. The result is compared with the Distributors Survey in Table IV-14. As shown on Table IV-14, the Distributors Survey results compare well with the facility survey results and there is a gradual decrease in the amount of Perc sold to the dry cleaning industry.

Table IV-14. Summary of Perc Usage[1]

	Sold to Dry Cleaning Industry In 2000 (Gallons)	Sold to Dry Cleaning Industry In 2001 (Gallons)	Sold to Dry Cleaning Industry In 2002 (Gallons)	Sold to Dry Cleaning Industry In 2003 (Gallons)
Distributors Survey	N/A[2]	378,000	346,000	320,000
Facility Survey	393,000	381,000	365,000	N/A[3]

1. Values are rounded off to the nearest thousand.
2. Value was not obtained from the Distributor Survey.
3. Value was not obtained from the Facility Survey.

The values obtained from the Distributors Survey are low when compared to an estimate by the Halogenated Solvents Industry Alliance, Inc. (HSIA). They estimated, based on population, that the volume sold to California dry cleaners is about 12 to 13 percent of the national volume, which in 2002 would have been 5.5 to 6 million pounds or 410,000 to 440,000 gallons (ARB, 2004k). This suggests that the California dry cleaning industry uses less Perc than the national average. In addition, current information from the Perc producers of 323,000 gallons and 236,000 gallons sold to the California dry cleaning industry in 2003 and 2004, respectively, confirmed the 320,000 gallons obtained from the Distributors Survey for 2003. (ARB, 2005e).

F. Perc and DF-2000 Sludge Test Results

To support emission analysis of the dry cleaning processes, liquid sludge from Perc machines and DF-2000 machines was tested for solvent content. The standard operating procedures for determining Perc and DF-2000 in sludge are shown in Appendix D and E, respectively. Eight Perc sludge samples and two DF-2000 sludge samples were obtained and tested. The test results compared well with the 50 percent Perc reported to the ARB by three waste haulers in 1992. The average results are similar to data provided by the South Coast AQMD. Detailed test results are shown in Appendix F. A summary of the test data compared with South Coast AQMD data is shown in Table IV-15.

Table IV-15. Summary of Perc and DF-2000 Sludge Tests

Machine Type	Number of tests	Wt% Solvent in Sludge[1]	Weighted Average Wt% Solvent in Sludge[1]	Sludge Density (lb/gal)	Weighted Average Sludge Density (lb/gal)
Perc Primary (ARB 2004-2005)	6	35%	45%	9.69	10.12
Perc Primary (South Coast)[2]	4	59%		10.77	
Perc Secondary (ARB 2004-2005)	2	44%	46%	9.88	9.92
Perc Secondary (South Coast)[3]	20	46%		9.92	
DF-2000 (ARB 2005)	2	20%	42%	7.55	7.68
DF-2000 (South Coast)[2]	10	46%		7.71	

1. Values are rounded off to the nearest integer.
2. South Coast, 2002.
3. Based on preliminary data from South Coast (3 quarters of data).

The test data shown on Table IV-15 include weight percent of solvent in sludge and sludge density. Also shown on Table IV-15 are calculated weighted average values of weight percent of solvent in sludge and sludge density. These weighted average values are used in emission calculations shown in Section H. Comparing the ARB and South Coast AQMD values for the weight percent of solvent in sludge shows the values obtained for the Perc secondary test series to differ by only two percent; however, for the Perc primary and the DF-2000 test series, the difference was 24 percent and 26 percent respectively. For the Perc Primary test series, with sample sizes of six and four and the range of the two series overlapping, the difference between the averages do not indicate systemic differences. The same is true with the DF-2000 test series. In all three cases, the weighted average of the ARB and South Coast AQMD test series combines the two sets of data to provide more representative data.

G. Leak Detector Evaluation

Based on observations during site visits and conversations with ARB training staff and local air districts, Perc facility operators do not use their halogenated hydrocarbon detector (HHD) as often as they are required. The reason is that most of the HHDs do not give quantitative results. A majority of the Perc facilities use HHDs made by TIF™ Instruments, Inc. (TIF detectors) and TIF detectors would beep when Perc or other volatile organic compounds (VOCs) were detected. The threshold level for beeping to begin is around eight ppm (ARB, 2004f). Because the Dry Cleaning ATCM requirement for the facility to fix the leak is at 50 ppm, the TIF detectors can not be easily used to accurately determine whether a facility is in violation.

Staff looked at what is available in the industry for Perc detection and conducted a limited evaluation. Nine portable detectors, in addition to a TIF detector and a photoionization detector (PID) that was available and served as reference, were evaluated. The range of technology tested included: PID, gas sensitive semiconductor, colorimetric tube, infrared, and heated diode sensor technology. Cost information for

the detectors is shown in Chapter VII. The evaluation included two phases. During the first phase, the detectors were evaluated under laboratory conditions to determine detection accuracy and response time to Perc standards. During the second phase, a TIF detector, the reference PID, and those detectors that had less than 30 second response time were selected and tested in dry cleaning facilities. The objective of this phase was to compare detector response time to Perc levels around the machines, to actual leaks, and were used to measure background Perc concentrations within the facilities.

A memorandum from ARB's Monitoring and Laboratory Division detailing the laboratory evaluation effort is shown in Appendix H. Based on laboratory evaluation results, staff tested eight detectors in dry cleaning facilities. One of the eight detectors was a modified Aeroqual detector that included a built-in fan in the sensor head. In addition to the eight detectors, staff also tested the TIF detector and compared readings with a PID (manufactured by PE Photoac International Inc.) used by staff of Sacramento AQMD. A summary of the results is shown in Table IV-16 below.

Table IV-16. Summary of Leak Detector Evaluation

Model and (Manufacturer)	Detection Principle	Sample Delivery	Display	Response Time[1] (sec)	Leak Check Suitability[2]
Gas Alert Micro 5 (BW Technologies)	Photoionization	Diffusion	LCD with audio and visual alarms	5 – 10	No
PhoCheck 1000 (Ion Solutions)	Photoionization	Internal pump	LCD	<5	Yes
MiniRAE 2000 (Rae Systems)	Photoionization	Internal pump	LCD with visual alarms	<5	Yes
Aeroqual 200 (Aeroqual)	Gas Sensitive Semiconductor	Diffusion	LCD	20 – 30	No
Aeroqual 500 (Aeroqual)	Gas Sensitive Semiconductor	Diffusion	LCD with audio alarm	20 – 30	No
Aeroqual 500 with build-in fan[3] (Aeroqual)	Gas Sensitive Semiconductor	Internal fan	LCD with audio alarm	5 – 10	No
C-21 (Eco Sensors,Inc.)	Gas Sensitive Semiconductor	Diffusion	LED bar with audible alarm	No Response[4]	No
D-Tek (Inficon)	Infrared	Internal pump	Audible with LED bar	No Response	No
Tek-Mate (Inficon)	Heated Diode Sensor Technology	Internal pump	Audible with low and high sensitivity options	<5	Yes
TIF-5100 (TIF Instruments)	Heated Diode Sensor Technology	Diffusion	Audible	<5	Yes
Draeger CMS (Draeger)	Colorimetric	Internal pump	LCD	110	No
HW 101 reference analyzer (h-nu Systems)	Photoionization	Internal pump	Analog Potentiometer	<5	No

1. Response time is the approximate time needed for the detector to display a stable concentration.
2. Leak check suitability based on response time of less than 5 seconds in the field.
3. Laboratory testing done after the memorandum in Appendix H was written.
4. No response to calibrated standards, may require humidified gas sample.

As shown in Table IV-16, in all cases, the PID detectors with an internal pump performed well and provided quantitative results. With the exception of TIF-5100, the detectors that used diffusion for sample delivery had response times of 5 seconds or more in the field and were deemed not suitable for leak detection. The Tek-Mate and the TIF-5100 were sensitive to Perc and will indicate leaks at levels below 50 ppm. The facility background concentrations were mostly non-detectable with the limit of detection of the PID detectors at around 1 or 2 ppm; the largest background concentration reading was between 5 to 10 ppm.

H. Emissions from Dry Cleaning Operations

Emissions from dry cleaning operations are calculated based on a material balance approach. The amount of solvent that is consumed by a dry cleaning operation is either emitted into the air or is embedded in the waste or in clothes that are removed from the facility. Equation 1 shows the material balance relationship.

(1) $$\mathbf{Solv_e = Solv_c - Solv_w - Solv_{clothes}}$$

where:

$Solv_e$ = volume in gallons of solvent emitted to the atmosphere from a dry cleaning facility,

$Solv_c$ = volume in gallons of solvent consumed in a dry cleaning facility,

$Solv_w$ = volume in gallons of solvent that exit a dry cleaning facility in the waste products, such as still bottom, separator water, and used cartridge filters, and

$Solv_{clothes}$ = volume in gallons of solvent that exit a dry cleaning facility in clothes.

Information from our workgroup and from our site visits showed that a three-year average of solvent purchased is a good indication of the amount of solvent used by a machine each year. The exception will be newly purchased machines because they initially use more solvent during the first year of operation due to the initial fill (ARB, 2004d). Therefore, the average volume of solvent used by a dry cleaning machine in California can be estimated from purchase amounts after excluding the newly purchased machines. For example, the three year average Perc purchased for a Perc primary machine is about 80 gallons per year, which happened to be the same as the amount consumed per year is estimated by calculating the three year average without newly purchased machines.

The three-year average method works well with Perc facilities; however, it did not work well with DF-2000 facilities because approximately 60 percent of the machines are two years or newer. If the newly purchased DF-2000 machines for the three years for which we had solvent usage data were not used, we would be left with a small subset of data. Since the difference in solvent usage from newly purchased machines occur during the first year of machine operation, it is assumed that excluding machines that were purchased in 2002 and using average 2002 solvent purchases would be a good approximation of average solvent consumption for DF-2000 machines. The average

DF-2000 consumption calculated is 89 gallons per year. This assumption was compared with Perc secondary machine data and the calculated amount of Perc purchased during 2002 without machines purchased in 2002 was 68 gallons, the same as the value calculated using a three year average excluding newly purchased machines.

Table IV-17 shows the amount of solvent consumed, three-year average of clothes dry cleaned, solvent consumed, still bottoms generated, and the number of filters used for facilities that used Perc primary machines, Perc secondary machines and DF-2000 machines. As shown on Table IV-17, there are three types of cartridge filters that are used in the machines. These are standard, split, and jumbo cartridge filters. A majority of the machines that use cartridge filters only use standard cartridges. Some of the machines have a combination of the three types of cartridge filters and they are designated as such on the table. In addition to cartridge filters, a portion of the machines have spin-disk filters. There are two types of spin-disk filters, powdered and non-powdered. As shown on Table IV-17, less than half of a percent of the Perc machines have both a powdered and a non-powered spin-disk. The machines that have cartridge filters may also have spin-disk filters; therefore, the sum of all the values on Table IV-17 under proportion of filters used is greater than 100.

Table IV-17. Facility Survey Summary for Emission Analysis

Emission Analysis Information	**Perc Facilities** Primary Machines	**Perc Facilities** Secondary Machines	**DF-2000 Facilities**
Amount of clothes cleaned	**Pounds[1]**	**Pounds[1]**	**Pounds[1]**
Average	44,000	52,000	53,000
Yearly solvent usage and waste produced	**Gallons[2,3]**	**Gallons[2,3]**	**Gallons[2,4]**
Solvent consumed	80	68	89
Average Still Bottom Removed	75	88	90
Average Separator Water Produced	141	191	210
Amount of Filters Used Per Year	**Count[2,3]**	**Count[2,3]**	**Count[2,4]**
Average number of Standard cartridge used	15	10	7
Average number of Split cartridges used	13	7	11
Average number of Jumbo cartridges used	7	5	9
Proportion of Filters Used	**Percent[3,5]**	**Percent[3,5]**	**Percent[4,5]**
Machine using Standard cartridge only	58	46	39
Machine using Split cartridge only	7	11	4
Machine using Jumbo cartridge only	5	10	6
Machine using a combination of Standard, Split, and Jumbo cartridges	4	8	9
Machine using non-powdered spin-disk	31	55	42
Machine using powdered spin-disk	13	11	27
Combo (non-powdered and powdered)	<0.5	<0.5	None

1. Values are rounded off to the nearest thousand.
2. Values are rounded off to the nearest integer, unless it is less than one.
3. Values are averaged from three years of data, excluding newly purchased Perc machines.
4. Value is obtained from 2002 data excluding data for machines purchased in 2002.
5. Values are rounded off to the nearest integer unless they are less than one and may not add up to 100 because of combined usage of spin-disk and cartridge filters.

The volume of Perc that is in the still bottoms is calculated from the average amount of still bottoms produced (from Facility Survey data) and the weight percent of Perc in still bottoms. The weight percent of Perc that is in the still bottom was measured previously by ARB as well as by South Coast staff. The results compared well with a test series conduced by ARB staff in 2004-2005 (see Section F) and average values from the two test series are used for the calculation. For example, the annual average amount of still bottoms produced by a primary Perc machine is about 75 gallons. With an estimated average solvent weight percent for primary machines of 45 percent and an average density of 10.12 pounds (lbs) per gallon, the annual average amount of Perc in the sludge of a primary machine is about 25 gallons.

The amount of Perc in separator water may be calculated from the volume of separator water produced by a facility and the Perc content in separator water. For example, the average volume of separator water produced by a primary machine is about 141 gallons (from Facility Survey, Table VI-17). The Perc content in separator water was measured during an ARB test program in 1997 and by an affiliate of ATC Associates Inc. (AVES). The average Perc content in separator water is about 150 ppm or 3.9 grams per gallon (gm/gallon) (AVES, 2000). Therefore, on average, about 1.2 lbs of Perc or less than 0.1 gallons of Perc is present in the separator water coming out of a primary machine in one year.

The amount of Perc in clothes is estimated based on available test data. AVES conducted a study in 1997 which showed the average amount of Perc in clothes was about 99 milligram per kilogram of clothes (AVES, 2000). For example, the amount of Perc in 52,000 lbs of clothes is about 0.3 gallons of Perc. This is higher than the 0.006 weight percent relative to the total Perc emitted from dry cleaning found in the Source Reduction Research Partnership in 1990 (ARB, 1993a).

The amount of Perc in standard and split filters is estimated to be 0.5 gallons and the amount of Perc in a jumbo cartridge filter is estimated to be one gallon (ARB, 2004d). For example, for a facility that uses 13 standard filters a year, the amount of Perc that is disposed of in the filters is about seven gallons.

A detailed look into machine types and amount of emissions shows that secondary machines are more efficient in Perc use compared to primary machines and converted machines. Because the number of converted machines is low (two percent of the total), it was not further divided into categories based on filter types. Within the categories of primary machines and secondary machines, the type(s) of filters used were identified and checked for difference in performance. There are three categories based on filter types: spin disk only, cartridge only, and combo. The category of spin disk only represent machines that operate with spin disk filtration and do not have any cartridge filters. The category of cartridge only represent machines that operate with cartridge filters only and do not have any spin disk filters. The combo category represents machines that have a combination of spin disk and cartridge filters. The percentage of each category is obtained from Facility Survey data and is shown on Table IV-18.

The amount of sludge, separator water, and number of filters used for converted machines and for each of the categories of primary and secondary machines was obtained from the Facility Survey. The emissions are then calculated based on Equation 1 and are then normalized to the same amount of material dry-cleaned (46,600 pounds per year). A comparison of the normalized emissions for each of the categories is shown on Table IV-18.

Table IV-18. Emissions Comparison[1]

Machine Type	Percent of Machine in Category	Solvent Usage (gal/yr)	Sludge Amt (gal/yr)	Amt Solvent in Sludge (Wt %)	No. of Filter	Solvent Emitted (gal/yr)	Solvent Emitted (Wt %)	Solvent Ems (lb/yr)
Converted	100	106	46	45	22	79	75	1073
Primary (Spin Disk Only)	28	73	86	45	0	44	60	589
Primary (Cartridge Only)	55	97	65	45	18	66	68	889
Primary (Combo)	17	79	78	45	14	45	57	613
Primary (Average)	100	86	74	45	10	56	65	759
Secondary (Spin Disk Only)	32	65	90	46	0	28	48	383
Secondary (Cartridge Only)	29	60	67	46	10	35	55	469
Secondary (Combo)	39	59	85	46	6	17	34	227
Secondary (Average)	100	61	81	46	5	30	50	410
DF-2000	100	78	79	42	4	36	46	230

1. Values are normalized to 46,600 pounds of material cleaned per year and rounded off to the nearest integer.

As shown on Table IV-18, the results show that Perc emissions calculated for the converted machines are the highest, with primary machines having lower emissions, and the secondary machines emitting the least amount of Perc for the same amount of clothes cleaned. When comparing primary machines, there is a distinct difference in emissions between machines that use spin disk filters and a combination of spin disk and cartridge filters versus those that use cartridge filters only. Primary machines that operate with only cartridge filters emit about 41 percent more Perc when compared with those that have a spin disk filter. The difference in emissions between filter types for secondary machines is relatively small. Comparing average Perc secondary machine to DF-2000 machines, the weight percent of solvent emitted is very close, with 50 percent and 49 percent, respectively. However, the actual amount in pounds per year emitted is higher for the Perc secondary machines when compared to DF-2000 machines (410 pounds per year versus 230 pounds per year) because Perc is higher in density.

V. POTENTIAL HEALTH IMPACTS

A. Perchloroethylene

Perchloroethylene (Perc) is the most common solvent currently being used in the dry cleaning industry. Exposure to Perc may result in both cancer and non-cancer effects. There are many human and animal studies which have been used to identify potential health impacts for exposure to Perc. Many of the human studies have been conducted on dry cleaning workers. The Office of Environmental Health Hazard Assessment (OEHHA) staff has performed an extensive assessment of the adverse health effects of Perc, including available carcinogenicity data. Summary information on human and animal studies can be found in OEHHA's Air Toxics Hot Spots Program Risk Assessment Guidelines, Part II, Technical Support Document for Describing Available Cancer Potency Factors, April 1999. The State of California, under Proposition 65, listed Perc as a carcinogen in April 1988.

The Air Resources Board (ARB) formally identified Perc as a toxic air contaminant in 1991. OEHHA concluded that Perc is a possible human carcinogen with no identifiable threshold below which no carcinogenic effects are likely to occur. In 1990, the United States Congress listed Perc as a hazardous air pollutant in subsection (b) of Section 112 of the federal Clean Air Act (42 U.S.C. 7412). The International Agency for Research on Cancer (IARC) has classified Perc in Group 2A, as a probable human carcinogen. The United States Environmental Protection Agency (U.S. EPA) is currently reevaluating Perc for carcinogenicity.

In addition to cancer effects, there are short-term (acute) and long-term (chronic) non-cancer health effects associated with exposure to Perc. Acute toxic effects resulting from short term exposure to high levels of Perc may include headaches, dizziness, rapid heartbeat, and irritation or burns on the skin, eyes, or respiratory tract. Chronic exposure to lower Perc concentration levels may result in dizziness, impaired judgement and perception, and damage to the liver and kidneys (ARB, 1996). Workers have shown signs of liver toxicity following chronic exposure to Perc, as well as kidney dysfunction and neurological effects. Effects on the liver, kidney, and central nervous systems from chronic inhalation exposure to Perc have been reported in animal studies (ARB, 1997).

1. Pollutant-specific Health Values

Dose-response or pollutant-specific health values are developed to characterize the relationship between a person's exposure to a pollutant and the incidence or occurrence of an adverse health effect. A unit risk factor (URF) or cancer potency factor is used when estimating potential cancer risk and

reference exposure levels (RELs) are used to assess potential non-cancer health impacts.

A URF is defined as the estimated upper-confidence limit (usually 95th percentile) probability of a person contracting cancer as a result of constant exposure to a concentration of 1.0 microgram per cubic meter (µg/m^3) over a 70-year lifetime. In other words, using the URF for Perc as an example, which is 5.9×10^{-6} (µg/m^3)$^{-1}$, the potential excess cancer risk for a person continuously exposed over a 70-year lifetime to 1.0 µg/m^3 of Perc is estimated to be no greater than 5.9 chances in 1 million. The URF of 5.9×10^{-6} (µg/m^3)$^{-1}$ is converted to the cancer potency factor of 2.1×10^{-2} (mg/kg - day)$^{-1}$ by multiplying the URF by 3500 and rounding to two significant figures. The factor of 3500 is derived from a 70 kilogram (kg) human body weight, 20 m^3 inhalation rate, and 1000 factor unit conversion.

An REL is a concentration at or below which adverse health effects are not likely to occur in the general population. RELs are designed to protect the most sensitive individuals in the population by including uncertainty factors in their development and can be created for both acute and chronic exposures. An acute exposure is defined as one or a series of short-term exposures generally lasting less than 24 hours. A one-hour exposure is used to determine acute non-cancer impacts. Chronic exposure is defined as long-term exposure usually lasting from one year to a lifetime.

As mentioned previously, exposure to Perc may result in both cancer and non-cancer effects. Table V-1 shows the health values currently adopted and approved for use in California. These health values have gone through a public comment and scientific peer review process. Of the currently used dry cleaning solvents, Perc is the only solvent for which there are adopted health values available for use in California. OEHHA has estimated interim RELs for several of the alternatives. Interim RELs are estimates based on approved OEHHA procedures; however, interim values have not gone through public comment and scientific peer review.

Table. V-1. Adopted Health Values for Perc

Health Effect	Health Value
Acute inhalation REL	2.0×10^4 µg/m^3
Chronic inhalation REL	35 µg/m^3
Inhalation unit risk factor	5.9×10^{-6} (µg/m^3)$^{-1}$
Inhalation cancer potency factor	2.1×10^{-2} (mg/kg-d)$^{-1}$

B. Perc Alternatives

There is relatively little health data available on the alternatives and no California health values have been adopted. As a result, ARB staff requested OEHHA to review the health effects of alternative dry cleaning solvents as they are used in the dry cleaning industry. Appendix G is a copy of OEHHA's December 2002 memorandum to ARB which provides both a summary of their literature review and toxicity data summaries for many of these compounds. Based on their literature review, OEHHA has estimated several interim RELs and is continuing to follow the peer-reviewed literature on toxicity studies for the alternative solvents.

1. Hydrocarbon Solvent Cleaning (DF-2000, PureDry, EcoSolv, Shell 140, Stoddard)

Hydrocarbon solvents, sometimes referred to as mineral spirits and petroleum solvents, are mixtures of hydrocarbons with or without other materials. Hydrocarbons have been used in the dry cleaning industry for many years and are some of the more common alternatives to Perc dry cleaning. The hydrocarbon solvents are a unique mixture of carbon and hydrogen molecules that co-exist as linear and branched chains, as well as in cyclic forms (U.S. EPA,1998).

For Stoddard solvent, the American Conference of Governmental Hygienists set a Threshold Limit Value (TLV) of 525 mg/m^3. The National Institute for Occupational Safety and Health (NIOSH) REL is 350 mg/m^3 time-weighted average (TWA). Stoddard solvent can be irritating to the eyes, nose, throat, and can also have effects on the nervous system.

A recent two-year inhalation study of Stoddard solvent conducted by the National Toxicology Program (NTP) concluded that there was some evidence of carcinogenic activity in male rats (NTP, 2004). In general, this study confirmed previous studies on toxicity for Stoddard. Most of the studies found in the literature for short and long-term toxicity identified the kidney and liver as the major target organs (NTP, 2004).

There is also very limited health information on other hydrocarbon mixtures. DF-2000™ Fluid (DF-2000) contains C_{11} to C_{13} aliphatic hydrocarbons. PureDry® (PureDry) contains 95 percent mineral spirits, which can cause neurotoxicity, and eye and respiratory irritation at high concentrations (OEHHA, 2003). EcoSolv® (EcoSolv) and Shell Sol 140 HT have similar hydrocarbon properties. However, information is lacking on the environmental persistence of these and other hydrocarbon mixtures.

For hydrocarbon mixtures, OEHHA has developed an interim chronic REL of 1,200 µg/m^3. The development of this interim value, which has not been

through scientific peer review, is based on a study by Phillips and Egan on male and female rates. Additional information on this study can be found in Appendix G.

An occupational exposure limit (OEL) can be calculated for various hydrocarbon solvents. Guidance values for individual hydrocarbon constituents or groups of constituents were recently published in an article *A Proposed Methodology for Setting Occupational Exposure Limits for Hydrocarbon Solvents* in the Journal of Occupational and Environmental Hygiene, October 2005. (JOEH, 2005). Information on calculating OELs and guidance values for other substance groups can be found in the article. Note however, these guidance values have not been approved for use in California's regulatory programs.

2. Volatile Methyl Siloxane Cleaning

Decamethylcyclopentasiloxane, or D_5, is a cyclosiloxane which is now being used as a dry cleaning solvent. Historically, it has been used as an ingredient in many personal health and beauty products. D_5 is present in GreenEarth® (GreenEarth) solvent. Dow-Corning, who manufacturers the solvent, conducted a two-year study with rats in which preliminary data showed an increase in tumors of the uterine endometrium. Preliminary findings may indicate that there is a potential carcinogenic hazard associated with D_5 (U.S. EPA, 2003). The observance of adverse effects on the uterus by D_5 is of concern (OEHHA, 2003). Because D_5 is lipophilic there is also concern that D_5 may bioaccumulate in the food chain.

A study by Burns-Naas *et al*. (1998) evaluated the subchronic toxicity of D_5. This study showed there were several minor changes observed in clinical biochemistry parameters; the most notable was an increase in gamma glutamyl transferase (a liver enzyme) in both sexes at the high dose. This study also showed that there was an increase in liver weight in rats. McKim et al. (1999) investigated the effects of D_5 on the expression and activity of selected rat hepatic phase I and phase II enzymes. Additional information on the Burns-Naas *et al*. and McKim *et al*. studies can be found in Appendix G.

In June 2005, D_5 manufacturers submitted final toxicity testing data to ARB, OEHHA, the Department of Health Services (DHS), and U.S. EPA. After these agencies review the data, a better assessment of the public health impacts from GreenEarth emissions can be made.

3. Propylene Glycol Ether (Rynex)

Rynex® (Rynex) is made up of mostly di-propylene glycol tert-butyl ether and water. Currently there is no toxicity data on Rynex.

Based on a recent study by NTP on the previous formulation for Rynex, propylene glycol t-butyl ether, OEHHA expressed concerns over the toxicity and carcinogenic potential of propylene glycol t-butyl ether. Of particular concern was the presence of tumors in mice. OEHHA has developed an interim chronic REL for propylene glycol t-butyl ether of 200 $\mu g/m^3$ to prevent adverse effects in the respiratory system. In addition, an interim inhalation unit risk factor for cancer was estimated to be 5.2×10^{-7} $(\mu g/m^3)^{-1}$, about one-tenth that of Perc. There are no developmental or reproductive studies on the chemical. Appendix G has more detailed information on the toxicological studies for propylene glycol t-butyl ether.

4. Carbon Dioxide Cleaning

As discussed in Chapter II, carbon dioxide (CO_2) cleaning used liquid CO_2. The CO_2 used in this process is an industrial by-product. There is no net increase in the amount of CO_2 emitted; therefore, this process does not contribute to global warming. CO_2 is naturally occurring and is routinely ingested in food products such as soft drinks. CO_2 is also used in packaging for many foods such as salads, potato chips, and cookies.

Design for the Environment (DfE), a cooperative project between the U.S. EPA and the garment and textile care industry, recognizes the CO_2 cleaning process as one example of environmentally preferable technology that can effectively clean garments. The DfE conducted a case study on a Micell Technologies, Inc., CO_2 system that uses CO_2 in conjunction with a cleaning agent that enhances the cleaning ability of the liquid CO_2. In the case study, Micell Technologies asserts that their cleaning system offers excellent cleaning performance across most garment components and a wide range of stains and soils. This system uses the same beverage-grade bulk CO_2 that is distributed to more than 50,000 restaurants and other fountain beverage dispensers located in the United States. (U.S. EPA, 1999)

5. Professional Wet Cleaning

Most detergents used in Professional Wet Cleaning (wet cleaning) are a complex mixture of water and a variety of chemicals. Most formulations are trade secrets. Because there are a wide variety of formulations, there is difficulty with determining toxicity of these substances. Chemicals used in wet cleaning process commonly include spotting agents, detergents, fabric conditioners and sizing products. Other products may be used for cleaning leather and suede including water repellants.

In general, detergents are approved for disposal into the sewer system by the sanitation districts. U.S. EPA examined the human health and environmental hazards of surfactants because they are the primary components of detergents. In general, they found that there was no expected health risk to general public.

(U.S. EPA, 1998). In addition, the draft report, Evaluation of New and Emerging Technologies for Textile Cleaning, indicates that detergents are low in toxicity (IRTA, 2005).

In U.S. EPA's Cleaner Technologies Substitute Assessment : Professional Fabricare Processes (CTSA), U.S. EPA provided health hazard summaries on surfactants and surfactant aids for some example detergents. The following surfactants were included in their example detergents: cellulose gum (CG), cocamidopropyl betaine (CAPB), ethoxylated sorbitan monodecanoate (P-20), lauric acid diethanolamide (Lauramide DEA), sodium laureth sulfate (SLS), sodium lauryl isethionate (SLI). Surfactant aids include: acetic acid, citric acid, sodium citrate, and sodium carbonate. It is unknown how representative these example detergents were for detergents currently being used. Below is some health information on some of the surfactant and surfactant aids presented in the CTSA.

a. Surfactants

Several studies have been conducted on CG, a water-soluble cellulose ether. This and other water-soluble cellulose ethers exhibit very low oral toxicity, and no neurologic, reproductive, or mutagenic effects. (U.S. EPA, 1998)

CAPB is reported as a potentially irritating substance. CAPB does not appear to have undergone any studies of reproductive or developmental toxicity or neurotoxicity or chronic studies of systemic effects. Results of one study, suggest that CAPB does not increase systemic tumors above background, but are not enough to be conclusive. (U.S. EPA, 1998)

In both animals and humans, P-20 has been found to be essentially nontoxic following acute and long-term oral ingestion and to exhibit little or no potential for skin irritation and sensitization. (U.S. EPA, 1998)

No human studies were located regarding the potential toxicity of lauramide DEA following oral or inhalation exposure. Lauramide DEA was not found to be mutagenic. The carcinogenic potential of lauramide DEA is currently being investigated. (U.S. EPA, 1998)

SLS, following oral exposures, is "moderately to slightly toxic" in acutely exposed animals and virtually non-toxic in chronically exposed animals. SDS does not appear to exhibit any reproductive, developmental, or carcinogenic effects in animals. (U.S. EPA, 1998)

Limited information on SLI suggests that this chemical may not be a skin irritant and is not mutagenic. (U.S. EPA, 1998)

b. Surfactant Aids

At high concentrations, acetic acid can result in severe irritation in both humans and animals. Based on short-term mutagenicity tests, acetic acid does not interact with genetic material. Although no direct information on the carcinogenicity of acetic acid was located, one chronic study in rats found no evidence of tumors. (U.S. EPA, 1998)

Citric acid is generally considered to be innocuous except in the case of ingestion of large quantities or chronic exposures. Citric acid has been shown to be a mild to moderate skin and eye irritant in humans following inhalation or dermal exposure. No information has been located discussing neurotoxic, mutagenic, or carcinogenic effects associated with citric acid exposures in animals or humans. Sodium citrate is expected to behave chemically like citric acid systemically, but may not have the irritant properties. (U.S. EPA, 1998)

Sodium carbonate is a skin and eye irritant. Sodium carbonate is not developmentally toxic to mice, rats, or rabbits. No information was available discussing reproductive, neurotoxic, mutagenic, or carcinogenic toxicity from exposure to humans or animals. (U.S. EPA, 1998)

6. Green Jet

The detergent used in the Green Jet® system is called DWX-44. The Material Safety Data Sheet (MSDS) states that the product is 100 percent biodegradable. It also states that it contains no petroleum solvents, volatile organic compounds, or products from the federal hazardous air pollutant list. ARB staff is not aware of any health studies on this detergent.

7. 1-Propyl Bromide

Although currently not in use in California, 1-propyl bromide, also known as 1-bromopropane, is a solvent that is currently being considered as an alternative to dry cleaning. This compound is a neurotoxicant and reproductive toxicant (OEHHA, 2003) and was listed under Proposition 65 as a reproductive toxicant in December 2004. It causes sterility in both male and female test animals, and harms developing fetuses when tested in pregnant animals. It can damage nerves, causing weakness, pain, numbness, and paralysis (CDHS, 2003). Because this is a relatively new chemical, most health information comes from animal testing.

OEHHA developed an interim chronic REL of 1100 $\mu g/m^3$ (220 parts per billion) for 1-propyl bromide from the reproductive toxicity data in the Ichihara (et.al.) study (OEHHA, 2003). Based on current toxicity data, OEHHA staff is concerned about its use as a dry cleaning solvent (OEHHA, 2003).

C. Interim Health Values

As mentioned earlier in this chapter, OEHHA has developed interim values for some of the dry cleaning alternatives. Interim RELs are estimates based on approved OEHHA procedures; however, interim values have not gone through public comment and scientific peer review. OEHHA is continuing to follow the peer-reviewed literature on toxicity studies for the alternative solvents. Table V-2 summarizes these values. Refer to Appendix G for a more detailed discussion on the applicability of these values to specific compounds.

Table. V-2. Summary of Interim Health Values

Compound	Acute REL[1]	Chronic REL	Cancer potency factor[1]
D5 (GreenEarth)	N/A	700 µg/m^3	N/A
1-Propyl bromide	N/A	1,100 µg/m^3	N/A
Hydrocarbon mixtures	N/A	1,200 µg/m^3	N/A
Hydrofluoroether (HFE 7200) (a compound in PureDry)	N/A	19,000 µg/m^3	N/A
Perc[2]	2.0x10^4 µg/m^3	35 µg/m^3	2.1x10^{-2} (mg/kg-d)$^{-1}$

1. N/A means not available - not enough health data is available to determine a health value for this compound.
2. The values for Perc are approved by OEHHA and are included for comparison.

VI. ENVIRONMENTAL IMPACTS

Several potential environmental impacts have been identified that are associated with the use of dry cleaning alternatives and perchloroethylene (Perc). This chapter discusses the impacts on wastewater, groundwater contamination, hazardous waste disposal, soil, flammability, energy usage and air pollution.

A. Wastewater

Sanitation districts have been concerned about the amount of chlorinated compounds found in the waste effluent at treatment plants and the potential for illegal disposal of Perc dry cleaning wastes down the sewers. Many treatment plants do not have the equipment necessary to process industrial wastes such as chlorinated solvents that have been detected at elevated levels at some facilities. However, Perc dry cleaners are not expected to significantly add to this burden. The impact of influent concentrations of Perc from the dry cleaning industry appears to be low due to the changes in dry cleaning operations and the implementation of environmental regulations (NC, 2001). Based on information gathered from the Dry Cleaning Facility Survey, dry cleaning facilities using Perc either use a wastewater treatment unit to recycle their Perc or they have their wastewater picked up by a registered hazardous waste transporter (in California, all hazardous waste must be managed offsite by a transporter that is registered with the California Department of Toxic Substances Control (DTSC)). It should be noted that spotting chemicals can also be a source of Perc.

In general, it is prudent to check with the local publicly owned treatment works (POTWs) in the State before discharging any wastewater into the sewer. However, potential wastewater impacts of the alternative solvents were assessed based on available information. The carbon dioxide (CO_2) cleaning process does not generate wastewater and would not have an impact. Dry cleaners that use other alternative solvents, including GreenEarth® (GreenEarth), hydrocarbon, and glycol ether, can release the solvents to water, mainly in separator wastewater. Separator water was analyzed in a project conducted by the Institute for Research and Technical Assistance (IRTA) and the Los Angeles County Sanitation Districts (LACSD). Separator water from three facilities, each using one of the alternative solvents mentioned, was analyzed for certain metals, toxic organics and aquatic toxicity (IRTA, 2005). In all cases, the metals concentrations and the toxic organic concentrations were below detection limits. Additionally, in all three cases, the separator water did not exhibit aquatic toxicity (IRTA, 2005).

In addition, IRTA and LACSD analyzed the wash and rinse effluents from four wet cleaning facilities for certain metals, toxic organics, and aquatic toxicity. None of the samples contained metals concentrations that exceeded hazardous waste levels. Perc and/or trichloroethylene (TCE) were found in the effluent from three of the wet cleaning facilities. In some cases, the concentrations of these toxics exceeded hazardous waste levels. The origin of the TCE and at least some of the Perc is most

likely spotting chemicals that are used to pre-spot garments. A few of the facilities had both wet cleaning and Perc machines and the Perc may have been entrained in garments cleaned in the wet cleaning machine. The analysis indicated that effluent samples from all four facilities did not exhibit aquatic toxicity despite the presence of Perc and/or TCE. (IRTA, 2005)

B. Groundwater Contamination

One of the concerns with the use of Perc is groundwater contamination. Perc is known to pass through porous surfaces, such as building walls, sewer lines, and cement floors (ARB, 1993). Therefore, Perc usage poses a significant threat to the safety of our groundwater. Perc has been detected in both wastewater and groundwater in the South Coast basin, with some levels in excess of the current drinking water standard of five parts per billion (South Coast, 2002). Perc has also been detected in 968 wells or approximately ten percent of the 9500 wells tested in California as of March 1996, creating a need for an estimated three billion dollar state cleanup (CFCA, 2002). The implementation of environmental regulations and changes in the dry cleaning industry will help minimize the impact on groundwater contamination from Perc.

Based on information available for the alternative solvents, groundwater contamination is not as large of an issue compared to Perc. When DF-2000™ Fluid (DF-2000), the more commonly used hydrocarbon solvent, is released into the environment, volatilization from water to the air is calculated to occur at a relatively rapid rate of a few days. Non-volatized product in the natural environment will biodegrade at a moderate rate and not persist. (ExxonMobil, 2003) Other high flash point hydrocarbon solvents are expected to behave similarly.

Based on preliminary findings from a study conducted by the Silicones Environmental, Health and Safety of North America Council (SEHSC), the GreenEarth solvent is unlikely to leach into groundwater because it is not very soluble in water and readily sticks to soil particles (GreenEarth, 2003). According to a study conducted by the International Fabricare Institute (IFI), GreenEarth solvent has low solubility in water (<100 parts per billion (ppb)) and is very close in density to water; therefore, if it is discharged to water, it will initially form a surface film and then will rapidly evaporate into the air. The half-life for GreenEarth in surface water is estimated at between one to five days. Acute studies with trout, daphnia, and algae show no significant effects at the highest doses prescribed by the test methodology. If larger amounts of GreenEarth solvent are kept in contact with soil, it will also be expected to decompose to carbon dioxide, silicon dioxide (sand), and water. (IFI, 2002)

Groundwater contamination is not a concern using the CO_2 process. At room temperature, CO_2 can exist as a liquid if kept in a closed system at an elevated pressure. The cleaning systems used for CO_2 are able to efficiently convert CO_2 from a gas to a liquid. One of these systems permits 98 percent of the CO_2 to be recycled

(U.S. EPA, 1999). In general, only a nominal amount of CO_2 is then vented to the atmosphere.

Environmental fate on the Rynex solvent is not readily available, but the Rynex formulation is a type of propylene glycol ether. Proplylene glycol ethers are known to be biodegradable. All propylene glycol ethers are liquid at room temperature and all are water-soluble. Propylene glycol ethers are unlikely to persist in the environment. Two specific types of glycol ethers, proplylene methyl ether and propylene glycol methyl ether acetate, have shown rapid biodegradation in soil. (SIDS, 2003)

C. Hazardous Waste

Hazardous waste is regulated in California by a federally authorized State program. Under this program, Perc is classified as hazardous waste. In California, all hazardous waste at a facility must be transported off-site by a registered hazardous waste transporter. In general, it is the facility owner's responsibility to determine whether the waste from the facility is hazardous.

Waste generated by the use of Perc in dry cleaning includes the still bottoms from solvent distillation and the spent cartridge filters used to remove lint and insoluble soil from the extracted Perc. Cartridge filters are typically replaced every six months or less, depending on workload and manufacturer recommendation. Reusable spin disc filters are also used and the removed lint and dirt from the spin disc filters generate perc-contaminated waste. (JE, 2003)

The change in the amount of waste generated from solvent-based technologies (i.e., hydrocarbon, GreenEarth, and Rynex) is relatively small compared to Perc (JE, 2003). In terms of waste volume, the CO_2 cleaning process is expected to generate the least amount of waste compared to Perc and the other alternative technologies (JE, 2003). In general, wastes from the mentioned alternative processes include spent filters and still bottoms. The still bottoms from four dry cleaning facilities that used hydrocarbon, GreenEarth, Rynex and CO_2, were analyzed in a study IRTA conducted with LACSD. The results of these tests showed excess levels of lead for one of the still bottom samples and three out of four of the still bottom samples exhibited aquatic toxicity (IRTA, 2005). Because the solvents do not contain lead and are not expected to exhibit aquatic toxicity, the results indicate that the spotting chemicals and detergents used may alter the characteristics of the waste streams. Alternately, waste streams from alternative processes can be handled as hazardous waste. Currently, registered hazardous waste transporters remove the wastes from hydrocarbon dry cleaning facilities as hazardous waste (ARB, 2004I).

The water-based cleaning technologies also generate spent filters. Again, in the absence of contamination from hazardous compounds, handling as municipal solid waste is an option (JE, 2003). Additionally, the detergents that are used are biodegradable and designed for discharge via the sanitary sewer. These detergents should be readily removed at the local treatment plant (JE, 2003).

D. Soil

Soil contamination has been a problem with Perc use. According to one report, Perc is found in more than 50 percent of the Superfund sites in the country (CFCA, 2002). However, all dry cleaning processes can result in soil contamination. Soil contamination can occur through accidental releases, such as spills, or during the distillation process from a boil-over. Although federal, state, and local environmental regulations have been developed to help minimize soil contamination, dry cleaners should take all necessary steps to contain spills and clean them up quickly.

E. Flammability

Flammable or combustible liquids are listed in different classes. The combustible liquids used in the dry cleaning industry are listed under classifications based on their flash point. Flash point is defined as the temperature at which a flame will ignite the solvent vapors. These combustible liquids are classified as Class II, Class IIIA, or Class IIIB. The use of these combustible liquids may require the issuance of fire permits. Class II liquids, like the Stoddard Solvent (Stoddard), have a flash point at or above 100 degrees Fahrenheit (°F) and below 140°F. Class IIIA liquids have a flash point at or above 140°F and below 200°F. The hydrocarbon solvents are an example of the Class IIIA liquids. Class IIIB liquids, like the Rynex solvent, have a flash point at or above 200°F. Class IV liquids, such as Perc, are considered noncombustible and, therefore, are not potential fire hazards. (JE, 2003)

As many may recall, Stoddard was a popular dry cleaning solvent that saw a significant usage decrease based on fire hazard concerns. As mentioned above, this solvent is classified as a Class II liquid and has a flash point of 110°F. This hazard encouraged the petroleum industry to develop a new group of solvents that have a higher flash point. These solvents are classified as Class IIIA and IIIB liquids and have a flash point above 140°F. It is important to know that these hydrocarbon solvents are still considered hazardous materials and a fire safety hazard by California Occupational Safety and Health Act (CAL/OSHA) standards. This group of solvents includes DF-2000™ Fluid (DF-2000), PureDry® (PureDry), Shell Sol 140 HT (Shell 140), and EcoSolv® (EcoSolv). DF-2000, with a flash point of 147°F, is currently the most popular hydrocarbon solvent being used.

There are a few more alternative solvents being used in the garment industry today. They are GreenEarth, Rynex, and CO_2. The GreenEarth solvent is classified as a Class IIIA liquid and has a flash point of 170°F. It is considered a potential fire safety hazard. Rynex, which has a flash point greater than 200°F, is classified as a Class IIIB liquid and a potential fire safety hazard. Based on a study conducted by the North Carolina Department of Environment and Natural Resources, CO_2 is a weak solvent; therefore, a detergent mixture is used as a supplement to the base solvent. The detergent mixture contains hydrocarbon chemicals in order to dissolve certain soils. The hydrocarbon compound used in the detergent mixture has a flash point above 140°F and is classified as a Class IIIA liquid. While the CO_2/detergent mixture is not

expected to be a fire safety hazard, the detergent mixture by itself is a fire safety hazard. (NC, 2001)

The water-based cleaning processes use detergents that are not considered a fire hazard. Therefore, there is no potential flammability risk involved with these processes. For comparison purposes, Table VI-1 below gives you a summary of the flash points and classifications of the commonly used solvents in the dry cleaning industry.

Table VI-1. Summary of Flash Points and Classification for Commonly Used Solvents[1]

Solvent	Flash Point	Classification
Perc	N/A	IV
Stoddard	110°F	II
DF-2000	147°F	IIIA
PureDry[2]	350°F	IIIB/IIIA
Shell 140	>143°F	IIIA
EcoSolv	>140°F	IIIA
Rynex	>200°F	IIIB
GreenEarth[3]	170°F	IIIA
CO_2[4]	N/A	N/A

1. Source: Material Safety Data Sheet, unless otherwise noted.
2. Dry cleaners and vendors have reported that the flash point can decline to the 140°F range during use because of the perfluorocarbon that is in the Pure Dry mixture. If this is the case, it is classified as a IIIA solvent.
3. Source: Cleaners Family, Volume 4.
4. The detergent mixture used as a supplement with the CO_2 solvent is a hydrocarbon and is classified as a IIIA solvent, but when used together with the CO_2 it is not considered a fire hazard.

E. Energy Usage

According to a report prepared by Jacobs Engineering for the City of Los Angeles, the overall amount of electricity used by a shop running either a new Perc system or a solvent-based technology (hydrocarbon, GreenEarth, Rynex) is about 1,100 Kilowatt-hour (kWh) per month. For water-based technologies, tests conducted by the Pollution Prevention Education and Research Center (PPERC) at a facility that switched from Perc to professional wet cleaning found a reduction in electricity use (to approximately 600 kWh per month). The CO_2 system requires a 70 to 150-amp service to operate the refrigeration system necessary to maintain the CO_2 in a liquid state. Peak load for the pumps and compressor could be up to 20 kWh. This is twice the peak load reported for the other alternative technologies and it could result in increased peak load demand charges. Therefore, the assumption is made that a CO_2 shop will utilize 30 percent more power than a shop using Perc. Based on available information, Table VI-2 shows monthly energy usage for Perc dry cleaning and alternatives. (JE, 2003)

Table VI-2. Estimated Monthly Electricity Usage[1]

Process	Electricity Usage (kWh)
Perc	1,100
DF-2000	1,100
GreenEarth	1,100
Wet Cleaning	600
CO_2	1,430

1. Source: JE, 2003.

Chapter VII gives additional information on electricity usage for each machine used in each dry cleaning process.

G. Air Pollution

1. Impacts on VOC Emissions and Global Warming

Tropospheric ozone ("bad" ozone) formation requires a mix of ozone-forming chemicals, also known as volatile organic compounds (VOCs), nitrogen oxides, oxygen, and sunlight. Any reduction in VOC emissions is expected to provide a beneficial environmental impact on air quality by reducing tropospheric ozone formation. The hydrocarbon solvents, as well as the Rynex solvent, used in the dry cleaning industry are classified as VOCs. An increase in the usage of these solvents may cause an environmental impact. For example, if the industry was to switch to the hydrocarbon dry cleaning process there would be an estimated increase of about two tons per day of VOCs Statewide.

Greenhouse gases, which alter the amount of heat, or infrared radiation, that can escape the Earth's surface, have been linked to a gradual warming of the Earth's surface and lower atmosphere. While CO_2 has been the traditional focus of greenhouse gas concerns, the CO_2 used in the dry cleaning process is an industrial by-product from other industrial operations and does not contribute to global warming. In the United States, the largest source of greenhouse gas emissions is from fossil fuel combustion, which accounted for approximately 81 percent of greenhouse emissions in 1996. (JE, 2003)

2. Workplace Exposure

CAL/OSHA regulates the concentration of many toxic air contaminants and VOCs in the workplace environment. CAL/OSHA has established a permissible exposure limit (PEL) for several of these compounds (the PEL is the maximum, eight-hour, time-weighted average concentration for occupational exposure). Perc has a PEL of 25 parts per million (ppm) and Stoddard has a PEL of 100 ppm. Although the remaining solvents do not have PELs, Table VI-3 gives a summary of any known acute and chronic health impacts.

Table VI-3. Potential Health Impacts and Permissible Exposure Limit (PEL)

Solvent	Acute	Chronic	PEL
Perc	central nervous system; irritation to eyes, skin, and respiratory tract	kidney, liver, and gastrointestinal system	25 ppm
Stoddard	central nervous system; irritation to eyes, skin, nose, and throat[1]	Unknown	100 ppm
DF2000	central nervous system; irritation to eyes, skin, and respiratory tract[2]	unknown	N/A
PureDry	central nervous system; irritation to eyes, skin, nose, throat, and respiratory tract[2]	unknown	N/A
EcoSolv	central nervous system; irritation to eyes, skin, and respiratory tract[2]	unknown	N/A
Shell 140	central nervous system; irritation to skin, nose, throat, and respiratory tract[2]	unknown	N/A
GreenEarth (D5)	mild eye irritation	increase in liver weight[3]	N/A
Rynex	headaches; irritation to eyes, nose, and throat[1]	unknown	N/A
CO_2	irritation to skin and eyes,[4] frostbite[5]	unknown	N/A

1. Source: U.S. EPA, 1998.
2. Information taken from Material Safety Data Sheets.
3. See Appendix G.
4. Due to exposure to detergents used with the CO_2 process.
5. Due to exposure to liquid CO_2.

VII. COST ESTIMATION

The data used in the cost analysis of the various dry cleaning processes was based on information collected from equipment manufacturers and distributors as well as from publicly available information. The categories covered in this analysis include estimates on the cost of machines, operation, installation, leak detectors, and control technology.

A. Machine Cost

Estimated machine costs are based on the Machine Manufacturers Survey and are presented in Table VII-1. As there are a variety of sizes and models that affect the actual price of each machine, costs are given in ranges for each technology.

Table VII-1. Summary of Machine Cost from Survey[1]

Solvent Type	Machine Type	Rated Capacity (lbs)	Cycle Time (minutes)	List Price ($)[2]
Water (wet cleaning)	Washer (soft mount)	15-42	12-35	8,800-30,400
Water (wet cleaning)	Washer (hard mount)	20-85	12-35	8,700-23,300
Water (wet cleaning	Dryer	15-135	12-30	2,100-12,900
Water (Green Jet)	Dry-to-Dry	45	32	30,000
Perc	Secondary Control	35-90	45-55	38,000-83,000
Hydrocarbon	Dry-to-Dry	30-90	45-60	36,000-98,000
Stoddard Solvent	Transfer	50-110	40	29,000-40,000
Stoddard Solvent	Dryer/Claimer	55-110	55	29,000-35,000
GreenEarth[3]	Dry-to-Dry	35-90	45-60	43,000-98,000
CO_2[4]	Dry-to-Dry	60	35-40	140,000

1. From Machine Manufacturers Survey (ARB, 2004), unless otherwise noted.
2. This reflects manufacture list price, machines can cost less. Also, does not include installation costs.
3. This does not include the annual GreenEarth "Affiliation Fee."
4. Source: ARB, 2005c.

Professional wet cleaning (wet cleaning) systems consist of a separate washer and dryer and require tensioning equipment. The two most common tensioning equipment pieces used are the form finisher, with an average cost of $11,000, and the pants topper, with an average cost of approximately $9,900 (PPERC, 2004). When selecting a wet cleaning washer, a dry cleaner needs to choose between a hard mount washer and a soft mount washer. Hard mount washers are less expensive than soft mount washers, but require a custom concrete foundation and are not suitable for

upper-floor or above-basement installations (PPERC, 2004). For example, a 35-pound soft mount washer is approximately $15,100 whereas a 40-pound hard mount washer is about $14,200 (ARB, 2004). The cost of a wet cleaning dryer with a 50-pound capacity is estimated at $4,500. Dry cleaners can expect to pay between $39,600 and $40,500 for a "typical" wet cleaning system (including tensioning equipment). Costs will be higher if a larger capacity washer or dryer is selected.

The Green Jet® (Green Jet) system uses one piece of equipment for cleaning and drying. The cost of the machine is $30,000 for a 45-pound capacity. This process does not require tensioning equipment because it intermittently rotates the garments to minimize shrinkage (as well as wrinkles) at the end of the cleaning cycle. (ARB, 2004)

The GreenEarth® (GreenEarth) dry cleaning machines with the capacity range of 35-pounds to 90-pounds are list priced at $43,000 to $98,000. There is also an annual GreenEarth "Affiliation Fee" of $2,500 per machine. If a facility has more than one machine, there is an annual "Affiliation Fee" of $1,250 for each additional machine. (ARB, 2004; ARB, 2005d)

According to the Dry Cleaning Facility Survey (Facility Survey) results, a typical perchloroethylene (Perc) dry cleaning facility has an average machine capacity of 40 to 45 pounds. If a Perc machine were to be replaced with an alternative dry cleaning machine, it would typically be replaced with a slightly larger machine (ARB, 2003). Table VII-2 gives a cost comparison of Perc secondary control machines and the alternatives, including hydrocarbon, GreenEarth, water-based cleaning, and carbon dioxide (CO_2).

Also shown on Table VII-2 are installation costs. The cost of installation varies according to the machine type. A Perc dry cleaning machine can be installed for $2,500 to $3,000 unless the facility needs to have a chiller or water tower included in the installation. If this were the case, the installation cost would range from $3,000 to $5,000. The installation cost for a hydrocarbon machine and a GreenEarth machine is basically the same. The installation cost range for these two types of machines is $5,000 to $6,000. The current installation cost for a CO_2 machine with a chiller is $50,000. As for wet cleaning, the installation cost for a complete wet cleaning process will range from $2,000 to 2,500. If a facility owner is replacing just one piece of equipment (e.g. the washer), the installation cost will be about $750 per piece. There is an increase in cost if the owner chooses to relocate the piece of equipment within the facility. If this were the case, this "relocation" cost would be $850 per piece. This increased cost is due to the installation of new lines and traps. (ARB, 2004d; ARB, 2004e, ARB, 2005c)

Table VII-2. Machine Cost Comparison for a Typical Dry Cleaning Facility[1]

Machine Solvent Type	Installation Cost	Typical Machine Cost	Machine Cost Difference Perc (dry-to-dry) to Alternative (dry-to-dry)[2]
Perc-Secondary Control (40-lb. capacity)	$2,500 – $3,000	$43,900	-
Perc-Secondary Control (40-lb. capacity) w/chiller or cooling tower	$3,000 - $5,000		
Hydrocarbon (50-lb. capacity)	$5,000 - $6,000	$61,000	+$17,100
GreenEarth (50-lb. capacity)[3]	$5,000 - $6,000	$63,000	+$ 19,100
Water-Based Cleaning	$2,000 - $2,500		
Green Jet (45-lb. capacity)		$30,000	-$13,900
Professional Wet Cleaning[4] (washer/dryer/tensioning equip.)			
Soft Mount (25-35 lb. capacity)		$37,800-$40,500	-$6,100 to -$3,400
Hard Mount (30-40 lb. capacity)		$35,700-$39,600	-$8,200 to -$4,300
CO_2 (60-lb. capacity)[5]	$50,000	$140,000	+$96,100

1. Based on information from ARB's 2004 Manufacturers survey, unless otherwise noted.
2. The cost estimates given for the soft and hard mount wet cleaning system are for washer/dryer combination.
3. This does not include the GreenEarth annual affiliation fee of $2,500 for the first machine purchased and the $1,250 for any additional machines purchased.
4. Source: ARB, 2005. Also note that typically 30-pound capacity washer/dryer wet cleaning machines can usually replace a 60-pound capacity Perc dry cleaning machine (PPERC, 2004).
5. Source: ARB, 2005c.

B. Operating Cost

There are various operating costs associated with the garment cleaning industry. The operating costs will vary according to the cleaning process. The most important operating cost variables include solvent cost, detergent and spotting agent cost, electricity cost, natural gas cost, waste disposal cost, filter cost, gasket cost and maintenance costs. Estimated natural gas cost was given only for those technologies for which ARB had therm usage information. The maintenance cost may include cleaning of traps and still, draining and cleaning the separator, cleaning and changing filters, lubricating machine parts, checking pressure level, and changing carbon filters.

Solvent costs will vary according to the dry cleaning technology used. The hydrocarbon technology has a variety of alternative solvents available. The most commonly used alternative solvent is DF-2000™ Fluid (DF-2000). Table VII-3 gives an overview of the available solvents and what the current cost is to the industry. Perc solvent costs given on this table include the current $4 Assembly Bill (AB) 998 fee. In the wet cleaning process, water is used as the solvent; therefore, there can be a change in water usage when switching to wet cleaning. A study conducted by Pollution Prevention Education and Research Center (PPERC) showed that there could be a 17 percent increase in water usage after switching to wet cleaning. This amounted to a $4 per month increase for water usage.

Table VII-3. Dry Cleaning Solvent Costs

Solvent	Cost
Perc	$19/gal.
Hydrocarbon	
DF-2000	$6.50-7.95/gal.
PureDry	$15/gal.
Shell	$5/gal.
EcoSolv	$6.50/gal.
Stoddard Solvent	$3.63/gal.
GreenEarth	$17.50/gal.
Rynex	$20/gal.
CO_2	$0.12-0.25/lb.
Green Jet	$12.80/gal.

1. There is no solvent cost for Professional Wet Cleaning. The cost impact for this technology would be in an increase of water usage which is shown on Table VII-5.

A comparison was made on total annual operating costs for a typical dry cleaning facility. These costs were derived using the assumption that a typical dry cleaning facility dry cleans an average of about 46,600 pounds of clothes each year, based on the Facility Survey. This estimate was used to normalize the annual operating costs of each process for a typical facility.

According to the Facility Survey, it is estimated that a Perc dry cleaning facility uses about ten standard filters each year and the remaining alternatives, with the exception of CO_2 and Green Jet, use about seven standard filters each year. Standard filters were used for the cost comparison because this is the size filter that is most commonly used by the industry. There is a minimal cost difference if the facility uses jumbo filters. Also, in some cases machines will require a spin disk filter which will incur an additional cost of $90 for each filter (PPERC, 2002). The CO_2 systems typically will use two filters and a lint filter. The lint filter is typically changed out every two weeks. (Smerling, 2004) The Green Jet machine uses a filter bag, foam filters, and felts which can be cleaned and reused. Since this system is relatively new, the lifespan of the felts and filters is unknown and it is difficult to estimate annual replacement costs. However, if these components were to be replaced, the cost would be $100 for the filter bag, $20 for the foam filters and $4 for the set of eight felts.

Table VII-4 list the average therm and kilowatt hour (kWh) usage per dry cleaning machine for each process. Information gathered from the Machine Manufacturers Survey was used to calculate kWh for each machine. Therm usage was estimated based on numbers taken from a study conducted by PPERC. Cost estimates for gas usages were made using the July 2005 Pacific Gas and Electric (PG&E) rates of $1.21 for summer months (April 1 through October 31) and $1.25 for winter months (November 1 through December 31). The 2005 Sacramento Municipal Utility District (SMUD) average rate of $0.10 per kWh was used to estimate electricity usage. Calculations used to estimate electrical cost can be found in Appendix J.

Table VII-4. Average Machine Gas and Electricity Usage for Each Dry Cleaning Process

Machine Type	Therm Usage/Month[1]	kWh Usage/Typical Load
Perc	531	6.2
Hydrocarbon		
DF-2000	243	6.2
PureDry	243	6.2
Shell	243	6.2
EcoSolv	243	6.2
Stoddard Solvent	unknown	4.1 transfer machine 5.1 dryer/claimer
GreenEarth	297	6.2
Rynex	unknown	6.2
CO_2	156	9.3 - 9.7
Green Jet[2] Option A (208 volts) Option B (240 volts)	 unknown unknown	 5.8 6.7
Professional Wet Cleaning	388	3.2 washer 5.8 dryer

1. Source: PPERC, 2002 and PG&E, 2005
2. The Green Jet machine is equipped with the option to run on 208 volts or 240 volts.

Facilities also incur a cost for gasket replacement. When leaks are detected, repairs consist of replacing gaskets. If a facility owner hires a maintenance person to replace the gaskets they would be charged about $70 per hour for labor costs. The replacement cost for a set of gaskets is estimated at $274. For comparison purposes, the assumption is made that all gaskets would get replaced annually with a three hour charge for labor.

Not all processes incur a hazardous waste disposal cost. For those processes that produce hazardous waste there will be an additional operating cost for disposal. Waste disposal costs for each of the technologies were calculated based on the amount of still bottom and separator water produced. The amount of still bottom and separator water produced were obtained from either the Facility Survey or the study conducted by the Institute for Research and Technical Assistance (IRTA). A complete comparison of all operating cost can be found on Table VII-5. The machine cost values on Table VII-5 are based on a five year loan with a ten percent interest rate. Therefore, the values for the total annual costs on the table reflect the cost of the first five years of operation. For years six through the life of the machine, the total annual cost would not include a machine cost. The numbers on Table VII-5 are rounded to the nearest dollar value.

Table VII-5. Annual Cost Comparison for the First Five Years of a Typical Size Dry Cleaning Facility[1]

Technology	Solvent	Average Cost Detergent/Spotting Agents	Electricity Cost	Gas Cost[2]	Average Maintenance[3]	Affiliation Fee	Filters[4]	Cost to Replace Gaskets	Machine Cost[5]	Waste Disposal ($/gal.)[6]	Total Annual Cost[7]
Perc	$1,159[8]	$1,500	$ 850	$7,800	$ 375	N/A	$320	$500	$12,372	$2,500	$27,376
Hydrocarbon:											
DF-2000	$ 546	$1,500	$ 850	$3,580	$ 250	N/A	$371	$500	$17,674	$2,640	$27,911
PureDry	$1,170	$1,500	$ 850	$3,580	$ 250	N/A	$371	$500	$17,674	$2,640	$28,535
Shell	$ 390	$1,500	$ 850	$3,580	$ 250	N/A	$371	$500	$17,674	$2,640	$27,755
EcoSolv	$ 507	$1,500	$ 850	$3,580	$ 250	N/A	$371	$500	$17,674	$2,640	$27,872
Stoddard Solvent	$ 283	$1,500	$1,160[9]	$3,580	$ 600	N/A	$371	$500	$17,674	$2,640	$28,308
GreenEarth	$1,715	$1,100[10]	$ 850	$4,370	$ 850	$2,500	$371	$500	$18,202	$2,260[11]	$32,718
Rynex	$1,000	$1,500	$ 850	$3,580	$ 625	N/A	$371	$500	$17,674	$ 120[12]	$26,220
CO_2	$ 552	$1,500	$ 940	$2,290	$2,250	N/A	$238[12]	$500	$50,121	$ 490	$58,881
Professional Wet Cleaning	$0-$48[13]	$2,355[14] (detergent/ conditioner only)	$ 660 (washer/ dryer)	$5,700	$ 320[14]	N/A	N/A	$500	$11,343	N/A	$20,926
Green Jet	$1,152	$1,500	$ 600	Unknown	$ 400	N/A	$124[15]	N/A	$ 8,573	N/A	>$12,349[16]

1. Where applicable, cost are normalized to about 46,600 pounds of clothes dry cleaned per year for a typical facility. Additionally, costs are rounded to the nearest value.
2. Therm usage is taken from PPERC, 2004a report using current PG&E gas rates. The gas usage for Stoddard and Rynex machines are assumed to be the same as DF-2000.
3. Source: ARB, 2004, unless otherwise noted.
4. Cost for standard filters is used for this comparison. Standard filters cost $32 each. Annual costs may vary slightly if the machine uses jumbo filters and spin disk.
5. Out of pocket costs assuming a five year loan and a ten percent interest rate.
6. Waste disposal costs range from $6.75 to $10 per gallon (ARB, 2005b). The average of $7 was used for this table.
7. Cost given are with the assumption that the facility has no waste water treatment unit.
8. Includes the current $4 Assembly Bill 998 fee.
9. This includes electricity cost for transfer machine and dryer/claimer.
10. Source: ARB, 2005c.
11. Required only in some local districts.
12. Filter cost for a CO_2 machine are $26 each and lint filter cost are $9 each.
13. The cost given is the yearly financial impact increase for water when switching from dry cleaning to Professional Wet Cleaning (PPERC, 2002).
14. Source: PPERC, 2002.
15. This cost includes $4 for the set of eight felts; $100 for the lint bag; and $20 for the foam filters.
16. It is important to note that the total operating cost shown for the Green Jet technology will increase because gas costs are unknown.

C. Leak Detector Cost

Most dry cleaners currently use a halogenated-hydrocarbon detector made by TIF™ Instruments, Inc. (TIF) to check for vapor leaks. The cost of these detectors range from $170 to $250 depending on the model. After conducting a comparison of available detectors on the market, we found that there are detectors that may be able to give a more accurate reading of Perc concentration. The more sophisticated portable analyzer is the photo ionization detector (PID) and it has a cost range of $1,305 to $2,745. The C-21, Aeroqual 200, and Aeroqual 500 Gas sensors are comparable to the detectors presently used by the dry cleaning operators, but use the gas sensitive semiconductor technology. The Aeroqual 200 and 500 monitors are equipped with a digital display window. In addition, there are the D-TEK and TEK-Mate detectors that are comparable in cost to the TIF detectors. These gas sensors range from $160 to $1,200. The Draeger detector is also available with a cost of $1,600, but requires the use of a measuring chip, which is an additional cost of $67. This measuring chip is good for ten leak checks before it needs replacement. Table VII-6 shows a price comparison of the various makes and models.

Table VII-6. Comparison of Cost for Perc Concentration Detectors

Product	List Price
TIFXL-1A[1]	$ 170
TIF 8800 Combustible Gas Detector	$ 210
TIF 8800A Combustible Gas Detector	$ 240
TIFRX-1A[1]	$ 240
TIF 5750A[1]	$ 240
TIF 8850 Combustible Gas Detector	$ 250
C-21 Gas Sensor	$ 300
TEK-Mate	$ 160
D-TEK	$ 350
Aeroqual Monitor Series 200	$ 580
Aeroqual Monitor Series 500	$1,200
Micro5 PID	$1,305
Draeger	$1,600[2]
ToxiRAE Plus PID	$2,050
MiniRAE 2000 PID	$2,995
PhoCheck 1000 PID	$2,745

1. The TIFXL-1A has replaced the TIF 5000, TIF 5050A and TIFXL-1. The TIFRX-1A sensor has replaced the TIF 5550A and TIFRX-1. The TIF 5750A sensor has replaced the TIF 5650A.
2. There is an additional cost of $67 for the measuring chip needed after ten leak checks.

D. Control Technology

There are several control options for the dry cleaning industry. Both Perc and hydrocarbon machines can be purchased with a secondary control system. For comparison purposes the average cost of a 35-pound capacity primary control machine is $38,000 and the average cost of a 35-pound secondary control machine is $43,000.

Secondary control can be added to an existing machine with primary control for about $6,000. However, these retrofits do not typically perform as well as machines with secondary control installed at the factory (ARB, 2004; ARB, 2004e). Spin disks are also used as secondary control and can also be added on to a machine. The 1998 and newer machines are equipped with convertible filters, which means that the housing can be changed from cartridge to spin disk. The cost for this would be under $1,000, but for machines older than 1998 it would most likely be more (ARB, 2004e).

Some local air districts require dry cleaning facilities to install room enclosures with ventilation systems. In a July 2000 report prepared by ATC Associates, Inc. (AVES) for the ARB, costs associated with room enclosures were identified. There are three different types of enclosure/ventilation systems: vapor barrier rooms (VBRs), partial vapor barrier rooms (PVRs), and local ventilation systems (LOCs). The capital costs between the three different types vary according to the size of the machine and how the machine is constructed and installed. Some rooms may need to be custom built to fit in a corner of a room or as a stand-alone structure. Cost of construction will vary due to dry cleaner's needs and local air district requirements. Construction may include walls or the installation of a blower, exhaust system, foil, or fan. AVES contacted several construction companies and found that VBR construction varies between $5,300 to $8,500. The construction of a PVR would cost about $4,800, and the LOC would be about $3,100 to $4,300. (AVES, 2000; BLS, 2003)

VIII. EFFICACY

Efficacy, or the ability to effectively clean clothes, is an important factor to consider when considering dry cleaning alternatives. Properties to consider include: cleaning ability, 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.

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 (e.g., time, temperature, and mechanical actions) (U.S. EPA, 1998). Over 95 percent of all the soils is water soluble (Cleaners Family 2004). However, the Kauri Butanol (KB) number is used to estimate the degreasing efficiency or cleaning ability of a solvent. High KB values generally indicate a strong cleaning ability, whereas a low KB value indicates a weaker cleaning ability. Higher KB values are usually more efficient in removing oil and grease stains, but a lower KB value may be safer on some dyes, adhesives, and trim fabrics. Therefore, a solvent with a high KB value may not be suitable for all applications. Table VIII-1 on page VIII-4 lists KB values and summarizes cleaning performance for perchloroethylene (Perc) and the alternatives.

A. Hydrocarbon Solvent Cleaning

Typically, solvents are more effective in cleaning oil stains, and water-based chemicals are more effective in cleaning sugar, salt, and perspiration stains. The cleaning process can be enhanced with the use of spotting agents, alternative detergents, surfactant additives, and other process modifications such as cleaning time, temperature, or mechanical action (U.S. EPA, 1998). With the use of specially formulated detergents it is believed that hydrocarbon solvents have a cleaning capability almost equal to Perc.

Hydrocarbon solvents include: DF-2000™ Fluid (DF-2000), PureDry® (PureDry), Stoddard, EcoSolv® (EcoSolv) and Shell SOL 140 HT (Shell 140). Many operators who have switched from Perc to hydrocarbon solvents have reported that fabrics come out fresher with no odor and that they could clean a wide range of items. Some operators have complained that clothes feel oily; however, that could be due to improper drying. Some users also report that the clothes felt softer, were easier to press, and have a better finish than clothes cleaned in Perc. (JE, 2003)

PureDry is a blend of isoparaffinic hydrocarbon with a chemical additive produced by 3M. Efficacy testing for PureDry was done at Walt Disney World Textile Services. The clothes were cleaned to exceptional standards and without residual solvent odor in the finished garment (JE, 2003).

B. Rynex

The Air Resources Board (ARB) staff was not able to locate any independent efficacy testing for Rynex® (Rynex). However, the manufacturer claims that Rynex is a superior, gentle cleaner (when compared to Perc) that can handle a wide variety of fabrics. They also claim that it removes water soluble stains better than other solvents (Rynex, 2005), although this has not been verified with independent testing.

C. Water-based Cleaning Systems

Several tests have been conducted on water-based cleaning systems. In 1999, the Pollution Prevention Education and Research Center (PPERC) published a study on the performance evaluation of a facility converting from Perc dry cleaning to Professional Wet Cleaning (wet cleaning). The performance evaluation showed that over 99.5 percent of the garments that would have been dry cleaned were able to be wet cleaned. Claims for ruined garments were the same for both Perc dry cleaning and wet cleaning. Although the rate for additional work (redos) initially increased when the facility switched to wet cleaning, the rate dropped after a three-month transition period (PPERC, 1999). This may indicate that operator training has a considerable impact on the reported efficacy of this technology.

In 2003, the PPERC published an assessment of the Green Jet® (Green Jet) System. The assessment consisted of interviews and site visits with facility owners using Green Jet. Several advantages and disadvantages were identified. The shop owner indicated that the advantages of the system were that Green Jet did not require as much experience or skill as the hydrocarbon equipment and that there was minimum wrinkling and shrinkage. Some of the disadvantages pointed out by the owner were that: 1) stain removal was difficult; 2) heavily soiled garments could not be processed; and, 3) additional technology was required for garments with a high level of oil or water based stains, or for heavily soiled items. Overall, the assessment indicated that although Green Jet does a good job removing surface soils, it may need to be supplemented by another cleaning system to handle the full range of textiles, particularly in situations where heavily-soiled garments need to be processed. (PPERC, 2003)

D. Carbon Dioxide Cleaning

Although ARB staff was not able to locate any independent efficacy testing on CO_2 cleaning, one CO_2 machine manufacturer performed testing that was published by the United States Environmental Protection Agency's (U.S. EPA) Design for the Environment. Design for the Environment is a cooperative project between U.S. EPA and the garment and textile care industry garment and textile care partnership. One advantage, according to the manufacturer, is that the color retention can meet or exceed that of Perc dry cleaning. One exception to this is certain triacetate and acetate fabrics with specific yellow dispersive dyes. There was some shrinkage for garments

that were triacetate-based only. However, these garments are quite rare. Triacetate based garments may be better handled by professional wet cleaning. (U.S. EPA, 1999)

E. GreenEarth

The International Fabricare Institute (IFI) conducted testing on the efficacy of GreenEarth solvent under a contract to GreenEarth (IFI, 2002). This solvent contains decamethylcyclopentasiloxane (D_5), which is the primary cleaning agent in GreenEarth. GreenEarth was ranked in several different categories including: cleaning performance, the ability to handle garments that dry cleaners currently process, affordability, capital costs, health issues, and contamination issues.

Based on the testing, IFI concluded that stain removal was comparable to Perc, although not quite as effective in removing solvent soluble stains. For the purpose of the testing, solvent soluble stains included ball point ink, vegetable oil, and shoe polish. Overall, IFI found that GreenEarth cleaning is a viable alternative to Perc.

Table VIII-1 on the following page lists KB values and summarizes cleaning performance for Perc and the alternatives.

Table. VIII-1. Summary of KB and Surface Tension Values and Cleaning Performance of Dry Cleaning Solvents

Solvent	KB Value	Cleaning Performance
Perc	92	Oil-based stains, most water-based stains, silks, wools, rayons. Not good for delicates.
Stoddard	32-39	Less aggressive than Perc for oil-based stains. Can handle delicate garments.
PureDry	37-40	Less aggressive than Perc for oil-based stains. Can handle delicate garments.
Shell 140	N/A	Less aggressive than Perc for oil-based stains. Can handle delicate garments.
EcoSolv	26-27	Less aggressive than Perc for oil-based stains. Can handle delicate garments.
DF-2000	27	Less aggressive than Perc for oil-based stains. Can handle delicate garments
Green Jet (DWX-44 detergent)	N/A	Less aggressive than Perc. More effective in cleaning sugar, salt, perspiration stains. Good for delicates. Not good for heavily soiled garments.
Rynex	70	Aggressive, cleans water-soluble and oil-based stains.
GreenEarth	<20	Less aggressive than Perc for oil-based stains. Good for water-based stains, delicates.
CO_2	<10[1]	Good for all stains and most fabrics. Very effective in removing oils, greases, sweats.
Wet cleaning	N/A	Aggressive, good for both oil and water-based stains. Can handle delicate garments.

1. KB value depends on machine. Lowering temperature provides for a higher KB value.

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Appendix A

Dry Cleaning Facility Survey

Air Resources Board

Alan C. Lloyd, Ph.D.
Chairman
1001 I Street • P.O. Box 2815 • Sacramento, California 95812 • www.arb.ca.gov

Winston H. Hickox
Agency Secretary

Gray Davis
Governor

September 16, 2003

Dear Dry Cleaning Professional:

The Air Resources Board (ARB), in cooperation with the California Cleaners Association, the Korean Dry Cleaners-Laundry Association, other industry representatives, and the local air districts, has developed the Dry Cleaning Facility Survey (Survey). Please note that this Survey is different from other surveys or information requests that you may have received from your local air district or other government agencies. We are asking each dry cleaning facility to complete and return the enclosed Survey.

The Survey has two parts. Part 1 of the Survey requests general information about your dry cleaning business. Part 2 of the Survey requests more detailed information about the type and operation of your dry cleaning machine. **If you have more than one machine, please make copies of Part 2 and fill out one Part 2 per machine.** Please complete the enclosed Survey and return it to us using the enclosed postage paid envelope by October 10, 2003 at the address shown below:

Attention SSD Dry Cleaning Survey
State of California
Air Resources Board
P.O. Box 2815
Sacramento, CA 95812-9987

Please be advised that your responses on the Survey will be kept confidential. No information specifically identifying your facility will be published or distributed by ARB. We are providing the Survey and this letter in both English and Korean (the Korean translation is on the reverse side). We ask that all responses or correspondence be in English (if possible).

If you are not a dry cleaner, please complete the Company Information area (question 1, Page 1), write “not a dry cleaner” in the Comments area (question 6, Page 2), and return the Survey to us.

Why is the ARB asking me to complete and return this survey?

The ARB is currently conducting a statewide assessment of the California dry cleaning industry. The purpose of the assessment is to improve our understanding of the various technologies being used in the dry cleaning industry and to collect information regarding cost, efficacy, and environmental impact of those technologies. The enclosed survey is an

important part of this assessment. The information obtained during the assessment will help us determine the effectiveness of the current statewide Airborne Toxic Control Measure for Emissions of Perchloroethylene from Dry Cleaning Operations (Dry Cleaning ATCM) and whether the Dry Cleaning ATCM continues to be adequately protective of public health.

Why does the ARB need economic information about my business?

While conducting the assessment, we want to ensure that we have a reasonable understanding of how the various technologies may affect your business economically. Without specific information from you and other dry cleaners in California, we would need to use nationwide estimates that may not be as accurate as the information you provide.

Does the ARB have the legal authority to request the information on the Survey?

Yes. State law (Health and Safety Code, section 39660) authorizes the ARB to request and gather information needed to evaluate toxic air contaminants, such as perchloroethylene (Perc), and other substances. The ARB listed Perc as a toxic air contaminant in October 1991.

When do I need to return the Survey?

We are requesting that you return the Survey to us by October 10, 2003. In appreciation for returning the Survey to us by this date, you will automatically be entered into a drawing for one of five **FREE** environmental training classes.

Thank you in advance for your assistance in providing us this information. If you have any questions or comments, please do not hesitate to contact Hafizur Chowdhury at (916) 322-2275, Sonia Villalobos at (916) 327-5983, or Mei Fong at (916) 324-2570.

Sincerely,

Richard Boyd, Manager
Emissions Evaluation Section
Stationary Source Division

Enclosure

cc: See next page.

cc: Hafizur Chowdhury
Air Resources Engineer
Emissions Evaluation Section

Sonia Villalobos
Air Pollution Specialist
Emissions Evaluation Section

Mei Fong
Air Resources Engineer
Emissions Evaluation Section

Winston H. Hickox
Agency Secretary

Air Resources Board

Alan C. Lloyd, Ph.D.
Chairman
1001 I Street • P.O. Box 2815 • Sacramento, California 95812 • www.arb.ca.gov

Gray Davis
Governor

September 12, 2003

드라이 크리닝업 종사자 분들께:

대기자원 관리국(ARB)에서는, 켈리포니아주 세탁협회, 한인 드라이 크리너-세탁협회, 그 외 관계 된 기타 업계 대표, 그리고 대기 관리 지역사무소의 협조아래 여기 동봉하는 질문서를 제작하였음니다. 이 질문서는 대기 관리 지역사무소나 다른 정부기관에서 실시한 질문서나 정보 요청서와는 다릅니다. 저희는 크리닝업 종사자 분들께서 이 질문서에 답변 후 제출하여주시기를 부탁드립니다.

여기에 동봉하는 드라이 크리닝에 관한 질문서는 두 부분으로 나누어저있읍니다. 첫 부분은 귀 업소에 관한 일반적인 질문입니다. 두번째 부분은 현 기계의 종류 및 가동상태에 대한 좀더 세부적인 질문입니다. **만약 세탁기게를 하나 이상 소유하고 계실경우, 질문서의 두번째 부분을 복사하여 각 세탁기계당 하나씩 제출해주십시요.** 동봉한 질문서에 답변하여서 October 10, 2003 까지 아래주소로 제출하여 주시기를 부탁드립니다.

Attention SSD Dry Cleaning Survey
State of California
Air Resources Board
P.O. Box 2815
Sacramento, CA 95812-9987

귀하의 답변내용은 기밀로 보장됩니다. ARB는 귀하의 업소가 타인에게 밝혀질만한 자료는 발표하거나 분포하지 않을것입니다. 영어와 한국어로 번역된 질문서와 편지를 보내드립니다 (한국어 번역은 뒷면). 대기자원관리국으로 보내는 모든 편지와 답변은 가능한 영어로 작성해 주시기바랍니다.

귀하의 업소에서 드라이 크리닝을하지않을 경우, 첫번째 페이지 1번 업소조사 란에 답하신 후, 두번째 페이지 6번 기타사항 란에 "드라이 크리닝을하지않음." 이라고 쓰신 후에 제출하여주시기를 부탁드립니다.

<u>대기자원관리국에서 나의 도움이 필요한 이유는 무엇입니까?</u>

ARB는 현제 켈리포니아 드라이 크리닝업소를 평가하려합니다. 이번 평가의 목적은, 드라이 크리닝업소에서 사용하는 기술에대한 저희의 이해를높이고 또, 그런 기술에 드는 비용과 효율성에대한 정보를 얻기위합입니다. 동봉한 질문서는 이번

The energy challenge facing California is real. Every Californian needs to take immediate action to reduce energy consumption. For a list of simple ways you can reduce demand and cut your energy costs, see our Website: http://www.arb.ca.gov.

평가에 쓰일 중요한 자료입니다. 이번 평가 자료는 현제의 드라이 크리닝업체로부터 대기에 유출되는 독성 물질 펄크 규제법안 (Dry Cleaning ATCM)의 유효성과, 또 이 법안 이 적합한 공중보건안으로 계속 쓰일수 있는지 결정하는데 도움이 될것입니다.

<u>대기자원관리국은 왜 나의 업소 경영정보를 필요로 합니까?</u>

저희는 이번 평가를 통하여, 여러가지 다양한 기술이 귀하의 사업에 미치는 경제적 영향에 대하여 저희가 잘 알고있는지 확인하고자 합니다. 귀하와 기타 켈리포니아에서 드라이 크리닝업에 종사하시는 분들로부터의 자료없이는 전국으로 통용되는 예산치를 기준으로 사용하게됨으로 귀하께서 제공하는 자료만큼 정확한 정보가 될수 없을 것입니다.

<u>대기자원관리국이 질문서에서 요구하는 정보를 요청할수있는 법적인 근거를 가지고 있읍니까?</u>

네. 켈리포니아주 법률(보건 및 안전에 관한 법 제 39660 조) 에 의하여 ARB 는 펄크 (Perc)와 같은 유해한 대기오염물질을 관리규정하는데 필요한 정보를 요구하고 수집할 권한이 있읍니다. 대기자원관리국은 펄크 (Perc) 를 유해한 대기오염물질로 1991년 10월에 지정하였읍니다.

<u>이 질문서는 언제까지 제출하여야 합니까?</u>

October 10, 2003 까지보내 주시기를 바랍니다. 날짜안에 제출하여 주시는것에 대한 감사의 뜻에서, 제출하신분 중 다섯 분을 추첨하여 드라이 크리닝 환경 연수교육을 무료로 드립니다.

저희의 자료수집에 도움 주신것에대하여 미리 감사드립니다. 이 드라이크리닝 질문서에대해 의문이 있거나 작성에 도움이 필요할경우, 주저없이 Hafizur Chowdhury (916) 322-2275, Sonia Villalobos (916) 327-5983 또는, Mei Fong (916) 324-2570 에게 연락해주십시요.

Sincerely,

Richard Boyd, Manager
Emissions Evaluation Section
Stationary Source Division

Enclosure

cc: Hafizur Chowdhury
Air Resources Engineer
Emissions Evaluation Section

Sonia Villalobos
Air Pollution Specialist
Emissions Evaluation Section

Mei Fong
Air Resources Engineer
Emissions Evaluation Section

California Environmental Protection Agency
AIR RESOURCES BOARD

DRY CLEANING FACILITY SURVEY

PART 1

QUESTIONS AND ASSISTANCE

Thank you for taking the time to complete this survey. Please be advised that the survey has two parts (Part 1 and Part 2) and your response on both parts is appreciated. If you have any questions about the dry cleaning facility survey or need assistance in completing the survey, please feel free to contact any of the following staff:

Hafizur Chowdhury
Phone: (916) 322-2275
E-mail: hchowdhu@arb.ca.gov

Sonia Villalobos
Phone: (916) 327-5983
E-mail: svillalo@arb.ca.gov

Mei Fong
Phone: (916) 324-2570
E-mail: sfong@arb.ca.gov

Please return the completed survey by October 10, 2003 and mail to:

Attention SSD Dry Cleaning Survey
California Air Resources Board
P. O. Box 2815
Sacramento, CA 95812

If you return the completed survey by October 10, 2003, you will automatically be entered into a drawing for one of five **FREE** Dry Cleaning Environmental Training Classes.

1. COMPANY INFORMATION *(do not include personal residential address)*

Date	_____	Company Name	_____
Contact Person	_____	Facility Address	_____
Phone Number	(____) _____	City, State, Zip	_____
Fax Number	(____) _____	Mailing Address	_____
E-mail Address	_____	City, State, Zip	_____

Survey responses will be kept confidential as provided under California law

2. BUSINESS INFORMATION

How long have you owned the facility? _____ Years _____ Months

Do you dry clean on-site? Yes [ ] No [ ] If no, please provide contact information of the dry cleaning facility you send your clothes to in number 6 (comments area on page 2) and return the survey to us.

Business Type: Plant/Retail [ ] Industrial [ ] Government [ ] Nonprofit [ ] Hotel/Motel [ ] Other [ ]

Business Status: Independently Owned [ ] Chain Operation [ ] Franchise [ ]

How many total dry cleaning machines are in the facility? Perc _____ Non-Perc _____

If facility is a chain operation: Owner's name _____ Phone (_____)_____

Annual Receipts From Total Operation :

Less than $100,000 [ ] $100,001 - $500,000 [ ] $500,001 - above [ ]

Percent Annual Receipts From Dry Cleaning Only:

Less than 25% [ ] 25-50% [ ] 50-75% [ ] more than 75% [ ]

Total Facility Employees:

Full Time _____ Part Time _____ Average Part Time Hours/week _____

Business Hours:

Monday thru Friday ____ AM to ____ PM

Saturday ____ AM to ____ PM

Sunday ____ AM to ____ PM

California Environmental Protection Agency
AIR RESOURCES BOARD

DRY CLEANING FACILITY SURVEY
PART 1 (continued)

3. OPERATING INFORMATION *(check all that apply)*

Solvent Type Used:

Perc [ ]
DF-2000 [ ]
Rynex [ ]
Stoddard [ ]
Green Earth [ ]
Other _____

Water (wet cleaning) [ ]
Green Jet [ ]
Pure Dry [ ]
Eco Solve [ ]
Liquid CO_2 [ ]

What do you do with your separator water?

Wastewater treatment unit [ ]
-Type: Evaporator [ ]
Atomizer [ ] Liquid Discharge [ ]
-Make _____ Model _____
Collected by waste hauler [ ]
Discharged to sewer [ ]
Used in a cooling tower [ ]
Used to generate steam [ ]
Other _____

From whom do you purchase your solvent?

Company name _____ Phone (_____)_____
Company name _____ Phone (_____)_____

Who collects your waste (e.g., still bottoms, separator water, filters)?

Company name _____ Phone (_____)_____
Company name _____ Phone (_____)_____

4. FACILITY INFORMATION *(only answer those you know)*

Facility Location: Do people live in the building where your facility is located? Yes [ ] No [ ] If yes, then
- Do people live above the building? Yes [ ] No [ ]
- Do people live next to the building (share a wall with your facility)? Yes [ ] No [ ]

Facility size:

Area _____ square feet Height _____ feet

Nearest neighbors:

Business _____ feet Residence _____ feet Park _____ feet
School (K-12) _____ feet Day Care _____ feet Hospital _____ feet Senior Community _____ feet

Type of ventilation systems used in dry cleaning facility *(check all that apply):*

Wall fan [ ] Powered exhaust fan (ceiling) [ ] Non-powered exhaust fan (ceiling) [ ] Open door [ ] Open window [ ]

Vapor barrier (room enclosure) around the machine: Yes [ ] No [ ] If yes, is it: Total [ ] Partial [ ]

Do you have a local ventilation system (such as fume/exhaust hood or shroud over machine)? Yes [ ] No [ ]

5. FUTURE MACHINE PURCHASE/REPLACEMENT *(check all that apply)*

If you had to purchase or replace a machine today, would you purchase a new or used machine? New [ ] Used [ ]

What type of solvent would you use for this future machine?

- Perc [ ] DF-2000 [ ] Rynex [ ] Stoddard [ ] Green Earth [ ] Liquid CO_2 [ ] Eco Solve [ ]
- Pure Dry [ ] Water (wet cleaning) [ ] Other _____

6. COMMENTS *(Optional)*

_____
_____
_____
_____

California Environmental Protection Agency
AIR RESOURCES BOARD

DRY CLEANING FACILITY SURVEY

PART 2

Please Copy and Complete This Page for Each Additional Machine

A. MACHINE INFORMATION

What year did you purchase your machine? _____ Did you buy it new or used? New [ ] Used [ ]

Machine brand _____ Model _____ Rated Capacity _____ pounds

Average pounds per load _____ Average number of loads per week _____

Total amount of clothes dry cleaned per year (pounds) 2000 _____ 2001 _____ 2002 _____

Machine Type:

Transfer [ ]
Dry-to-dry with primary control [ ]
Dry-to-dry with secondary control [ ]
Converted (vent to no-vent) [ ]
Wet Cleaning [ ]
Other _____

Solvent purchased per Machine (gallons):

	2000	2001	2002
Perc	_____	_____	_____
DF-2000	_____	_____	_____
Rynex	_____	_____	_____
Stoddard	_____	_____	_____
Green Earth	_____	_____	_____
Liquid CO_2	_____	_____	_____
Eco Solve	_____	_____	_____
Pure Dry	_____	_____	_____
Other _____	_____	_____	_____

Normal machine operating schedule: _____ AM to _____ PM days/week _____

B. WASTE INFORMATION

Still Bottoms Removed (gallons) 2000 _____ 2001 _____ 2002 _____

Separator Water Produced (gallons) 2000 _____ 2001 _____ 2002 _____

Filters Used:

(1) Cartridge

Number of filters disposed of in:

(a) Standard (7-inch diameter, 14 inches high) 2000 _____ 2001 _____ 2002 _____

(b) Split (13-inch diameter, 9 inches high) 2000 _____ 2001 _____ 2002 _____

(c) Jumbo (13-inch diameter, 18 inches high) 2000 _____ 2001 _____ 2002 _____

(2) Spin-Disk

Non-Powdered [ ] Powdered [ ]

C. MAINTENANCE INFORMATION

How often do you inspect the machine?

Daily [ ] Weekly [ ] Monthly [ ] Bi-monthly [ ] Quarterly [ ] Twice a year [ ] Yearly [ ] Never [ ]

-What type of leak detector (instruments) is used during inspection? _____

How many certified operators do you have on-site? _____

If your machine has a secondary control, how often do you regenerate the carbon?

According to machine manufacturer's specification [ ]

Machine regenerates carbon automatically [ ]

Never [ ]

Other _____

California Environmental Protection Agency
AIR RESOURCES BOARD

드라이크리닝 업소 질문서
파트 1

문의사항과 도움

시간를 내주셔서 감사합니다. 이 질문서는 두 파트로 나누어저있음을 유의하시고, 두 파트(파트1 과 파트2) 모두에 응답하여주시기를 부탁드립니다. 이 드라이크리닝 질문서에대해 의문이 있거나 작성에 도움이 필요할경우, 아래 직원에게 연락해주십시요.

Hafizur Chowdhury
Phone: (916) 322-2275
E-mail: hchowdhu@arb.ca.gov

Sonia Villalobos
Phone: (916) 327-5983
E-mail: svillalo@arb.ca.gov

Mei Fong
Phone: (916) 324-2570
E-mail: sfong@arb.ca.gov

질문서에 답변하여서 October 10, 2003 까지 아래주소로 제출하여주시기를 부탁드립니다.

Attention SSD Drycleaning Survey
California Air Resources Board
P. O. Box 2815
Sacramento, CA 95812

이 질문서에 답변하셔서 October 10, 2003 까지 제출하시면, 그중 다섯 분을 추첨하여 드라이 크리닝 환경 연수교육을 무료로 드립니다.

1. 업소 조사 (개인거주지 주소는 쓰지말아주십시요).

오늘날짜	_____	업소 이름	_____
연락처 사람 이름	_____	업소 주소	_____
전화번호	( ) _____	시, 주, 짚 코드	_____
팩스 번호	( ) _____	우편물 배달 주소	_____
이메일 주소	_____	시, 주, 짚 코드	_____

답변내용은 켈리포니아 법에의하여 기밀로 보장됩니다.

2. 사업경영 조사

현 상업 소유기간은 얼마나 됩니까? _____ 년 _____ 월

현 장소에 드라이 크리닝기계가 있읍니까? 네 [ ] 아니요 [ ] "아니요" 일 경우드라이 크리닝을보내는 거래 연락처를 6번 질문칸(기타 사항) 에 써서 이 질문서를 제출해 주십시요.

업체 종류: 공장/소매 [ ] 산업체 [ ] 관영 [ ] 비영리법인 [ ] 호텔/모텔 [ ] 기타 [ ]

업체소유형태: 개인소유 [ ] 체인형태 소유 [ ] 푸렌차이스 [ ]

현 업소에 있는 총 드라이 크리닝 기계는 몇대입니까? 펄크사용기계 _____ 펄크외 사용 기계 _____

체인형태업소일 경우, 소유주의 이름 _____ 전화번호 (_____)_____

총 연수입:

$100,000 이하 [ ] $100,001 - $500,000 사이 [ ] $500,001 이상 [ ]

총 연수입중 드라이 크리닝수입이 차지하는 비율:

25%이하 [ ] 25-50% 사이 [ ] 50-75% 사이 [ ] 75% 이상 [ ]

종업원 수 :

풀타임 _____명 파트타임_____ 명 평균 파트타임 시간 주 ___ 시간

영업시간 :

월요일 – 금요일 ____ AM 부터 ____ PM 까지

토요일 ____ AM 부터 ____ PM 까지

일요일 ____ AM 부터 ____ PM 까지

California Environmental Protection Agency
AIR RESOURCES BOARD

드라이크리닝 업소 질문서
파트 1 (계속)

3. 기계 가동 (해당사항 모두 표시)

사용하는 쏠벤트 종류 :

펄크 [ ]
DF-2000 [ ]
Rynex [ ]
Stoddard [ ]
Green Earth [ ]
기타 _____

물 (물세탁) [ ]
Green Jet [ ]
Pure Dry [ ]
Eco Solve [ ]
Liquid CO_2 [ ]

분리된 물처리는 어떻게하십니까 ?

폐수처리 장치 [ ]
-종류 : 증발기 [ ]
아토마이저 [ ] 액체배수 [ ]
-상표 _____ 모델 _____
폐수처리자가 수거[ ]
하수구에 버림 [ ]
냉각수조에 (쿨링타월)에 사용 [ ]
스팀에 사용 [ ]
기타 _____

쏠벤트구입은 누구에게서 합니까 ?

회사 이름 _____ 전화번호 (_____)_____
회사 이름 _____ 전화번호 (_____)_____

폐기물 수거는 누가합니까 ?

회사 이름 _____ 전화번호 (_____)_____
회사 이름 _____ 전화번호 (_____)_____

4. 건물조사 (아는대로 기입해 주십시요.)

건물 위치: 건물내에 사람이 거주합니까 ? 네 [ ] 아니요 [ ] "네" 일경우,
- 현업소 바로 윗층에 사람이 거주합니까? 네 [ ] 아니요 [ ]
- 담을 같이한 바로 옆건물에 사람이 거주합니까? 네[ ] 아니요[ ]

업소크기 :

면적 _____ 스퀘어피트 높이 _____ 피트

주변지역과의 거리 :

상가 _____피트 주택가 _____피트 공원 _____피트
국민학교 _____ 피트 유아원 _____ 피트 병원 _____ 피트 노인 컴뮤니티 _____ 피트

드라이 크리닝 작업장에 있는 환기시설 (해당사항 모두 표시):

벽에 고정된 환풍기 [ ] 전동환풍기 (천장) [ ] 통풍기 (천장) [ ] 문을열음 [ ] 창문을 열음 [ ]
기계주위 습기차단 장치(작업장 내): 네 [ ] 아니요 [ ] "네" 일경우, 전체 [ ] 부분 [ ]
부분환기시설이 있읍니까? (예로, 환기후드나 덮개) 네 [ ] 아니요 [ ]

5. 장래 기계구입/교체 여부 (해당사항 모두 표시)

만약 오늘 당장 세탁기계를 구입이나 교체할 경우, 어느 기계를 선택하시겠읍니까? 새 기계 [ ] 중고 [ ]
어떤 종류의 쏠벤트를 사용하시겠읍니까?
- 펄크 [ ] DF-2000 [ ] Rynex [ ] Stoddard [ ] Green Earth [ ] Liquid CO_2 [ ] Eco Solve [ ]
- Pure Dry [ ] 물 (물세탁) [ ] 기타 _____

6. 기타 사항

_____
_____
_____
_____

California Environmental Protection Agency
AIR RESOURCES BOARD

드라이크리닝 업소 질문서

파트 2

이 페이지를 복사하여서 각 기계당 한장씩 작성 제출해 주십시요 .

A. 기계 조사

몇년도에 이 기계를 구입하셨읍니까? _____ 새 기계 구입 [ ] 중고 구입 [ ]

기계 상표 _____ 모델_____ 용량 _____ 파운드

평균 한번 세탁 파운드 량 _____ 주 평균세탁 수 _____

년 드라이크리닝한 세탁물의 총 무게 (파운드) 2000 _____ 2001 _____ 2002 _____

기계 종류 :

트렌스퍼 [ ]
드라이 투 드라이 일차 제어 장치 [ ]
드라이 투 드라이 이차 제어 장치 [ ]
개조된 기계 (배기에서 무 배기용) [ ]
물 세탁 [ ]
기타 _____

기계당 쏠벤트구입량 (갈론):

	2000	2001	2002
펄크	_____	_____	_____
DF-2000	_____	_____	_____
Rynex	_____	_____	_____
Stoddard	_____	_____	_____
Green Earth	_____	_____	_____
Liquid CO_2	_____	_____	_____
Eco Solve	_____	_____	_____
Pure Dry	_____	_____	_____
기타 _____	_____	_____	_____

기계가동 시간 : _____ AM 부터 _____ PM 까지 주당 _____일

B. 폐기물 조사

증류기 바닥에서 제거된 폐기물 양 (갈론) 2000 _____ 2001 _____ 2002 _____

분리기에서 나온 물 (갈론) 2000 _____ 2001 _____ 2002 _____

사용하는 필터:

(1) 카트리지 **소모한 필터 수 :**

(a) 스탠다드 (지름 7인치, 길이14 인치) 2000 _____ 2001 _____ 2002 _____

(b) 스프릿(지름13인치, 길이9인치) 2000 _____ 2001 _____ 2002 _____

(c) 점보 (지름 13인치, 길이18 인치) 2000 _____ 2001 _____ 2002 _____

(2) 스핀 디스크

파우더가 아닌 종류 [ ] 파우더 종류 [ ]

C. 정비 조사

얼마나 자주 기계정비를 합니까?

매일 [ ] 매주한번 [ ] 매월한번 [ ] 두달마다 [ ] 세달마다 [ ] 일년에두번 [ ] 매년 한번 [ ] 안함 [ ]

-기계정비 과정중, 누수조사는 어떻게(무슨점검 기계로) 확인 하십니까? _____

작업장에 정식허가받은 기계가동자가 몇 명이 있읍니까? _____

이 기계에 이차 제어 장치가 있으면, carbon(카본)은 얼마나 자주 재 생산합니까?

기계제작 회사의 설명서에 따라서 [ ]

기계가 자동으로 카본생산 [ ]

안함 [ ]

기타 _____

Appendix B

Dry Cleaning Site Visit Survey

California Environmental Protection Agency
AIR RESOURCES BOARD

DRY CLEANING SITE VISIT SURVEY 2003

1. COMPANY INFORMATION

Date	_____	Facility Name	_____
Contact Person	_____	Street Address	_____
Phone Number	( ) _____	City, State, Zip	_____
Fax Number	( ) _____	Cross Street	_____
E-mail Address	_____	GPS Lat/Long	_____

2. BUSINESS INFORMATION

How long have you own the facility _____

Type of business/ Business Status _____

How much do you charge to dry clean a pair of pants? _____

Amount of annual receipt (dollar) from total operation _____

Percent of annul receipts from dry cleaning only _____

Number of employees both full-time/part-time _____

Average part time employee hours per day _____

Business Hours:

Monday thru Friday ____ AM to ____ PM Saturday ____ AM to ____ PM

Sunday ____ AM to ____ PM

3. OPERATING INFORMATION

What type of solvent(s) used in the machine(s)? _____

What do you do with separator water? _____

From whom do you purchase your solvent? Company _____ Phone _____

Who collects your waste? Company _____ Phone _____

4. FACILITY INFORMATION

Physical location of the facility _____

Do people live in the building where facility is located? _____

Do people live above the building? _____

Do people live next to (share a facility wall) the building? _____

Area of the facility _____ square feet

Facility Height _____ feet

Front Door height _____ feet, width _____ feet

Back Door height _____ feet, width _____ feet

Window height _____ feet, width _____ feet

California Environmental Protection Agency
AIR RESOURCES BOARD

DRY CLEANING SITE VISIT SURVEY 2003

4. FACILITY INFORMATION *(continued)*

Is the facility a part of a larger building? _____ Stand alone building? _____

Dimension of the building: Length _____ feet Width _____ feet Height _____ feet

Does the facility have a stack? _____

Stack height _____ feet Stack diameter _____ feet

Does the stack has a raincap/horizontal release? _____ Stack airflow _____ cfm

Does each machine have separate stacks or do they combine into single stack? _____

Distance measured from door to door:

Nearest business _____ feet Residence _____ feet

Nearest (School/Day Care/Hospital/Park/Senior Community) _____ feet

What type of fan(s) do you have in your facility? _____

Is there a vapor barrier (room enclosure) around the machine? _____

Do you still keep your doors open when the weather is bad? _____

5. FUTURE MACHINE PURCHASE/REPLACEMENT

If you had to purchase or replace a machine today, would you purchase a new or used machine? _____

What type of solvent would you use for this future machine? _____

What do you think of the alternative solvents? (write in comments, section 9)

6. MACHINE INFORMATION

What year did you purchase your machine? _____ Did you buy it new or used _____

Machine brand type _____ Model _____

Rated Capacity _____ pounds Machine age _____

Average pounds per load _____ Average number of loads per week _____

Total amount of clothes dry cleaned per year (pounds) 2000 _____ 2001 _____ 2002 _____

Have you done any retrofit to the machine? _____

Does machine have a shroud? _____ Does machine have a lock-out device? _____

How much **solvent** used per machine(gallons) in year 2000 _____ 2001 _____ 2002 _____

What is your normal machine operating hours? _____ AM to _____ PM

How many days do you operate the machine per week? _____

In a year, how many times do you have a minor spill of solvent? _____

In a year, how many times do you have a major spill of solvent?_____

California Environmental Protection Agency
AIR RESOURCES BOARD

DRY CLEANING SITE VISIT SURVEY 2003

7. WASTE INFORMATION

How much still bottoms (gallons) removed in year 2000 _____ 2001 _____ 2002 _____

How much separator water (gallons) produced in year 2000 _____ 2001 _____ 2002 _____

What type of cartridges do you use in your machine? (e.g.: standard, split or jumbo) _____

What do you do in preparation to changing the filters? _____

How do you dispose of the filters? _____

How many filters disposed in year 2000 _____ 2001 _____ 2002 _____

If your machine needs Spin-Disk filter, then is it powdered or non powdered? _____

8. MAINTENANCE INFORMATION

How often do you inspect the machine? _____

What type of leak detector used during inspection? _____

In a year, how many time is a leak being detected? _____

Do you have extra gaskets handy?_____

How often do you replace gaskets? _____

How many certified operators do you have on-site? _____

If your machine has a secondary control, how often do you regenerate the carbon? _____

9. COMMENTS

_____

_____

_____

_____

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_____

Appendix C

Machine Manufacturer’s Survey

California Environmental Protection Agency
AIR RESOURCES BOARD

MACHINE MANUFACTURER SURVEY

QUESTIONS AND ASSISTANCE

Thank you for taking the time to complete this survey. If you have any questions about the manufacturer survey or need assistance in completing the survey, please feel free to contact any of the following staff:

Hafizur Chowdhury
Phone: (916) 322-2275
E-mail: hchowdhu@arb.ca.gov

Sonia Villalobos
Phone: (916) 327-5983
E-mail: svillalo@arb.ca.gov

Mei Fong
Phone: (916) 324-2570
E-mail: sfong@arb.ca.gov

Please return the completed survey by April 30, 2004 and mail to:

Attention SSD Dry Cleaning Survey
California Air Resources Board
P. O. Box 2815
Sacramento, CA 95812

1. COMPANY INFORMATION *(do not include personal residential address)*

Date	_____	Company Name	_____
Contact Person	_____	Facility Address	_____
Phone Number	( ) _____	City, State, Zip	_____
Fax Number	( ) _____	Mailing Address	_____
E-mail Address	_____	City, State, Zip	_____

2. NOTES FOR TABLE ON PAGE 2 AND PAGE 3

Instruction: The description of each item on page 2 and page 3 are elaborated below to complete the survey accurately:

a:	Specify the solvent types for each machine brand (for example: perc, DF-2000™, Rynex®, Stoddard™, Green Earth®, Water (wet cleaning), Green Jet™, Pure Dry®, Eco Solve™, Liquid CO_2 or others).
b:	Specify each machine brand (for example: Bowe Permac, Multimatic, Crown, Fluormatic, Lindus etc.).
c:	Specify types of machine (for example: Dry-to-dry primary control, Dry-to-dry secondary control, Transfer, Wet Cleaning - Washer, Wet Cleaning - Dryer, or others).
d:	Specify each model for its type (for example: P546, 380BC, ML45, RS373, BT37 etc.).
e:	Specify each model rated capacity (for example: 35 lbs, 40 lbs, 45 lbs, 60 lbs etc.).
f:	Provide the cycle time in minutes.
g:	Provide the list price ($US) for each type of machine that is sold in the State of California.
h:	Specify each model power requirement to operate the machine such as 110V, 220V, Amperes, average hours
i:	Specify gas or steam requirements to operate the machine (for example: average monthly cost ($US) of gas or steam generation).
j:	Estimated yearly maintenance cost ($US) for each model stated in column 10 of page 2.
k:	Provide the maintance requirements for each model as stated in page 3 (for example: daily, weekly, monthly etc.)
l:	Specify the type of control equipment for each model.
m:	Briefly describe how each modeled machine operates. In addition, specify if and when any part of the machine is under pressure or under vacuum. Please use extra sheet as an attachment if necessary.
n:	If you have different types of machine maintenance schedule besides daily, weekly, monthly etc., then specify under 'Other'.

California Environmental Protection Agency
AIR RESOURCES BOARD

MACHINE MANUFACTURER SURVEY

Solvent[a] Type	Machine[b] Brand	Machine[c] Types	Model[d]	Rated[e] Capacity (lbs)	Cycle[f] Time (minutes)	List[g] Machine Price ($)	Electrical[h] Requirement	Gas/Steam[i] Requirement	Yearly[j] Maintenance Cost ($)
.									

California Environmental Protection Agency
AIR RESOURCES BOARD

MACHINE MANUFACTURER SURVEY

Maintenance Requirements[k]								Control[l] Equipments	Short Description of Equipment Operation[m]
Model[d]	Every 4th Load	Daily	Weekly	Monthly	Every 3 Months	Every 6 Months	Every 12 Months		
	Other[n] _____	Other[n] _____	Other[n] _____	Other[n] _____	Other[n] _____	Other[n] _____	Other[n] _____		
.									

California Environmental Protection Agency
AIR RESOURCES BOARD

MACHINE MANUFACTURER SURVEY

COMMENTS

Appendix D

Standard Operating Procedure for the Determination of Tetrachloroethylene in Dry Cleaning Sludge by Gas Chromatograhy - FID

California Environmental Protection Agency

Air Resources Board

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF TETRACHLOROETHYLENE IN DRY CLEANING SLUDGE BY GAS CHROMATOGRAPHY-FID

January 31, 2005, Revision 1.0

DISCLAIMER: Mention of any trade name or commercial product in Method 310 and associated Standard Operating Procedures does not constitute endorsement or recommendation of this product by the Air Resources Board. Specific brand names and instrument descriptions listed in the Standard Operating Procedures are equipment used by the ARB laboratory. Any functionally equivalent instrumentation can be used.

1 INTRODUCTION

The procedure follows closely MLD SOP SAS07, with modifications to analyze perchloroethylene from dry cleaning sludge.

This method is suitable for the determination of the exempt compounds: ethanol (AP/DO only), acetone, methyl acetate and tetrachloroethylene (perchloroethylene). Additional analytes are methanol, isopropanol, 1-propanol, isobutanol, and limonene.

2 SUMMARY OF METHOD

The dry cleaning sludge samples from each machine is collected in triplicate in a 250 milliliter (ml) glass jar. One aliquot is used to determine sample density and another aliquot is used to determine tetrachloroethylene concentration. The samples of dry cleaning sludge are prepared as 1:10 wt. / volume dilutions in 1-methoxy-2-propanol (MPA). After dilution and thorough mixing, the insoluble material is allowed to settle out, or the sample filtered to remove insoluble material. The diluted sample is then analyzed on a gas chromatograph equipped with a flame ionization detector(FID). The data is reported as percent perchloroethylene in the dry cleaning sludge.

3 INTERFERENCES AND LIMITATIONS

With the potential increase in the number of interfering compounds, overlap of perchloroethylene's retention time may occur. Care must be taken to make certain of the identity of the compound, if possible through gas-chromatography-mass spectrometry.

4 INSTRUMENTATION AND EQUIPMENT

4.1 Gas Chromatograph (GC) configured with a Flame Ionization Detector (FID),

4.1.1 GC Column: J & W DB-624, 30 m x 0.32 mm I.D. with 1.8 µm film,

4.1.2 GC Parameters are as follows:

<u>Oven Conditions</u>	
Initial temperature:	35℃
Initial time:	5.0 min
Rate:	10℃/min
Final temperature:	200℃
Final time:	1.0 min

Run time:	22.5 min
Oven equilibration:	0.3 min
Injector temperature:	250℃
Detector temperature:	250℃
Carrier gas (He):	10 psi (26 cm/sec)
DET B FID:	ON
EPP B:	9.5 psi @ 35°C
Split Flow:	100 mL/min

4.2 Volumetric Flasks:

4.2.1 10 and 500 ml,

4.3 Rainin Pipettors:

4.3.1 250 µL, 1.0 ml, 2.5 ml with tips,

4.4 Vials and Jars:

4.4.1 20 mL, for standards,

4.4.2 8 mL with PTFE-lined cap, for standards and dilutions,

4.4.3 2 mL with caps, for GC analysis,

4.4.4 250 ml widemouth glass jars with PTFE –lined caps,

4.4.5 15 ml graduated disposable polypropylene conical tubes,

4.5 Analytical Balance:

4.5.1 Sartorious ME215S,

4.5.2 Sartorious MC1,

4.5.3 Sartorious LC6201S,

4.6 Vortex Mixer, variable speed.

5 REAGENTS

5.1 1-Methoxy-2-propanol (MPA), 98%,

5.2 Analyte, tetrachloroethylene, spectrophotometric grade,

5.3 Stock Standards: The 80 mg/mL stock standard is prepared gravimetrically.

5.4 Control/Check Stock Solution: A control/check stock solution is prepared using acetone in MPA. The analyte is weighed in the preparation of the stock, so the concentration is in g/mL.

5.5 Helium, grade 5,

5.6 Air, compressed, ultra high purity,

5.7 Hydrogen Generator, Whatman, model 75-32 or equivalent.

6 PROCEDURE

6.1 Sample Collection:

6.1.1 Samples are collected in triplicate from each dry cleaning machine.

6.1.2 Using a long wooden or metal stirring rod, stir the collected sludge to resuspend the solid material as much as possible.

6.1.3 Using a cup or jar fill a 250 ml jar with the stirred dry cleaning sludge.

6.1.4 Clean the jar, seal the container, and attach the sample identification label.

6.1.5 Repeat this process two more times making sure the sludge is remixed between each sampling.

6.1.6 Place the triplicate samples in a travel container (such as an ice chest) at ambient temperature for transport back to the laboratory.

6.2 Sample Preparation:

6.2.1 The collected samples are given a unique identification number and entered into the laboratory information management system (LIMS).

6.2.2 The samples are stored at ambient temperature prior to analysis.

6.2.3 Density Determination:

6.2.3.1 Tare a polypropylene conical tube (Becton-Dickinson 15 ml) on a top loading balance.

6.2.3.2 For the determination of water density as a control check, fill the conical

tube with water and cap making sure no air bubbles are present.

6.2.3.3 Weigh the tube to the nearest 0.00 grams. The tubes will hold approximately 16 ml when filled to capacity

6.2.3.4 Repeat the water density determination two more times. The average water density should be 1.0 g/ml.

6.2.3.5 Mix the sludge samples well and aliquot into a pouring beaker. Pour into a 15 ml conical tube as described in 6.2.3.2.

6.2.3.6 Weigh the tube and record the weight.

6.2.3.7 Repeat the sludge density determination two more times using a clean tube for each determination.

6.2.3.8 Enter weights in the dry cleaning ATCM spreadsheet. The density is calculated as weight per 16 mls and recorded in g/ml.

6.2.3.9 The tubes should be disposed in the hazardous waste container.

6.2.4 Tetrachloroethylene Determination:

6.2.4.1 Weigh a one (1) milliliter aliquot of sludge into a 10 ml volumetric flask.

6.2.4.2 Fill to the mark with 1-methoxy-2-propanol.

6.2.4.3 Mix well and transfer into an eight (8) ml disposable vial with a PFTE lined cap.

6.2.4.4 Transfer an aliquot to a 1.8 ml autoinjector vial.

6.3 Instrument Preparation:

6.3.1 Turn on the main valve for the air cylinder; verify cylinder pressure is above 500 psi.

6.3.2 Verify helium cylinder pressure is above 500 psi.

6.3.3 Check that the water level in hydrogen generator is above the refill line.

6.3.4 Press the FID igniter on the front of the GC.

6.4 Analysis Preparation:

6.4.1 Solvent Blank: Prepare solvent blank by filling a GC vial with the same MPA used to make the dilutions in steps 6.2.2 – 6.2.4. Cap the vial.

6.4.2 Calibration Standards: Prepare the five calibration standards in 10 mL volumetric flasks as follows:

Concentration	Volume of Stock Standard
1.0 mg/mL	0.125 mL
10 mg/mL	1.25
20 mg/mL	2.50
40 mg/mL	5.0
80 mg/mL	----

Bring to volume with MPA, mix thoroughly and place in dilution vials.

6.4.3 Transfer an aliquot of each standard into a GC vial and cap.

6.4.4 Control/Check: Prepare the control/check by diluting 1.0 mL of the control/check stock standard to 10 mL with MPA. The control is analyzed after the calibration. The check is run after every ten samples and at the end of the run.

6.4.5 Transfer an aliquot of each control/check and sample into appropriately labeled GC vials and cap.

6.5 Sample Analysis:

6.5.1 Place vials in the autosampler in the following order: MPA blank, calibration standards, control/check, and diluted samples. The check standard is run every tenth sample and at the end of the run. Additional blanks between standards and samples maybe used if carryover is suspected.

6.5.2 Calculate the value for each analyte found by dividing the amount from the report (mg/mL) by the sample dilution weight (see Section 8).

7 QUALITY CONTROL

7.1 An MPA solvent blank must be analyzed for each batch of samples. The analyte concentration in the blank must be less than 0.1% wt./volume. An MPA blank is run before the control and each check to prevent carry over from the previous sample.

7.2 The correlation coefficient for compounds present in the calibration must be greater than 0.995. If the calibration fails, the sequence is stopped and corrective action is implemented.

7.3 A control sample is run after the calibration. The control must fall within the control limits. If the control is not within the control limits, it may be necessary to recalibrate and rerun the sequence.

7.4 A check sample is run after every ten samples and at the end of the run. The check must fall within the control limits. If one of the checks is out of the control limits, re-run the check and any samples that follow until the next check.

8 CALCULATIONS

The weight fraction of analyte in the product is calculated as follows:

$$\text{Weight Fraction of Analyte} = \left(\frac{\text{analyte}\ (\text{mg/mL})}{\text{sample dilution}\ (\text{g})}\right) \times 10^{-2}$$

Appendix E

Standard Operating Procedure
For the Determination of DF2000™ in Dry Cleaning Sludge
by Gas Chromatography – Mass Selective Detector

California Environmental Protection Agency

Air Resources Board

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF DF2000™ IN DRY CLEANING SLUDGE BY GAS CHROMATOGRAPHY-MASS SELECTIVE DETECTOR

May 24, 2005

DISCLAIMER: Mention of any trade name or commercial product in Method 310 and associated Standard Operating Procedures does not constitute endorsement or recommendation of this product by the Air Resources Board. Specific brand names and instrument descriptions listed in the Standard Operating Procedures are equipment used by the ARB laboratory. Any functionally equivalent instrumentation can be used.

1 INTRODUCTION

This method was developed to look specifically for components of the dry cleaning solvent DF2000™. DF2000™ is a complex mixture of C11-C13 isoparaffinic hydrocarbons containing a low percentage of cycloparaffins.

This method is suitable for the determination of aliphatic hydrocarbons in the range of decane (C10) to octadecane (C18) with boiling points ranging from 174 to 316 degrees centigrade.

2 SUMMARY OF METHOD

The dry cleaning sludge samples are collected in triplicate in a 250 milliliter (ml) glass jar. One aliquot is used to determine sample density and another aliquot is used to determine DF2000™ concentration. The samples of dry cleaning sludge are prepared as 1:20 wt. / volume dilutions in methylene chloride ($MeCl_2$). After dilution and thorough mixing, the insoluble material is allowed to settle out, or the sample filtered to remove insoluble material. The diluted sample is then analyzed on a gas chromatograph equipped with a mass selective detector (MSD). The data is reported as percent DF2000™ in the dry cleaning sludge.

3 INTERFERENCES AND LIMITATIONS

Since the method looks for the generic class of hydrocarbons from decane to octadecane there is an increased likelihood of interference from hydrocarbon contribution from sources other than the sludge sample. Method blanks should be analyzed to insure the solvent and instrument are free of hydrocarbon contaminants.

4 INSTRUMENTATION AND EQUIPMENT

4.1 Gas Chromatograph (GC) configured with a Mass Selective Detector (MSD),

4.1.1 GC Column: J & W DB-1, 60 m x 0.32 mm I.D. with 1.0 µm film,

4.1.2 GC Parameters are as follows:

<u>Oven Conditions</u>

Initial temperature:	40℃
Initial time:	2.0 min
Rate:	2.0℃/min
Intermediate temperature:	200℃
Intermediate hold time:	5.0 min

Rate:	40°C/min
Final Temperature:	320℃
Final Hold Time:	1.0 min
Run time:	91.0 min
Oven equilibration:	0.3 min
Injector temperature:	300℃
Interface temperature:	300℃
Carrier gas (He):	1.46 ml/min
Source Temperature:	150℃
MSD scan range:	40 to 500 amu
Split Flow:	Splitless for 1.0 min

4.2 10 ml Volumetric Flasks,

4.3 Rainin Pipettors: 250 µl, 1.0 ml, 2.5 ml with tips,

4.4 Vials and Jars:

4.4.1 8 mL with PTFE-lined cap, for standards and dilutions,

4.4.2 2 mL with caps, for GC-MSD analysis,

4.4.3 250 ml widemouth glass jars with PTFE –lined caps,

4.4.4 15 ml graduated disposable polypropylene conical tubes,

4.5 Analytical Balance capable weighing to 0.1 milligram,

4.6 Vortex Mixer, variable speed.

5 REAGENTS

5.1 Dichloromethane, Pesticide grade or better,

5.2 DF2000™ directly from the manufacturer or the dry cleaners supply,

5.3 Stock Standards: The 15 mg/mL stock standard is prepared gravimetrically,

5.4 Helium, grade 5.

6 PROCEDURE

6.1 Sample Collection:

6.1.1 Samples are collected from eight (8) liter buckets of dry cleaning sludge which represents the total contents of the dry cleaning machine sump.

6.1.2 Using a long wooden or metal stirring rod, stir the collected sludge to resuspend the solid material as much as possible.

6.1.3 Using a cup or jar fill a 250 ml jar with the stirred dry cleaning sludge.

6.1.4 Clean the jar, seal the container, and attach the sample identification label.

6.1.5 Repeat this process two more times making sure the sludge is remixed between each sampling.

6.1.6 If the aliquoted samples are not to be analyzed immediately store either in a laboratory hood or in a refrigerator.

6.2 Sample Preparation:

6.2.1 The collected samples are entered into the laboratory information management system (LIMS) and given a unique identification number.

6.2.2 If the samples were stored in the refrigerator allow them to warm to ambient temperature prior to analysis.

6.2.3 Density Determination:

6.2.3.1 Tare a polypropylene conical tube (Becton-Dickinson 15 ml) on a top loading balance.

6.2.3.2 For the determination of water density as a control check, fill the conical tube with water and cap making sure no air bubbles are present.

6.2.3.3 Weigh the tube to the nearest hundreth of a gram. The tubes will hold 16 ml when filled to capacity

6.2.3.4 Repeat the water density determination two more times. The average water density should be 1.0 g/ml.

6.2.3.5 Mix the sludge samples well and aliquot into a pouring beaker. Pour into a 15 ml conical tube as described in 6.2.3.2.

6.2.3.6 Weigh the tube and record the weight.

6.2.3.7 Repeat the sludge density determination two more times using a clean tube for each determination.

6.2.3.8 Enter weights in the dry cleaning ATCM spreadsheet. The density is calculated as weight per 16 mls and recorded in g/ml.

6.2.3.9 The tubes should be disposed in the hazardous waste container.

6.2.4 DF2000™ Determination:

6.2.4.1 Weigh approximately 0.5 ml of sludge into a 10 ml volumetric flask.

6.2.4.2 Fill to the mark with $MeCl_2$.

6.2.4.3 Mix well and transfer into an eight (8) ml disposable vial with a PFTE lined cap. Allow the solids to settle out before analysis.

6.2.4.4 Make a serial dilution such that the final concentration of sludge is in the three (3) to five (5) milligram per milliliter range.

6.2.4.5 Transfer an aliquot to a 1.8 ml autoinjector vial.

6.3 Instrument Preparation:

6.3.1 Verify helium cylinder pressure is above 500 psi.

6.3.2 Load the Exxon method into the GC/MSD.

6.3.3 After system equilibrates TUNE the MSD using the Standard Tune command.

6.3.4 After tuning the MSD check to insure the calibration is acceptable.

6.4 Analysis Preparation:

6.4.1 Solvent Blank: Prepare solvent blank by filling a GC vial with the same $MeCl_2$ used to make the dilutions in steps 6.2.2 – 6.2.4. Cap the vial.

6.4.2 Calibration Standards: Prepare the five DF2000™ calibration standards in 10 mL volumetric flasks as follows:

Concentration	Volume of Stock Standard
0.1 mg/mL	0.0665 mL
0.2 mg/mL	0.133
0.5 mg/mL	0.333
1.0 mg/mL	0.667
2.0 mg/mL	1.333

Bring to volume with $MeCl_2$, mix thoroughly and place in dilution vials.

6.4.3 Transfer an aliquot of each standard into a GC vial and cap.

6.5 Sample Analysis:

6.5.1 Place vials in the autosampler in the following order: $MeCl_2$ blank, calibration standards, continuing calibration verification, and diluted samples. The continuing calibration verifcation standard is run every tenth sample and at the end of the run. Additional blanks between standards and samples maybe used if carryover is suspected.

6.5.2 Calculate the value for each analyte found by dividing the amount from the report (mg/mL) by the sample dilution weight (see Section 8).

7 QUALITY CONTROL

7.1 An $MeCl_2$ solvent blank must be analyzed for each batch of samples. The analyte concentration in the blank must be less than 0.1 mg/ml. An $MeCl_2$ blank is run before the control and each check to prevent carry over from the previous sample.

7.2 The correlation coefficient for compounds present in the calibration must be greater than 0.995. If the calibration fails, the sequence is stopped and corrective action is implemented.

7.3 A continuing calibration verification (CCV) sample is run after every ten samples and at the end of the run. The CCV must fall within +/- 25% of the true value. If one of the CCV's is out of the control limits, re-run the CCV and any samples that follow until the next acceptable CCV.

8 QUANTIFICATION

8.1 Because DF2000™ is a complex mixture, seven (7) peaks are used to represent the entire complex mixture during quantitation. The peaks are identified as Peaks 1 through 7.

8.2 Peaks 1 through 7 are identified by retention times which are listed in Table 1.

Table 1

Peak Number	Retention Time (mins)
1	40.24
2	41.26
3	43.00
4	43.45
5	44.52
6	48.20
7	51.72

8.3 The weight fraction of Peaks 1 through 7 in the sludge are calculated as follows:

$$Weight\ Fraction\ of\ Analyte = \left(\frac{analyte\,(mg/mL)}{sample\ dilution\,(g)} \right) \times 10^{-2}$$

8.4 These seven peaks are then reported as the average of peaks 1 through 5, peaks 6 and 7, and peaks 1 through 7.

Appendix F

Sludge Sampling Results

Table F-1. Perc Sludge Test Results (Primary Machines)

Machine	*Test No.*	*Make*	*Model Year*	*Sludge Density (g/ml)*	*Sludge Density (lb/gal)*	*% solvent in sludge*	*# of filter*
Machine A	1	Bowe Permac	1994	1.20	10.00	44	0
Machine A	2	Bowe Permac	1994	1.13	9.39	17	0
Machine A	3	Bowe Permac	1994	1.08	9.03	18	0
Machine B	1	Bowe Permac	1991	1.08	9.03	21	0
Machine B	2	Bowe Permac	1991	1.07	8.95	14	0
Machine B	3	Bowe Permac	1991	1.07	8.92	11	0
Machine C	1	Bowe Permac	1999	1.02	8.50	14	0
Machine C	2	Bowe Permac	1999	1.16	9.70	29	0
Machine D	1	Midwest	1988	1.37	11.45	67	0
Machine D	2	Midwest	1988	1.20	10.00	41	0
Machine D	3	Midwest	1988	1.33	11.06	69	0
Machine E	1	Columbia	1993	1.26	10.50	61	0
Machine E	2	Columbia	1993	1.17	9.78	39	0
Machine E	3	Columbia	1993	1.30	10.81	65	0
Machine F	1	Columbia	2000	1.18	9.84	40	0
Machine F	2	Columbia	2000	1.09	9.09	31	0
Machine F	3	Columbia	2000	1.11	9.25	33	0

Table F-2. Perc Sludge Test Results (Secondary Machines)

Machine	*Test No.*	*Make*	*Model Year*	*Sludge Density (g/ml)*	*Sludge Density (lb/gal)*	*% solvent in sludge*	*# of filter*
Machine A,B[1]	1	Columbia	1997	1.19	9.92	43	0
Machine A,B[1]	2	Columbia	1997	1.21	10.09	51	0
Machine A,B[1]	3	Columbia	1997	1.20	9.98	41	0
Machine C	1	Victory	1996	1.20	10.00	45	3
Machine C	2	Victory	1996	1.17	9.75	38	3
Machine C	1	Victory	1986	1.15	9.56	44	3

1. Machines A and B have a common still.

Table F-3. DF-2000 Sludge Test Results

Machine ID	*Test No.*	*Make*	*Model Year*	*Sludge Density (g/ml)*	*Sludge Density (lb/gal)*	*% solvent in sludge*	*# of filter*
Machine A	1	Realstar	1997	0.898	7.49	26	12
Machine A	2	Realstar	1997	0.892	7.44	29	12
Machine A	3	Realstar	1997	0.891	7.43	24	12
Machine B	1	Realstar	2003	0.920	7.67	12	10
Machine B	2	Realstar	2003	0.922	7.68	11	10
Machine B	3	Realstar	2003	0.913	7.61	15	10

Appendix G

OEHHA Memorandum

Office of Environmental Health Hazard Assessment

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Terry Tamminen
Agency Secretary

Arnold Schwarzenegger
Governor

MEMORANDUM

TO: Peter Venturini, Chief
Stationary Source Division
Air Resources Board

FROM: George V. Alexeeff, Ph.D., D.A.B.T
Deputy Director

DATE: December 2, 2003

SUBJECT: HEALTH EFFECTS OF EXPOSURE TO ALTERNATIVE DRY CLEANING SOLVENTS

In response to your memorandum of December 17, 2002, staff of the Office of Environmental Health Hazard Assessment (OEHHA) have reviewed the health impacts for non-perchloroethylene dry cleaning solvents, specifically decamethylcyclopentasiloxane (D5), which is present in GreenEarth® solvent, and propylene glycol tert-butyl ether, which is the principal (93%) component of Rynex® solvent. We recently reviewed the literature on these for the Bay Area Air Quality Management District (BAAQMD) and are providing you with updated versions of those reviews. We included information on octamethylcyclotetrasiloxane (D4), another cyclosiloxane with potential for use in dry cleaning. Also included are a review of toxicity data on 1-propyl bromide for the BAAQMD (originally done in 2001 and recently updated) and a review of Pure Dry for the BAAQMD (from 2002 and recently updated). Pure Dry contains by weight 95% odorless mineral spirits (OMS), 3.6% HFE-7200 (a mixture of ethyl perfluoroisobutyl ether and ethyl perfluorobutyl ether), 0.9% FC-43 (perfluoro compounds of primarily 12 carbons), 0.3% PF-5070 (perfluoro compounds of primarily seven carbons), and 0.2% PF-5060 (perfluoro compounds of primarily six carbons). It should be noted that the toxicity databases for all these perchloroethylene alternatives is limited. However, in order to aid in risk characterization, we have derived interim inhalation chronic Reference Exposure Levels (RELs) for the chemicals. The following paragraphs summarize concerns of OEHHA staff:

D5 and D4: While basic testing is still underway for D4 and D5, staff has evaluated the available data. We have concerns about the potential carcinogenicity of D5 and the estrogenic activity of D4. Since D5 is very lipophilic, we are concerned that it will bioaccumulate in the food chain. Dow-Corning conducted a two year study of D5 by inhalation in rats. After both 12 and 24 months, female rats showed an increase in tumors of the uterine endometrium. Dow-Corning noted that the usual progression of hyperplasia to adenoma to adenocarcinoma was not observed in the experiments and that the statistically significant increase in adenocarcinomas alone is lost when the other tumors (adenomas) are added in. However, a statistically significant increase in a malignant tumor due to D5, a chemical that is bioconcentrated and is a candidate to

replace perchloroethylene, indicates a potential hazard for workers in the dry cleaning industry and perhaps for the general public. D4 has estrogenic activity in animals. For D5 an interim inhalation chronic REL of 700 $\mu g/m^3$ to prevent adverse effects in spleen and liver was derived.

Propylene glycol t-butyl ether: Based on a very recent study by the National Toxicology Program (NTP) staff have concerns about the toxicity and carcinogenic potential of propylene glycol t-butyl ether. The NTP conducted a two-year bioassay by inhalation in mice and rats. Data from mice showed multiple hepatocellular adenomas and non-neoplastic eosinophilic foci in the liver, especially at the top dose of 1200 ppm. No tumors were seen in rats, but effects on the nasal epithelia were seen as were male rat specific renal effects. The presence of tumors in mice is a cause for concern. For propylene glycol t-butyl ether an interim chronic REL of 200 $\mu g/m^3$ to prevent adverse effects in the olfactory epithelium (respiratory system) was derived. In addition an interim inhalation unit risk for cancer of 5.2×10^{-7} $(\mu g/m^3)^{-1}$ was derived.

1-Propyl bromide: Staff has concerns about the adverse effects of 1-propyl bromide on the reproductive system and on the nervous system. A recent review by the National Toxicology Program confirmed the concerns about the reproductive toxicity of this compound. The Department of Health Services has approved the issuance of a hazard alert for workers exposed to the chemical based on the reproductive toxicity observed in animal studies. The Hazard Alert is attached. The National Toxicology Program (NTP) is conducting a two year bioassay by inhalation in mice at 0, 62.5, 125, or 250 ppm and in rats at 0, 125, 250, or 500 ppm which may give robust dose-response data and fill in some data gaps. For 1-propyl bromide an interim chronic REL of 1100 $\mu g/m^3$ to prevent adverse effects in the male reproductive system was derived.

Mineral spirits: ExxonMobil Chemical Dry Cleaning Fluid 2000 contains C_{11} to C_{13} aliphatic hydrocarbons. Pure Dry contains 95% mineral spirits, a mixture of mainly C_9 to C_{12} paraffin hydrocarbons. Mineral spirits can cause neurotoxicity. For C_{10}-C_{11} hydrocarbons an interim inhalation chronic REL of 1200 $\mu g/m^3$ to prevent adverse effects in the kidney and the blood was derived. The remainder of Pure Dry consists of several perfluorinated chemicals, whose toxicology is limited to a few members of the class (HFE-7100 and HFE-7200) and relatively high doses and whose environmental persistence is unknown. We have included a copy of a Toxicity Summary for HFE-7100 and HFE-7200, which OEHHA staff previously sent to the Board. For HFE-7200 an interim chronic REL of 19,000 $\mu g/m^3$ to prevent adverse effects in the liver and the blood was derived.

OEHHA staff plans to continue to follow the peer-reviewed literature and also to obtain whatever information we can from the manufacturers of the solvents on the toxicity of the components, such as the final toxicity data of the Dow-Corning study on D5. We could pursue a Freedom of Information Act request of the U.S. EPA to determine if there is additional toxicity

information about the proposed dry cleaning alternatives to perchloroethylene. We are especially interested in data from studies designed to address data gaps, most importantly in developmental and chronic toxicity. We could also conduct an analysis to see if any of the proposed substitutes pose less risk than perchloroethylene. Moreover, staff wants to have a better understanding on all possible dry cleaning alternatives, not just the ones discussed above. For example, carbon dioxide (CO_2) is a viable cleaning agent when compressed, and would have much less of a problem with toxicity.

OEHHA staff cannot at this time indicate which of the proposed alternatives would be the least risky. We do not have modeled air concentrations to compare with the REL and we do not have a complete database characterizing the toxicity. However, since the recently signed AB 998 will result in an annual increase in cost of perchloroethylene until 2013 and since the South Coast Air Quality Management District plans to phase out perchloroethylene by 2020, one or more alternative chemicals will be used. The following table gives some advantages and disadvantages of use of each chemical summarized.

Chemical	*Pros*	*Cons*
D5 and D4	Not volatile	Very lipophilic (high Koc), so potential to bioaccumulate; possible animal carcinogen and/or endocrine disrupter
Propylene glycol t-butyl ether	Member of less toxic propylene glycol ether family	Possible water contaminant; possible animal carcinogen
1-Propyl bromide	Less volatile than perchloroethylene	Toxic to nervous and reproductive systems
Mineral spirits	Long use in industry; toxic properties fairly well known	Flammable; VOC
HFE-7100 and HFE-7200	Relatively inert	Environmental fate unknown; potential stratospheric ozone depletion

OEHHA staff is aware of potential cross-media issues, i.e., that dry cleaning chemicals are not just an air issue. Perchloroethylene itself is a problematic water contaminant as well as a toxic air contaminant. In order to more fully understand the cross-media impact of the compounds, further research on environmental fate and transport of the new materials is required.

Finally, we could develop drinking water action levels for those compounds that could enter the aqueous environment.

If you have questions about our analysis, or would like additional information, please call Dr. Jim Collins, of my staff, at CALNET 8-561-3146.

Attachments

cc: Melanie A. Marty, Ph.D., Chief
Air Toxicology and Epidemiology Section

James F. Collins, Ph.D., D.A.B.T.
Air Toxicology and Epidemiology Section

Richard Boyd
Air Resources Board

TOXICITY DATA REVIEW

CYCLIC SILOXANES (D5 AND D4)

(decamethylcyclopentasiloxane and octamethylcyclotetrasiloxane)

CAS Registry Number: 541-02-6 (D5); 556-67-2 (D4)

Summary

Decamethylcyclopentasiloxane is an alternative to perchloroethylene in dry cleaning and is already in use under the Green Earth trademark. Decamethylcyclopentasiloxane (D5) is lipophilic and can bioconcentrate (log K_{ow} = 5.2). Inhalation of 160 ppm for 12 or 24 months by female rats led to adenocarcinomas of the endometrium. D4 was shown to be estrogenic in rats. This review includes material made available by the manufacturer in 2003.

Chemical and physical properties

Decamethylcyclopentasiloxane (D5) (CAS Registry Number 541-02-6) is a low molecular weight (370.8 daltons) cyclic siloxane used for industrial (silicone fluids and elastomers) and consumer product (cosmetics and toiletries) applications. The chemical is not listed as a hazardous air pollutant (HAP). D5 is an oily liquid that boils at 210°C. One ppm in air equals 15.1 mg/m^3. It has low solubility in water (0.24 mg/L at 25°C) and a very high lipid solubility; the logarithm of its octanol water partition coefficient is 5.2. Thus it has a 100,000 times greater preference for lipid than water. Its bioconcentration factor (BCF) is estimated to be 5000. According to HSDB, a national survey of human adipose tissue in 1982 found D5 in 28 of 46 samples. Unfortunately the original survey was not available for OEHHA review. Neither D5 nor any other siloxane was measured for the recent Second National Report on Human Exposure to Environmental Chemicals released in January 2003 by the National Center for Environmental Health. [A recent study found that several years after ruptured silicone implants were removed, siloxanes including D3 and D4, but not D5 and D6, could still be found in blood samples from several women. In addition, D4, D5, and D6 could be detected leaking from current implants.]

Health effects information on D5 in the peer-reviewed literature

HSDB (Hazardous Substances Data Bank), citing Hayden and Barlow (1972), reports that several siloxanes are estrogenic in animals and that the cyclic compounds were more active than the linear compounds. The study did not examine D5 but did find weak (not statistically significant) estrogenic activity with the cyclic tetrasiloxane D4 in the ovariectomized immature female rat uterus following oral administration. Some cyclic siloxanes with phenyl groups (rather than methyl groups as in D5) had stronger estrogenic activity in the assay.

Burns-Naas *et al.* (1998a) assessed potential toxic consequences and immune system modulation of inhalation exposure to D5 in male and female Fischer 344 rats exposed by whole body inhalation to 0, 10, 25, 75, or 160 ppm D5 6 h/day, 7 days/week for 28 days. D5 inhalation

exposure did not alter humoral immunity and caused only minor, transient changes in hematological, serum chemistry, and organ weight values. Histopathological changes were confined to the respiratory tract and appeared to be reversible. The no-observed-adverse-effect-level (NOAEL) for systemic toxicity, based primarily on the liver weight changes, was 75 ppm for this 28 day study.

Burns-Naas *et al.* (1998b) evaluated the subchronic toxicity of D5 using a 3-month, nose-only inhalation exposure. Control and high dose groups were also allowed a 4-week recovery period to observe reversibility, persistence, or delayed occurrence of any potential adverse effects. Male and female Fischer 344 rats were exposed for 6 h/day, 5 days/week for 3 months to target concentrations of 0, 26, 46, 86, and 224 ppm D5. There were several minor changes observed in clinical biochemistry parameters; the most notable was an increase in gamma glutamyl transferase (gamma-GT) in both sexes at the high dose. In females, this effect was dose-related between 46 and 224 ppm and did not return to control levels upon cessation of exposure. Additionally, there was a decrease in serum lactate dehydrogenase (LDH) observed in females at 86 and 224 ppm, which did not resolve during recovery. There was an increase in absolute and/or relative liver weight in rats of both sexes. Taken together, these data suggest that the female rat is more sensitive to the actions of D5 on the liver. Exposure-related increases in absolute and relative lung weights were observed in both sexes at terminal necropsy. This observation was not noted in males in the recovery phase, but was still present in females. Histopathology indicated that the primary target organ following D5 inhalation is the lung, with an increase in focal macrophage accumulation and interstitial inflammation in the lungs of male and female rats exposed to 224 ppm D5. This observation did not appear to resolve at the end of a 1-month period of non-exposure. The incidence of these changes was also slightly increased in rats of both sexes exposed to 86 ppm D5. These data suggest that nose-only D5 vapor inhalation provokes minimal changes in the lung, which are similar in incidence and severity to spontaneously occurring changes in control animals after nose-only exposures. There were no histopathological findings noted in the livers, despite the observed changes in organ weight and in some serum chemistry parameters.

Effects of inhalation of increasing D5 levels in female rats

D5 concentration	*Liver wt (g)*	*Triglycerides (mg/dL)*	*Serum γ-glutamyl tranferase (U/L)*
0 ppm	3.71±0.46[#]	42.88±7.88	0.70±0.15
26 ppm	3.94±0.26	39.38±4.38	1.10±0.34
46 ppm	4.26±0.60**	33.25±3.5**	1.49±0.37**
86 ppm	4.02±0.50	31.50±3.5**	1.56±0.53**
224ppm	4.31±0.59**	35.00±3.5	3.35±0.51**

[#] mean ± standard deviation; ** $p<0.01$

McKim *et al.* (1999) investigated the effects of D5 on the expression and activity of selected rat hepatic phase I and phase II enzymes. The results suggested that the profile for enzyme induction following inhalation exposure of female Fischer-344 rats to D5 vapors is similar to that reported for phenobarbital, and therefore D5 may be described as a weak "phenobarbital-like" inducer.

Lieberman *et al.* (1999a) injected female CD-1 mice intraperitoneally with different doses of distillate (3.5-35 g/kg body weight) containing cyclosiloxanes (CSs) D3, D4, D5, and D6. The distillate was found to be lethal at high doses and all the mice injected with 35 g/kg died within 5-8 days. The median lethal dose (LD_{50}) for distillate was estimated to be approximately 28 g/kg. The mice developed inflammatory lesions of the lung and liver as well as liver cell necrosis with elevated serum levels of alanine aminotransferase, aspartate aminotransferase, and lactic acid dehydrogenase. Administration of D4 alone produced lethality in these mice with an LD_{50} of 6-7 g/kg. D4-treated mice exhibited pulmonary and hepatic lesions and elevated serum enzymes. The authors stated that analysis of LD_{50} data indicated that CS-D4 is about as acutely toxic as carbon tetrachloride or trichloroethylene. The authors measured hydroxyl radical formation in CS-D4-treated mice and found increases of approximately 20-fold in liver and approximately 7-fold in lung on day 4 following injection. They believe that the findings are significant because in vitro experiments have demonstrated that CSs can migrate out of breast implants. Additionally in mouse experiments CSs have been shown to be widely distributed in many organs after a single subcutaneous injection and to persist for at least a year (Kala *et al.*, 1998).

At first glance the results may appear alarming. However when a chemical requires a dose greater than 15 g/kg to exert lethality, the chemical is considered to be practically non-toxic. It is unfortunate that none of the journal's peer-reviewers noted this, but several other scientists did and submitted critiques:

Five letters (individually written by Carlton, Meeks, Witschi, Burin, and Dost) were critical. (Dr. Witschi was formerly a member of the Board's Scientific Review Panel on Toxic Air Contaminants.) These letters pointed out (1) the practically non-toxic classification of the chemicals based on the LD_{50}s reported by Lieberman et al., (2) the likelihood that the distillation pretreatment of the chemicals by the investigators altered the chemicals including opening of the cyclosiloxane ring structure, and (3) the lack of mass balance calculation in the study of distribution of the chemical. The letter by Lukasiak, Jamrogiewicz, and Falkiewicz was complimentary and pointed out that related chemicals were used to treat intestinal gas in humans. Lieberman *et al.* (1999b) defended their study and said that it was the first time an LD_{50} had been reported for cyclic siloxanes. In addition, they reported effects at doses below the LD_{50}. They state that effects similar to those obtained with the distillate were seen with commercial D4; thus heat treatment of the distillate did not cause the effects.

Varaprath *et al.* (2003) report that rats metabolize D5 to at least ten metabolites identifiable by GC-MS analysis. No parent D5 was found in the urine.

HSDB reports that D5 is non-clastogenic; it does not cause chromosomes to fragment and thus is not genotoxic by this criterion. No other tests for mutagenicity were reported by HSDB.

Siloxane Product Stewardship Program

OEHHA staff obtained a copy of the "Siloxane Product Stewardship Program" 2002 Annual Progress Report of Dow Corning Corporation to the USEPA. D5, marketed as Dow Corning® 245 Fluid, is one of the siloxanes included. The report draws on two papers by Burns Naas and colleagues mentioned above and many of Dow Corning's internal reports. Dow Corning tested D5 for various effects, including organ effects and reproductive effects, by the inhalation, oral, and dermal routes of exposure for up to 13 weeks, and for potential genetic activity. The acute inhalation LC_{50} in rats was calculated to be 8.67 mg/liter (8670 mg/m^3). Results from the 28 day and 13 week inhalation studies are presented in the summaries of the two reports by Burns-Naas *et al.* above. Some other studies showed an increase in liver weight at high concentrations (e.g., inhalation at 160 ppm), which was reversible in animals that were allowed to recover from exposure to D5. D5 had no effect on fertility at 132 ppm, the highest concentration studied. In a 2-generation study D5 had no effect on parental toxicity, reproductive toxicity, neonatal toxicity, and developmental neurotoxicity at 160 ppm, the highest concentration studied. D5 was inactive in the Ames test and in the L5178L mouse lymphoma cell mutation assay.

Two year chronic toxicity/oncogenicity study of D5 in rats

Dow Corning has also conducted a 24 month combined chronic toxicity/oncogenicity study in male and female Fischer 344 rats exposed to 0, 10, 40, or 160 ppm D5 6 hr/day; 5 days per week. Dow Corning's Environment, Health and Safety Office reported preliminary results to the U.S. EPA's Office of Pollution Prevention and Toxics in a letter dated February 4, 2003. After both 12 and 24 months, female rats showed an increase in tumors of the uterine endometrium. The experiment was conducted with 4 groups:

Group	*Rats*	*Exposure*	*Recovery*	*Analysis*
A	6/sex/dose	6 months	none	D5 levels in liver, fat, plasma
B	10/sex/dose	12 months	none	Necropsy and organ/tissue analysis
C	20/sex/dose	12 months	12 months	Necropsy and organ/tissue analysis
D	60/sex/dose	24 months	none	Necropsy and organ/tissue analysis

No uterine tumors were seen in groups A and B. Results in group C females were:

Tumor	*0 ppm*	*10 ppm*	*40 ppm*	*160 ppm*
Endometrial adenocarcinoma	1	1	0	2
Endometrial adenomatous polyp	0	0	0	1
Total tumors	*1*	*1*	*0*	*3*
Number rats in group	20	20	20	20

In group D, after 24 months of exposure, the results in female rats were:

Tumor	*0 ppm*	*10 ppm*	*40 ppm*	*160 ppm*
Endometrial adenocarcinoma	0	1	0	5
Endometrial adenoma	0	1	0	0
Endometrial adenomatous polyps	1	0	1	0
Total tumors	*1*	*1*	*1*	*5*
Number of rats in group	60	60	60	60

The authors note that the progression of hyperplasia to adenoma to adenocarcinoma was not observed in the experiments. They also state that the statistically significant increase in adenocarcinomas alone is lost when the other tumors are added in. (OEHHA staff obtained a p value of 0.029 comparing 0/60 adenocarcinomas in the control group versus 5/60 in the 160 ppm D5 exposure. Comparing 1/60 total tumors in the control versus 5/60 in the 160 ppm group gave a p value of 0.10.) However, a statistically significant increase in a malignant tumor (adenocarcinoma) due to D5, a chemical that is bioconcentrated and is a candidate to replace perchloroethylene, indicates a potential hazard for workers in the dry cleaning industry and perhaps for the general public. Based on a meeting with Dow Corning and others interested in D5 on April 14, 2003 in Sacramento, a final report on the 2 year study will be available in 12 months. Dow Corning is also investigating possible mechanisms by which the tumors were induced.

Health effects of D4 (octamethylcyclotetrasiloxane) in animals

D4 is a cyclosiloxane with one less Si-O link than D5. There are also several reports on D4 in the literature. At least three have shown effects on the uterus of female rats. The observance of adverse effects on the uterus by both D5 and D4 is of concern.

Hayden and Barlow (1972) administered 32 organosiloxane compounds orally to ovariectomized immature female rats and compared their effects on the uterus. Scoring was on a scale of 0 to +4, where 0 was no effect and +4 was an increase equal to or greater than estrogen treated controls. D4 gave a +1 response, a less than 20% increase in uterine wet weight, which was not statistically significant. The dose of D4 given was not clearly described in the paper.

McKim *et al.* (2001) examined potential estrogenic and anti-estrogenic activities of D4 by the oral route in Sprague-Dawley (SD) and Fischer 344 (F-344) rats. Estrogenicity of D4 was determined by measuring absolute and relative uterine weights in immature rats and by monitoring uterine epithelial cell height. In order to determine relative estrogenicity, D4 at 0, 10, 50, 100, 250, 500, and 1000 mg/kg/day was compared to ethinyl estradiol (EE) (1 to 30 μg/kg/day), diethylstilbestrol dipropionate (DES-DP) (0.5 to 15 μ/kg/day), and coumestrol (CE), a plant estrogen (10 to 150 mg/kg/day). Anti-estrogenic effects were evaluated by co-administering D4 (500 mg/kg/day) with EE at 1, 3, 10, and 30 μg/kg/day. All compounds were administered by gavage in sesame oil at 5 mL/kg. Beginning on postnatal day (PND) 18 in SD rats or PND 21 in F-344 rats, each pup (12 per group) received a single dose of test compound once a day for 4 consecutive days. The morning after the last treatment the female pups were euthanized and their uteri removed, weighed, and processed. EE and DES-DP produced a significant dose-dependent increase in absolute and relative uterine weights and cell height.

(Maximum increase in uterine weight following EE exposure = approx. 350% vs. controls) At the highest dose, CE increased uterine weight by approx. 230% vs. controls. D4 exposure led to statistically significantly increases in absolute and relative uterine weights and in uterine epithelial cell height at 250, 500, and 1000 mg/kg/day. D4 was approximately 0.6 million times less potent than EE or DES-DP in SD pups and 3.8 million times less potent than EE or DES-DP in F-344 pups in its (D4) ability to increase uterine weight. The maximal increase produced by D4 at 1000 mg/kg/day was approximately 160% in SD rats and 86% in F-344 rats. D4 co-administered over a wide range of EE doses, resulted in a significant reduction in uterine weight compared to EE alone. The authors concluded that D4 showed weak estrogenic and anti-estrogenic activity.

Burns-Naas and co-workers (who also investigated D5 in a 3-month inhalation study) evaluated the subchronic toxicity of D4 following a 3-month nose-only inhalation exposure (Burns-Naas *et al.*, 2002). They exposed male and female F-344 rats (20/sex/group) 6 h/day, 5 days/week for 3 months to vapor concentrations of 0, 35, 122, 488, and 898 ppm D4. An additional 10 rats per sex in the 0 and 898 ppm groups were given a 4-week recovery period to observe reversibility, persistence, or delayed occurrence of effects. Females showed a concentration-dependent increase in absolute and relative liver weight at 488 and 898 ppm and a significant decrease in ovarian weight at 898 ppm D4. Exposure to 35 to 898 ppm D4 produced minor alterations in hematological and serum chemistry parameters that the authors considered either to not be toxicologically significant, or to suggest metabolic adaptation in response to hepatomegaly. No histopathology was seen in the liver. Histopathologically the primary target was the female reproductive tract. Reversible changes were observed in the ovary (hypoactivity) and vagina (mucification) of female rats in the high-dose group only. (Increased incidence and severity of macrophage accumulation, interstitial inflammation, and eosinophil infiltration were observed in the lungs of rats exposed to D4 in this experiment. The authors considered the toxicological significance of lung effects to be uncertain since other inhalation studies at similar concentrations failed to show these effects.)

Interim inhalation chronic REL estimate for D5

A chronic REL is a level at or below which adverse noncancer health effects would not be expected to occur even in sensitive subpopulations. An interim chronic REL for D5 can be estimated from the spleen and liver changes reported by Burns-Naas *et al.* (1998a).

Study	Burns-Naas *et al.* (1998a)
Study population	Male and female Fischer 344 rats
Exposure method	Discontinuous whole-body inhalation to 0, 26, 46, 86, and 224 ppm
Critical effects	Spleen and liver changes
LOAEL	46 ppm
NOAEL	26 ppm
Exposure continuity	6 hours/day, 5 days/week
Exposure duration	3 months
Average experimental exposure	4.6 ppm for NOAEL group (26 x 6/24 x 5/7)
Human equivalent concentration	4.6 ppm for NOAEL group
LOAEL uncertainty factor	1
Subchronic uncertainty factor	3 (NOAEL is based on a 3 month study in rats)
Interspecies uncertainty factor	3 (see below)
Intraspecies uncertainty factor	10
Cumulative uncertainty factor	100
Interim Reference Exposure Level	46 ppb; 700 $\mu g/m^3$

The NOAEL from the 3 month (subchronic) study of Burns-Naas *et al.* (1998a) was 26 ppm (although an argument might be made that the spleen and liver changes at 46 ppm were statistical fluctuations and not part of a dose-response relationship). The NOAEL was time adjusted to an equivalent continuous exposure of 4.64 ppm. Use of OEHHA's methodology for developing a chronic Reference Exposure Level (REL) (division by a subchronic UF of 3, an interspecies UF of 3 to account for residual susceptibility differences in rats not accounted for by U.S. EPA Human Equivalent Concentration (HEC) approach, and an intraspecies UF of 10) results in a chronic inhalation REL of 46 ppb (700 $\mu g/m^3$). [HSDB reports several measurements of D5 indoors. None exceeded 1 ppb.] This interim value is an estimate based on our approved procedure (OEHHA, 2000), but it has not been reviewed by the Scientific Review Panel.

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TOXICITY DATA REVIEW

PROPYLENE GLYCOL TERT-BUTYL ETHER

(propylene glycol mono-t-butyl ether; tert-butoxypropanol)

CAS Registry Number: 57018-52-7

Summary

Rynex, which contains 93% propylene glycol tert-butyl ether, has been proposed as an alternative to perchloroethylene in dry cleaning. In a two year inhalation study, propylene glycol tert-butyl ether exposure resulted in neoplastic and non-neoplastic lesions of the liver in mice. Rats showed hyaline degeneration of olfactory epithelium in males and females, basophilic liver foci in males, and several kidney lesions in males. This review includes data from a draft report released by the National Toxicology Program (NTP) in 2003. There are no developmental or reproductive studies on the chemical.

Rynex and propylene glycol tert butyl ether

OEHHA staff reviewed a toxicology report on Rynex, an azeotropic mixture of propylene glycol tert-butyl ether (93%) and water (7%), which was submitted to the Bay Area Air Quality Management District by ARCO Chemical and Rynex Holdings. Staff also obtained additional information on propylene glycol tert-butyl ether (PGtBE) (CAS Registry Number 57018-52-7) from RTECS® and from the National Toxicology Program (NTP) web site (www.niehs.nih.gov). Propylene glycol tert-butyl ether [1-Methyl-2-tert-butoxyethanol; 1-tert-Butoxy-2-propanol; Arcosolv PTB; 2-Propanol, 1-(1,1-dimethylethoxy)-] is not currently listed as a hazardous air pollutant. The molecular weight of PGtBE is 132.23; thus 1 ppm in air = 5.4 mg/m^3. PGtBE would likely be hydrolyzed in vivo to propylene glycol and tert-butyl alcohol or oxidized to a ketone.

Acute lethality

The submission by ARCO/Rynex (on page 4-1) reports an acute oral LD_{50} of 3771 mg/kg in Sprague-Dawley rats and designates the chemical as "not classified" in regard to toxicity. However, the tables on levels of toxicity found in a standard toxicology text, such as Loomis' Essentials of Toxicology (1978), would designate a material having such an acute oral toxicity level as "moderately toxic." A waste or material, subject to Title 22 in California, with this LD_{50} would be designated "hazardous."

The submission (pages 4-3 and 4-4) reports a 4 hour LC_{50} test in rats. No deaths were seen in 5 male and 5 female rats at 2.68 mg/liter (496 ppm), the only level tested. RTECS® reports an LC_{50} in rats for propylene glycol methyl ether (PGME) of 10,000 ppm. The test submitted gives a free-standing NOEL for lethality and is not an adequate

lethality test. In fact, 496 ppm is not far above the workplace 8 hour ACGIH TLVs of 100 ppm for propylene glycol monomethyl ether.

Ninety day inhalation study

The submission (on pages 4-14 through 4-17) describes a 90-day inhalation study in which groups of rats (50 males and 50 females) were exposed 6 hours/day, 5 days per week to 1 of 4 levels of Rynex or to air. The report states that the target doses were 0, 25, 80, 250, and 750 ppm. The concentrations given on page 4-15 are 0, 0.00454, 0.01452, 0.04538, and 0.13613 mg/L. But 0.00454 mg/L equals 4.54 mg/m^3 which is equal to 0.84 ppm, not 25 ppm. Increases in absolute and relative liver and kidney weights were seen at all concentrations, such that the lowest level was a LOAEL, and the NOAEL was below the lowest level tested (page 4-16, item 4). Based on our calculations this LOAEL is 0.84 ppm, not 25 ppm. This needs to be clarified.

Genetic toxicity

Negative tests for mutation in *Salmonella* up to 5000 micrograms Rynex per plate, with or without metabolic activation, are reported on page 4-18. The report also notes that NTP observed a positive result at 3,300 and 10,000 PGtBE micrograms per plate. NTP reported that PGtBE was negative in causing chromosomal aberrations (CA) and sister chromatid exchange (SCE).

Water pollution

Currently there is concern about methyl tert butyl ether (MTBE) in California water. Allowing another water soluble, tert-butyl ether compound, which could be used by a large number of small businesses dispersed in or near residential areas and some of which would likely end up in the water, is of concern to OEHHA.

National Toxicology Program bioassay

The National Toxicology program (NTP) has conducted 14 day and 90 day inhalation tests and a 2 year inhalation test of 0, 75, 300, or 1200 ppm PgtBE in Fischer 344 rats and B6C3F1 mice. OEHHA has received the NTP Board Draft (TR 515) on the chemical. The draft was scheduled for review by the NTP in May 2003. The NTP released some of the pathology data on its website: http://ntp-server.niehs.nih.gov/htdocs/LT&ST_Pages/TR515_T&C.html which then appeared in the draft report. Data from mice showed neoplastic (multiple hepatocellular adenoma) and non-neoplastic (eosinophilic foci) lesions of the liver, especially at the top dose.

Incidence data from NTP study of PGtBE in mice – liver lesions

Sex	Lesion	Control	75 ppm	300 ppm	1200 ppm
female	eosinophilic focus	11/49 = 22%	10/50 = 20%	9/50 = 18%	27/49 = 55%
female	hepatocellular adenoma, multiple	6/49 = 12%	0/50 = 0%	3/50 = 6%	32/49 = 65%
male	eosinophilic focus	9/50 = 18%	14/49 = 29%	11/50 = 22%	29/50 = 58%
male	hepatocellular adenoma, multiple	3/50 = 6%	7/49 = 14%	12/50 = 24%	23/50 = 46%

In mice there was evidence of a positive dose-response. NTP tentatively concluded that there was clear evidence of carcinogenicity in both male and female mice. While NTP found only equivocal evidence of carcinogenicity in male rats, some non-neoplastic lesions in the rats were noteworthy.

Incidence data from rats – olfactory, liver, and kidney lesions

Sex	Lesion	Control	75 ppm	300 ppm	1200 ppm
female	hyaline degeneration of olfactory epithelium	10/49 = 20%	22/49 = 45%	48/50 = 96%	50/50 = 100%
male	"	0/50 = 0%	25/49 = 51%	45/49 = 92%	50/50 = 100%
male	Liver focus, basophilic	6/50 = 12%	18/50 = 36%	15/49 = 31%	17/50 = 34%
male	hyaline droplet accumulation in renal tubules	1/50 = 2%	2/50 = 4%	9/50 = 18%	17/50 = 34%
male	renal tubule hyperplasia	0/50 = 0%	3/50 = 6%	7/49 = 14%	19/50 = 38%
male	mineralization of papilla	0/50 = 0%	8/50 = 16%	28/49 = 57%	41/50 = 82%
male	transitional epithelium hyperplasia, renal pelvis	2/50 = 4%	1/50 = 2%	6/49 = 12%	15/50 = 30%

The rat data indicate a LOAEL of 75 ppm (the lowest dose tested) for chronic effects on the nose (hyaline degeneration of olfactory epithelium) in males and females, the liver in males, and the kidney in males. The mouse data show induction of multiple hepatocellular adenomas in both sexes; the data from female mice show a dose response to the propylene glycol tert-butyl ether for multiple hepatocellular adenomas.

Interim inhalation chronic REL estimate

Chronic RELs are concentrations at or below which adverse health effects are not likely to occur in the general population, even in sensitive individuals. An interim chronic REL was estimated from the NTP data that show degeneration of olfactory epithelium in the rat.

Study	NTP (2003)
Study population	Male rats (50/group)
Exposure method	Discontinuous whole-body inhalation to 0, 75, 300, and 1200 ppm
Critical effects	Hyaline degeneration of olfactory epithelium
LOAEL	75 ppm
NOAEL	Not determined
Exposure continuity	6 hours/day, 5 days/week
Exposure duration	2 years
Average experimental exposure	13 ppm for LOAEL group (75 x 6/24 x 5/7)
Human equivalent concentration	13 ppm for LOAEL group
LOAEL uncertainty factor	3
Subchronic uncertainty factor	1
Interspecies uncertainty factor	10
Intraspecies uncertainty factor	10
Cumulative uncertainty factor	300
Interim Reference Exposure Level	40 ppb; 200 $\mu g/m^3$

The NTP data indicate a LOAEL of 75 ppm, the lowest dose tested, for degeneration of olfactory epithelium in the rat. This chronic REL is an estimate based on our approved procedure (OEHHA. 2000), but it has not been reviewed by the Scientific Review Panel.

Inhalation unit risk for cancer

OEHHA staff derived an inhalation unit risk factor for cancer using the standard default procedure for air toxics by fitting the linearized multistage model to the incidence data for (benign) multiple hepatocellular adenoma in male mice in the NTP study. The inhalation unit risk was estimated to be 5.2×10^{-7} $(\mu g/m^3)^{-1}$, about one-tenth that of perchloroethylene.

References

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TOXICITY DATA REVIEW

1-PROPYL BROMIDE

(n-propyl bromide; 1-bromopropane)

CAS Registry Number: 106-94-5

Summary

1-Propyl bromide has been proposed as an alternative to perchloroethylene in dry cleaning. 1-Propyl bromide is a neurotoxicant and a reproductive toxicant. This review includes peer-reviewed material published in 2003 as well as earlier. The database is incomplete since a 2 year chronic toxicity/oncogenicity study has not been completed in animals.

Description

1-propyl bromide (n-propyl bromide; 1-bromopropane, 1-PB) is a non-ozone depleting chemical and the principal component of the Leksol family of solvents. Comexsol-one, a member of the family which contains >95% 1-propyl bromide, is proposed for use in the Bay Area as a dry cleaning solvent. OEHHA staff have reviewed both the materials submitted by the proponent (an MSDS and Amity Product Information Bulletin Sheets) and papers in the peer-reviewed literature.

Human case report

In a case report Sclar (1999) described a 19-year-old male who developed complaints including weakness of both legs and of the right hand, numbness, and difficulties in swallowing and urinating following a two month exposure to an industrial solvent constituted mainly of 1-propyl bromide. However, the solvent also contained butylene oxide, 1,3 dioxolane, nitromethane, and other components. Nerve conduction studies revealed evidence of a primary, symmetric demyelinating polyneuropathy. Evidence of central nervous system (CNS) involvement came from gadolinium enhanced magnetic resonance imaging (MRI) scans of the brain. The scans showed patchy areas of increased T2 signal in the periventricular white matter. Similar scans of the spinal cord revealed root enhancement at several lumbar levels. The patient's symptoms had started to resolve following the discontinuation of the exposure, before he was lost to follow-up. Since similar findings have been reported following 1-bromopropane exposure in rats (see following section), Sclar hypothesized that the patient's symptoms may have been due to 1-bromopropane-induced neurotoxicity.

Animal studies of neurotoxicity

In order to clarify the dose-dependent effects of 1-propyl bromide on the nervous system, forty-four Wistar male rats were randomly divided into four groups of eleven each (Ichihara *et al.*, 2000a). The groups were exposed to 200, 400, or 800 ppm of 1-propyl bromide or only fresh air eight hours per day for twelve weeks. Grip strength of forelimbs and hind limbs, maximum motor nerve conduction velocity (MCV), and distal latency (DL) of the tail nerve were measured in nine rats of each group every four weeks. The other two rats of each group were perfused at the end of the experiment for morphological examinations. The rats of the 800-ppm group showed poor kicking activity and were not able to stand still on the testing slope. After a twelve-week exposure, forelimb grip strength decreased significantly at 800 ppm and hind limb grip strength decreased significantly at both 400 and 800 ppm. MCV and DL of the tail nerve deteriorated significantly at 800 ppm. Ovoid or bubble-like debris of myelin sheaths was prominent in the unraveled muscular branch of the posterior tibial nerve in the 800-ppm group. Swelling of preterminal axons in the gracile nucleus increased in a dose-dependent manner. Plasma creatine phosphokinase (CPK) decreased dose-dependently with significant changes at 400 and 800 ppm. 1-propyl bromide induced weakness in the muscle strength of rat limbs and deterioration of MCV and DL in a dose-dependent manner, with morphological changes in peripheral nerve and preterminal axon in the gracile nucleus. The authors concluded that 1-bromopropane may be seriously neurotoxic to humans and should thus be used carefully in the workplace. OEHHA staff determined that 200 ppm was a NOAEL and 400 ppm was a LOAEL for neurotoxicity of 1-propyl bromide in rats in this twelve-week study.

The same research group extended the above study to specific biochemicals and reported biochemical changes in the cerebrum including lower glutathione levels, decreased activity of the neuron-specific enzyme gamma-enolase, and decreased creatine kinase (Wang *et al.*, 2003).

Exposure of male Wistar rats to 1000 ppm of 1-BP eight hours per day for five or seven weeks caused a significant decrease in body weight and MCV and elongation in DL. Linearly arranged ovoid- or bubble-like debris of the axons and myelin sheaths in the teased tibial nerves and axonal swelling in gracilis nucleus were found in this group. This report (Yu *et al.*, 2001) extends the dose response relationship seen for neurotoxicity above.

Animal studies of reproductive and developmental toxicity

Yamada *et al.* (2003) studied the effects of 1-propyl bromide on female reproductive function in rats. Groups of ten female Wistar rats were exposed daily to 0, 200, 400, or 800 ppm 1-propyl bromide for eight hours a day. After 7 weeks, all rats at the highest dose became ill and were necropsied during the 8th week. The other groups were exposed for 12 weeks. In the 800-ppm group only, body weight was significantly less than the control at each time point from 2 through 7 weeks. Vaginal smears showed a significant increase in the number of irregular

estrous cycles; extended diestrus was noted at 400- and 800-ppm. Histopathological examination of the ovary showed a significant, dose-dependent reduction of the number of normal antral follicles and a decrease in the number of normal growing follicles at 400-ppm. No significant change was found in plasma concentrations of LH or FSH in any group as compared with the control. The authors concluded that 1-bromopropane can induce a dose-dependent ovarian dysfunction in non-pregnant female rats which is associated with disruption in follicular growth process.

Thirty-six Wistar male rats were randomly divided into four groups of nine and exposed to 200, 400, or 800 ppm 1-propyl bromide or only fresh air, eight hours per day for twelve weeks (Ichihara *et al.*, 2000b). Epididymal sperm indices were evaluated. The testes, epididymides, seminal vesicle, prostate, and other organs were weighed and examined histopathologically. Spermatogenic cells, in stage VII seminiferous tubules, and retained spermatids, at the basal region of stages IX-XI seminiferous epithelium, were counted. Plasma testosterone levels were measured by radioimmunoassay. The testicular weight did not significantly change, but the weight of epididymides, seminal vesicle, and prostate dose-dependently decreased. The weight of seminal vesicle decreased significantly at the lowest concentration of 200-ppm and above. 1-Propyl bromide induced a dose-dependent decrease in the epididymal sperm count and in motility, as well as an increase in tailless sperm and sperm with an immature head shape. The spermatogonia, preleptotene spermatocytes, pachytene spermatocytes, and round spermatids (various stages of sperm development) did not decrease significantly at stage VII. Retained, elongated spermatids near the basement membrane at the postspermiation stages IX-XI increased dose-dependently. Plasma testosterone levels significantly decreased at the 800-ppm dosage. 1-Bromopropane caused failure of spermiation. The authors concluded the solvent may have serious reproductive toxic effects in men, and should be used very cautiously in the workplace.

Data from Ichihara *et al.* (2000b) on inhalation of 1-propyl bromide in male rats

1-Propyl bromide	*Body weight (g)*	*Seminal vesicle (g)*	*Seminal vesicle relative wt (mg/g bw)*	*Sperm count ($x10^6$/g cauda)*
0 (n=8)	432±21[#]	1.88±0.27	4.35±0.62	792±199
200 ppm (n = 9)	426±25	1.38±0.26**	3.23±0.55**	772±221
400 ppm (n = 9)	403±25*	1.27±0.25**	3.17±0.67**	588±132*
800 ppm (n = 9)	382±16**	1.00±0.36**	2.62±0.87**	240±240**

[#] mean±standard deviation; * $p<0.05$; ** $p<0.01$

Interim inhalation chronic REL estimate

A chronic REL is a concentration at or below which adverse health effects are not likely to occur in the general population. An interim chronic REL for 1-propyl bromide was estimated from the reproductive toxicity data in the Ichihara *et al.* (2000b) study.

Study	Ichihara *et al.* (2000)
Study population	Male rats (9/group)
Exposure method	Discontinuous whole-body inhalation to 0, 200, 400, and 800 ppm
Critical effects	Male reproductive; weight of seminal vesicle
LOAEL	200 ppm
NOAEL	Not determined
Exposure continuity	8 hours/day, 7 days/week
Exposure duration	12 weeks
Average experimental exposure	67 ppm for LOAEL group (200 x 8/24)
Human equivalent concentration	67 ppm for LOAEL group
LOAEL uncertainty factor	3
Subchronic uncertainty factor	3 (LOAEL is based on a 12 wk study in rats)
Interspecies uncertainty factor	3 (see below)
Intraspecies uncertainty factor	10
Cumulative uncertainty factor	300
Interim Reference Exposure Level	220 ppb; 1100 $\mu g/m^3$

From the Ichihara *et al.* (2000b) study OEHHA staff determined that 200 ppm was a subchronic LOAEL for reproductive toxicity in male rats. The LOAEL was time adjusted from 8 hours to an equivalent continuous 24-hour exposure of 67 ppm. Use of OEHHA's methodology for developing a chronic Reference Exposure Level (REL) (division by a LOAEL uncertainty factor (UF) of 3, a subchronic UF of 3, an interspecies UF of 3 to account for residual susceptibility differences in rats not accounted for by U.S. EPA Human Equivalent Concentration (HEC) approach, and an intraspecies UF of 10) results in a chronic inhalation REL of 220 ppb (1100 $\mu g/m^3$). This is an estimate based on our approved procedure (OEHHA, 2000), but it has not been reviewed by the Scientific Review Panel.

Genotoxicity

1-Propyl bromide is not genotoxic. In the CytoMed cell death assay 1-propyl bromide was effective in causing cell death at 500 ppm but not at a lower concentration (presumably 100 ppm). The chemical was not effective in an altered enzyme function bioassay and in two DNA damage bioassays at 500 ppm. (Amity Product Information Bulletin Sheet Ref No: 01-005)

Evaluation by other agencies

The ACGIH currently has no workplace TLV for 1-propyl bromide. The California Department of Health Services has released a Hazard Alert on the chemical for workers based on the reproductive and nervous system toxicity observed in animal studies.

The Center for the Evaluation of Risks to Human Reproduction of the National Toxicology Program convened an expert panel to study the reproductive and developmental toxicity of the chemical. In March 2002 the panel completed its report (NTP-CERHR-1-BP-02) and found that the human data were insufficient to draw conclusions. However, the available data from animals were sufficient to conclude that 1-propyl bromide can induce reproductive and developmental toxicity in rats and that the rat data are relevant to assessing potential for human reproductive effects (NTP, 2000).

The National Toxicology Program (NTP) is currently conducting a two year bioassay by inhalation in mice at 0, 62.5, 125, or 250 ppm and in rats at 0, 125, 250, or 500 ppm, which may give better, more robust dose-response data and fill in any data gaps.

Based on the above, OEHHA staff are concerned about the neurotoxicity and reproductive toxicity of 1-propyl bromide and would be concerned about its use as a dry-cleaning solvent.

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1-Bromopropane (n-Propyl Bromide)

1-Bromopropane can harm the reproductive system and the nervous system. It causes sterility in both male and female test animals, and harms the developing fetus when tested in pregnant animals. 1-Bromopropane can damage the nerves, causing weakness, pain, numbness, and paralysis. It will soon be tested in animals to find out if it can cause cancer, as many similar chemicals do. The effects of 1-bromopropane on human health have not been well studied. However, a few human case reports suggest that 1-bromopropane can harm the nervous system. 1-Bromopropane is a new solvent intended to replace solvents like trichloroethane and some Freons that damage the upper ozone layer. HESIS is issuing this Hazard Alert because 1-bromopropane is being considered for widespread use and is not regulated to protect workers, consumers, or the environment.

Health Hazard ALERT

How to find out if you are working with 1-bromopropane

1-Bromopropane is a solvent. It might be used wherever there is a need to dissolve fats, waxes, or resins. So far, two of its main uses are in degreasing and in spray adhesives. It is being considered for use in drycleaning and for many other uses as a replacement for other organic solvents that damage the upper ozone layer.

Your employer must tell you if you are working with 1-bromopropane, and must train you to use it safely (California Code of Regulations, Title 8, Sections 3203 and 5194). If you think you may be exposed to 1-bromopropane on the job, ask to see the Material Safety Data Sheets (MSDSs) for the products you are using. The MSDS for a product that contains 1-bromopropane must identify it in Section 2, by the CAS number 106-94-5. 1-Bromopropane is also called n-propyl bromide. Some MSDSs do not fully describe the hazards of the product.

How 1-bromopropane enters your body

1-Bromopropane enters your body when you breathe its vapor or drops of spray in the air. Some can enter your body through your skin.

Your risk of health effects depends on the amount of 1-bromopropane that enters your body. That depends mainly on the amount (the concentration) of 1-bromopropane in the air, your skin contact, and how long you are exposed.

How 1-bromopropane can affect your health

The toxic effects of 1-bromopropane in humans have not yet been well studied. Because it is a recently introduced chemical, most information comes from animal testing, not from experience with human use.

In most of the animal tests, the animals breathed 1-bromopropane in the air. However, you can also absorb 1-bromopropane through your skin.

HEALTH HAZARD ALERT

HESIS
HAZARD EVALUATION SYSTEM & INFORMATION SERVICE
California Department of Health Services
Occupational Health Branch
1515 Clay Street, Suite 1901, Oakland, CA 94612
510-622-4300 • www.dhs.ca.gov/ohb

JULY 2003
California Department of Health Services • California Department of Industrial Relations

REPRODUCTIVE SYSTEM

1-Bromopropane damages the reproductive systems in both male and female animals. In males, it damages the sperm, testicles, prostate, epididymis, and seminal vesicles, and reduces testosterone levels, causing sterility. In females, it damages the ovaries and interferes with the estrous cycle, again causing sterility. 1-Bromopropane also caused delayed growth in the offspring of animals exposed during pregnancy. Some of these effects were seen at exposure levels as low as 200 parts per million (200 "ppm") in air, and possibly even at 100 ppm.

Reproductive toxicity of 1-bromopropane has not been studied in humans, but the closely related chemical 2-bromopropane has been found to cause long-lasting ovarian failure and absence of sperm in workers.

NERVOUS SYSTEM

1-Bromopropane damages the nerves in the arms, legs, and body. There is evidence that 1-bromopropane may also damage the brain itself. Animal tests have found these effects with exposures as low as 400 ppm. Case reports show that similar effects can occur in humans.

EYES, NOSE, THROAT, AND SKIN

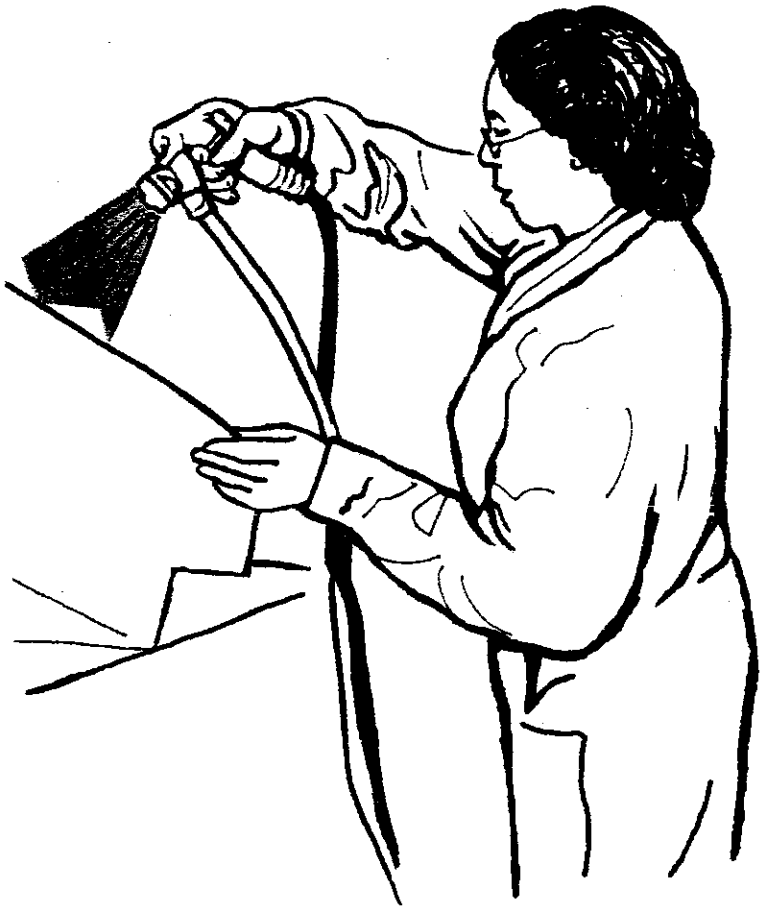
1-Bromopropane is irritating to the eyes, nose, and throat, at exposure levels of perhaps 30 ppm. Like other organic solvents, the liquid can dissolve the natural protective oils on your skin and cause dermatitis (dry, rough, red, cracked skin). It can also be absorbed into your body through the skin.

LIVER

Very high exposures may harm the liver. We don't know whether there's any risk to the liver from exposure levels likely to be found in the workplace.

CANCER

1-Bromopropane will soon be tested to see whether it can cause cancer. Many similar chemicals, such as dibromochloropropane (DBCP), do cause cancer. In some tests, but not in others, 1-bromopropane has caused genetic mutations. Chemicals that cause mutations often can cause cancer.



HOW TO REDUCE YOUR EXPOSURE

Even though there is no Permissible Exposure Limit (PEL) for 1-bromopropane (see page 4), Cal/OSHA's Title 8, Section 5141 requires your employer to protect you from being exposed to chemicals at levels that harm your health. See **www.dir.ca.gov/title8/5141.html**.

Cal/OSHA and the Cal/OSHA Consultation Service can help you and your employer – see "Where to Get Help" on the last page.

- **Substitution.** The best way to reduce exposure is to switch to products that don't contain 1-bromopropane. Avoid using products for which you do not have an MSDS.

  Switch to water-based adhesives, when possible, for flexible foam fabrication. Hot water-based aqueous cleaning detergents often can be substituted for 1-bromopropane products for vapor degreasing and cold cleaning operations.

  If you can't switch to 1-bromopropane-free products, take other steps to limit your exposure.

- **Using Less.** If you must use 1-bromopropane products, use as little as possible. Keep containers closed between uses. 1-Bromopropane can evaporate from 1-bromopropane-soaked rags, so make sure that used rags are kept in a well-ventilated area or sealed in an airtight container.

- **Ventilation.** Make sure that there is good ventilation. "Local exhaust ventilation" is most effective; it captures contaminated air at the source, before 1-bromopropane can spread into your breathing zone. In a study conducted by the National Institute for Occupational Safety and Health (NIOSH), for example, improving the local exhaust ventilation reduced 1-bromopropane levels by about 70% in a cushion manufacturing plant. Next best is general ventilation, which uses a fan-powered system to bring fresh air into the work area. Open doors and windows usually provide very little ventilation. An indoor fan that just blows contaminated air around without removing it from your work area is not effective.

- **Other Engineering Controls.** Vapor degreasing systems should include controlled hoists, effective cooling coils, and lids. Vapor degreasing should be isolated from other work areas. If parts are removed wet, the drying area should be vented to the outdoors.

- **Respiratory Protection.** Respirators may be used only if ventilation and other control methods are not effective and feasible. A half-face respirator with organic vapor cartridge can reduce your exposure. In spraying operations, this should be combined with a mist pre-filter cartridge. A "dust mask" will not protect you, and may even increase your exposure by giving a false sense of confidence. Employers must comply with the Cal/OSHA Respiratory Protection Standard (Title 8, Section 5144). See **www.dir.ca.gov/title8/5144.html**.

- **Skin Protection.** It may be hard to avoid getting 1-bromopropane on your hands if you use it for cleaning or gluing. If you must use 1-bromopropane products and it is likely that it will get on your skin, wear protective gloves and replace them often. Chemical protective clothing, such as aprons or sleeves, may also be needed if skin contact occurs at areas other than your hands. California regulation (Title 8, Section 3384) requires employers to supply gloves or any other necessary protective equipment. Viton, Silvershield, and 4H glove materials may resist penetration by 1-bromopropane longer than most other materials. 1-Bromopropane can penetrate some common glove materials within 30 minutes to two hours.

Legal exposure limits

1-Bromopropane is a virtually unregulated chemical. Cal/OSHA does not have a Permissible Exposure Limit (PEL) for workplace exposure. Neither the U.S. Environmental Protection Agency (U.S. EPA) nor Cal/EPA has set any limits on 1-bromopropane in the environment. U.S. EPA is considering approving 1-bromopropane for use as an alternative to chemicals that damage the ozone layer in the upper atmosphere.

Recommended exposure limits

HESIS recommends that workplace exposure be limited to about 1 ppm in order to protect against the reproductive and nerve toxicity of 1-bromopropane. HESIS also recommends a skin notation to require protection against skin contact exposure.

Many manufacturers and distributors have made recommendations for occupational exposure limits. These proposals range from 5 ppm to 100 ppm.

Measuring your exposure

The amount of 1-bromopropane in the air in your workplace can and should be measured. However, until 1-bromopropane is regulated by Cal/OSHA, there may not be any legal standard to compare the results to.

Are there medical tests for exposure and health effects?

1-Bromopropane levels in urine reflect recent exposure fairly accurately, but the test is difficult and expensive. Bromine levels in urine also reflect recent exposure, but other exposures may influence the test. Standard tests for reproductive function, nervous system damage, and blood effects may be appropriate if you work with 1-bromopropane.

Regulations that help to protect workers

HAZARD COMMUNICATION STANDARD. Under this standard (Title 8, Section 5194), your employer must tell you if any hazardous substances are used in your work area, must train you to use them safely, and must make MSDSs available. See **www.dir.ca.gov/title8/5194.html.**

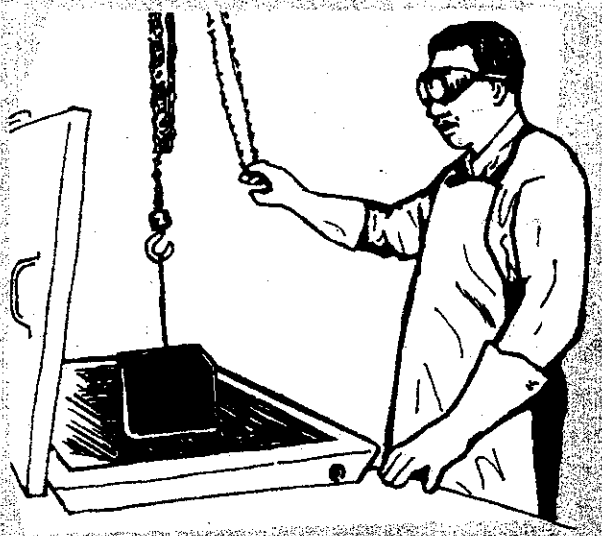
INJURY AND ILLNESS PREVENTION PROGRAM. Every employer must have an effective, written Injury and Illness Prevention Program (IIPP) that identifies a person with the authority and responsibility to run the program (Title 8, Section 3203). The IIPP must include methods for identifying workplace hazards, methods for correcting hazards quickly, health and safety training at specified times, a system for communicating clearly with all employees about health and safety matters (including safe ways for employees to tell the employer about hazards), and record-keeping to document the steps taken to comply with the IIPP Standard. See **www.dir.ca.gov/title8/3203.html.**

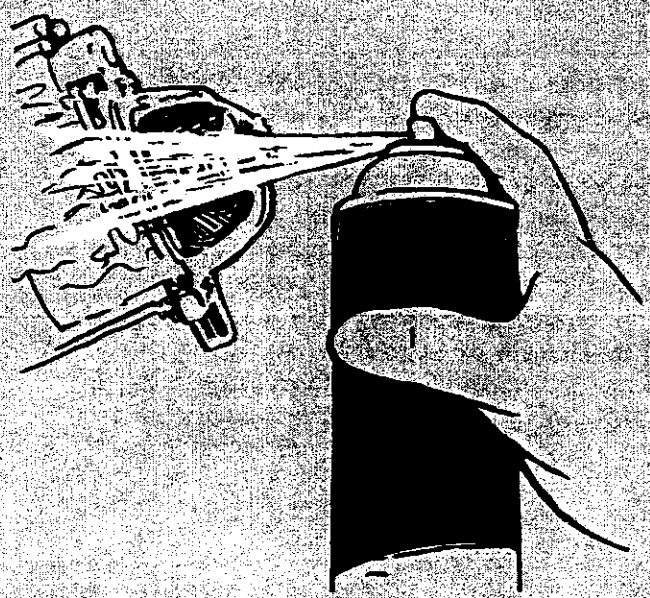
ACCESS TO MEDICAL AND EXPOSURE RECORDS. You have the right to see and copy your own medical records, and any records of toxic substance exposure monitoring (Title 8, Section 3204). These records are important in determining whether your health has been affected by your work. Employers who have such records must keep them and make them available to you for at least 30 years after the end of your employment. See **www.dir.ca.gov/title8/3204.html.**

DO YOU USE ANY OF THESE PRODUCTS?

Abzol
Albatross VDS-3000
Alpha Metals VaporEdge 1000
Amrep Misty Safety Solvent 2000
Ceramichrome Overglazes 6, 8, 9, or 18
Ecolink Hypersolve
Ecolink Triagen
EnSolv; EnSolv-A; EnSolv-CW
Hypersolve NPB; Hypersolve ASC
K-Grip 501 Spray Adhesive
Leksol
LPS Instant Super Degreaser II
Micro Care PowrClean Solvent
NPB Heavy Duty Cleaner Degreaser
NPB Heavy Duty Contact Cleaner
NPB Heavy Duty Flux Remover
Nye Lubricants Fluorosolvent 507
Nye Lubricants Nyetact 502H-20
Pensolve PB2000
Petroferm Lenium
Petroferm nPB Stabilizer Booster
Rite-Off Generation 2000 Bromo-Clean
Solvon PB, PBA, AER, ACS, DR, or IP
Techtride DG
Tek-Rap Series 200-20D Low-VOC/HAPs Liquid Adhesive Coating
United C174 Aerosol Contact Cleaner
Western Chemical

These are some products with MSDSs showing that they contain 1-bromo-propane. However, products like these can change their ingredients quite often. Be sure to check the current MSDS for whatever products you're using.





WHERE TO GET HELP

➤ **HESIS** answers questions about 1-bromopropane and other workplace hazards and has many free publications available.

For information on workplace hazards: **(510) 622-4317**. Please leave a message and your call will be returned.

For HESIS Publications: **(510) 622-4138**. Call, or visit our website www.dhs.ca.gov/ohb, or write to HESIS, 1515 Clay Street, Suite 1901, Oakland, CA 94612.

- *HESIS Guide to Solvent Safety.* Discusses health and safety hazards and protective measures.
- *Workplace Chemical Hazards to Reproductive Health: A Resource for Worker Health and Safety Training and Patient Education.* Explains how chemicals can affect reproduction.
- *HESIS Publication List.* Fact sheets, booklets, and medical guidelines on workplace hazards including chemicals, repetitive motion, and infectious diseases. Visit our website, call, or write for the list.

➤ **California Division of Occupational Safety and Health (Cal/OSHA)** investigates workers' complaints, makes enforcement inspections, and answers questions about workplace health and safety regulations. Complainants' identities are kept confidential. Contact the Cal/OSHA Enforcement District office nearest to your workplace. Offices are listed in the blue government section near the front of the phone book, under "State Government / Industrial Relations / Occupational Safety and Health / Enforcement," or visit their website at www.dir.ca.gov/DOSH/districtoffices.htm.

➤ **Other resources for employees** may include your supervisor, your union, your company health and safety officer, your doctor, or your company doctor.

➤ **Cal/OSHA Consultation Service** helps employers who want free, non-enforcement help to evaluate the workplace and improve the health and safety conditions. Employers can call **(800) 963-9424**.

➤ **Occupational health services** can be found at:

- UC San Francisco/SFGH Occupational and Environmental Medicine Clinic: (415) 885-7580.
- UC Davis Occupational and Environmental Medicine Clinic: (530) 754-7635.
- UC Irvine Center for Occupational and Environmental Health: (949) 824-8641.
- UC San Diego Center for Occupational and Environmental Medicine: (619) 471-9210.

Gray Davis, Governor
State of California

Grantland Johnson, Secretary
Health and Human Services Agency

Diana M. Bontá, R.N., Dr.P.H.
Director, Department of Health Services

Steve Smith, Acting Secretary
Labor and Workforce Development Agency

Chuck Cake, Acting Director
Department of Industrial Relations

JANE NORLING DESIGN

OSP 03 79401

TOXICITY DATA REVIEW

Hydrocarbons (PureDry, D-2000)

(mineral spirits, paraffins, cycloparaffins)

Summary

Mixtures of hydrocarbons, with or without other materials, have been proposed as alternatives to perchloroethylene in dry cleaning. PureDry contains 95% mineral spirits, which can cause neurotoxicity, and eye and respiratory irritation at high concentrations. Perfluorinated chemicals constitute 5% of PureDry; additional information is needed on their environmental persistence. Another proposed substitute is ExxonMobil Chemical Dry Cleaning Fluid D-2000, which contains C_{11} to C_{13} aliphatic hydrocarbons.

Description

ExxonMobil Chemical Dry Cleaning Fluid D-2000 contains only C_{11} to C_{13} aliphatic hydrocarbons. It is a synthetic mix of ~90% paraffins and ~10% cycloparaffins (naphthenes) and boils between 185-211°C.

PureDry contains by weight 95% odorless mineral spirits (OMS). The odorless mineral spirits are a mixture of aliphatic hydrocarbons. PureDry also contains 3.6% HFE-7200 (a mixture of ethyl perfluoroisobutyl ether and ethyl perfluorobutyl ether), 0.9% FC-43 (perfluoro compounds of primarily 12 carbons), 0.3% PF-5070 (perfluoro compounds of primarily seven carbons), and 0.2% PF-5060 (perfluoro compounds of primarily six carbons). The toxicity of HFE-7200 is described in a separate toxicity summary.

OEHHA staff have reviewed a preliminary MSDS for PureDry, an MSDS for Shellsol® odorless mineral spirits (OMS), and toxicity tests on PureDry by Product Safety Labs in New Jersey. OEHHA also reviewed the peer-reviewed literature.

Hazards to humans of hydrocarbon mixtures

The occupational hazards of mineral spirits in the dry cleaning industry are known. Stoddard solvent has been used in the past in dry cleaning. Stoddard solvent is a mixture of 48% C_9 to C_{12} straight and branched chain hydrocarbons, 38% naphthenes (cycloparaffins such as cyclohexane), and 14% aromatic hydrocarbons (ACGIH, 1998). PureDry is an alternative to Stoddard Solvent and does not contain aromatic hydrocarbons (including benzene, a known human carcinogen). Shellsol®, the brand of mineral spirits in PureDry, contains naphtha, petroleum, and heavy alkylates and is described in the MSDS as a complex stream of

predominately C_9 to C_{12} hydrocarbons. Neurotoxicity, eye irritation and respiratory irritation at high levels of exposure are common effects of solvents. For Stoddard solvent the TLV is 100 ppm (525 mg/m^3) and was calculated by the American Conference of Governmental Hygienists (ACGIH) from data on the toxicity of its major components.

Acute toxicity of PureDry

Product Safety Labs found that the single dose LD_{50} for PureDry was greater than 500 mg/kg in 5 male and 5 female rats, since all 10 rats survived that dose. Ten rats survived a one hour inhalation exposure to 20.68 mg/L PureDry (20,680 mg/m^3). All rats survived a single dermal dose of 2000 mg/kg. The lab also reported that, based on applying the material directly to rabbit skin and eyes, PureDry was not a primary skin or eye irritant. These results indicate that the material does not have severe acute toxicity. However, no data for longer exposures were presented.

Toxicity studies of hydrocarbons in animals

OEHHA does not have a chronic Reference Exposure Level (REL) for Stoddard solvent or for odorless mineral spirits. However, chronic RELs have been developed for several hydrocarbons including (aliphatic) hexane (7,000 μg/m^3), (aromatic) benzene (60 μg/m^3), and three alkylbenzenes: ethylbenzene (2,000 μg/m^3), toluene (300 μg/m^3), and xylenes (700 μg/m^3). The chronic RELs are also are available on OEHHA's website (www.oehha.ca.gov).

Carpenter *et al.* (1975a,b) exposed groups of 25 male Harlan-Wistar rats and four beagle dogs by inhalation to 0, 84, 190, or 330 ppm Stoddard solvent 6 hours/day, 5 days per week for 13 weeks. Parameters tested included body, liver, and kidney weights, hematological counts and blood chemistry. No adverse effects were seen in dogs. The only adverse effects in rats were in the kidney, which the authors attributed to the "inherent murine nephrosis" in the strain.

Phillips and Egan (1984a) exposed groups of 50 male and 50 female Fischer 344 rats by inhalation to 0, 300 ppm (1.83 g/m^3), or 900 ppm (5.48 g/m^3) of C_{10}-C_{11} isoparaffins 6 hr/day, 5 days/week for 8 weeks. Some were allowed a 4-week period of recovery. The urine concentrating ability of male rats was reduced after 4 and 8 weeks at both 300 and 900 ppm. After recovery, the urine concentrating ability showed evidence of recovery. After 4 and 8 weeks exposure, glucose, protein, and epithelial cell excretion in urine of males were higher in exposed than controls. Creatinine clearance decreased after 8 weeks in the males at 900 ppm. After 4 weeks of recovery, urine glucose, protein, epithelial cell exfoliation, and creatinine clearance returned to control levels in exposed male rats. Overall, the effect on kidney function in male rats was mild and reversible. Histologic changes in exposed males included an increased

regenerative tubular epithelia and dilated tubules with proteinaceous debris. No changes were observed in females.

In a 12 week study, Phillips and Egan (1984b) exposed groups of 35 male and 35 female Sprague-Dawley rats to either Dearomatized White Spirit (DAWS) vapor at 1.97 and 5.61 g/m^3 or C_{10}-C_{11} Isoparaffinic Hydrocarbon (IPH) vapor at 1.91 g/m^3 (313 ppm) and 5.62 g/m^3 (921 ppm) for 6 hours/day, 5 days/week. (The vapor levels were targeted to equal the occupational exposure limit of 300 ppm and three times the limit (900 ppm), respectively, recommended by Exxon.) After 4, 8, and 12 weeks of exposure, a total of 10, 10, and 15 rats, respectively, from each group were necropsied. No deaths related to either vapor occurred during the study. Average body weights were significantly lower than controls in male rats following exposure to 5.61 g/m^3 DAWS, and 5.62 or 1.91 g/m^3 IPH. Body weights were not affected in females. The primary effects from DAWS or IPH were in the kidneys of male rats only and began at week 4. The corticomedullary junction showed signs of mild tubular toxicity (regenerative tubular epithelia and dilated tubules containing proteinaceous casts). The incidence and severity appeared to increase with increasing concentration and exposure duration. There were instances of statistically significant increases in liver and kidney weights in both males and females.

Effects of C_{10}-C_{11} IPH vapor on male rats after 12 weeks (Phillips and Egan, 1984b)

Isoparaffinic hydrocarbon (IPH) vapor	Erythrocyte count in males (10^6/mm^3)	Relative kidney weight in males	Relative liver weight in males
0 ppm	8.12±0.09	0.69±0.06	3.60±0.42
313 ppm	7.68±0.08*	0.77±0.08*	3.72±0.33
921 ppm	7.74±0.10*	0.81±0.08**	3.88±0.24*

* $p<0.05$; ** $p<0.01$

Interim inhalation chronic REL estimate for hydrocarbon mixtures

A chronic REL is a level at or below which adverse noncancer health effects would not be expected to occur even in sensitive subpopulations. An interim chronic REL for hydrocarbon mixtures can be estimated from the data on body weight, kidney, and erythrocyte count changes in male rats by Phillips and Egan (1984b).

Study	Phillips and Egan (1984b)
Study population	Male and female rats
Exposure method	Inhalation of 0, 313, and 921 ppm C_{10} & C_{11}
Critical effects	Body weight, kidney, and erythrocyte count changes in male rats
LOAEL	313 ppm
NOAEL	Not determined
Exposure continuity	6 hours/day, 5 days/week
Exposure duration	12 weeks
Average experimental exposure	56 ppm
Human equivalent concentration	56 ppm
LOAEL uncertainty factor	3
Subchronic uncertainty factor	3 (12 week study)
Interspecies uncertainty factor	3
Intraspecies uncertainty factor	10
Cumulative uncertainty factor	300
Interim Reference Exposure Level	0.19 ppm (~ 1.2 mg/m^3 for C_{11})

The study by Phillips and Egan (1984b) was selected as the key study to use to develop the chronic REL since C_{10} and C_{11} isoparaffinic vapor was considered to be closer to the C_9-C_{12} hydrocarbon composition of PureDry than Stoddard solvent is (e.g., Stoddard solvent contains aromatic hydrocarbons). The LOAEL was time adjusted to an equivalent continuous exposure of 56 ppm. Use of OEHHA's methodology for developing a chronic Reference Exposure Level (REL) (division by a LOAEL of 3, a subchronic UF of 3, an interspecies UF of 3 to account for residual susceptibility differences in rats not accounted for by U.S. EPA Human Equivalent Concentration (HEC) approach, and an intraspecies UF of 10) results in a chronic inhalation REL of 0.19 ppm (1.2mg/m^3). This interim value is an estimate based on our approved procedure (OEHHA, 2000), but it has not been reviewed by the Scientific Review Panel.

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TOXICITY SUMMARY

HFE-7100 and HFE-7200

Summary

The hydrofluoroethers (HFEs) are being developed as alternatives to industrial solvents due to their greatly lower ozone depleting potential (ODP) compared to the Freons. PureDry, a dry cleaning alternative to perchloroethylene, contains 3.6% HFE-7200.

Physical and Chemical Properties

HFE-7100 (denoted as T-6334 in study reports) (3M Corporation, 1999), except where noted).

Description	Clear, colorless liquid at room temperature. Mixture of approximately (1) 68.7% 2-(difluoromethoxymethyl)-1,1,1,2,3,3,3-heptafluoropropane and (2) 29.6% 1-ethoxy-1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy-butane (Mitsubishi Chemical Safety Institute Ltd., 1996b).
Molecular formula	(1) $(CF_3)_2CF-CF_2-O-CH_3$ (2) $CF_3-CF_2-CF_2-CF_2-O-CH_3$ (Mitsubishi Chemical Safety Institute Ltd., 1996b).
Molecular weight	250.06 for both (1) and (2)

HFE-7200 (denoted as T-6333 in study reports) (3M Corporation, 1999), except where noted).

Description	Clear, colorless liquid at room temperature. Mixture of approximately (1) 70.2% 2-(ethoxydifluoromethyl)-1,1,1,2,3,3,3-heptafluoropropane and (2) 29.6% 1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane (Mitsubishi Chemical Safety Institute Ltd., 1996a).
Molecular formula	(1) $(CF_3)_2CF-CF_2-O-C_2H_5$ (2) $CF_3-CF_2-CF_2-CF_2-O-C_2H_5$ (Mitsubishi Chemical Safety Institute Ltd., 1996a).
Molecular weight	264.09 for both (1) and (2)

Acute Toxicity: Inhalation

One test group of 5 male and 5 female rats (Sprague-Dawley, 8-9 weeks of age) was exposed to a test atmosphere containing HFE-7200 at a target concentration in air of 10% (v/v) (actual observed concentration was 9.2%, or 917 g/m^3) for four hours (Huntingdon Life Sciences Ltd., 1997c). Use of a control group was not reported. The rats were observed during the exposure period and for 14 days post exposure. Bodyweight was measured daily throughout the study. One female rat died during exposure to HFE-7200. Clinical signs seen in test rats during exposure included partial closing of the eyes, wetness around the snout/mouth and restless behavior. Wet staining on the body and a staggering gait were seen in all test rats immediately following exposure. All surviving rats were normal in appearance and behavior from Day 4 following exposure. The authors stated that exposure did not affect body weight during either the exposure or observation periods; however, no control group was available for comparison. Macroscopic pathology examination revealed slight lung congestion in the female rat that died during the exposure period. No microscopic pathology data were reported. The data indicated that the Lowest Observable Adverse Effect Level (LOAEL) for this study based on clinical signs and lethality was 917 g/m^3; a No Observable Adverse Effect Level (NOAEL) was not available for this study.

Acute Toxicity: Oral

One test group of 5 male and 5 female Sprague-Dawley rats (225 to 286 grams body weight, age not specified) was exposed to a single gavage dose of 5000 mg/kg-bodyweight HFE-7100 (Hazelton Wisconsin, 1995a). The rats were observed for 14 days post exposure. All animals were killed and examined macroscopically on day 14, the end of the observation period. No visible gross pathology lesions were observed at necropsy. No microscopic pathology data were reported. The authors stated that the acute lethal oral dose to rats of HFE-7100 was demonstrated to be greater than 5000 mg/kg-bodyweight.

Huntingdon Life Sciences Ltd. (1997d) assessed the toxicity of HFE-7200 following a single oral dose in the rat. A group of ten rats (Sprague-Dawley; five males, five females, 4-7 weeks of age) received a single oral gavage dose of the test substance administered at a dose level of 2000 mg/kg-body weight. Use of a control group was not reported. The rats were observed for 14 days post exposure. All animals were killed and examined macroscopically on day 15, the end of the observation period.

Clinical signs of reaction to treatment comprised piloerection and hunched posture in all rats; pallor of the extremities was seen in males only. No other clinical signs were observed and all animals had fully recovered by the afternoon of day 8. The authors stated that all animals achieved satisfactory bodyweight gains throughout the study; however, no control group was available for comparison. No macroscopic pathology abnormalities were observed at the study termination necropsy. No microscopic pathology data were reported. The authors stated that the acute lethal oral dose to rats of HFE-7200 was demonstrated to be greater than 2000 mg/kg-body weight.

Acute Toxicity: Dermal

Hazelton Wisconsin (1995b) studied the potential dermal toxicity of HFE-7100 in New Zealand White rabbits. Three male rabbits (2,408 to 2,575 grams body weight) were used in the study. Use of a control group was not reported. On the day before treatment, the back and/or flanks of each animal were clipped free of hair to obtain an unblemished skin site. A 0.5 ml amount of the test substance was applied under a 25 mm x 25 mm gauze pad to one intact skin site on each animal, then covered with a dressing for four hours. At the end of the exposure period, the dressing and gauze pad were removed and the treatment site was washed with warm water to remove any residual test substance. Approximately 30 minutes after removal of the test material, the degree of erythema and edema at each test site was read according to the Draize technique (recorded as the 4-hour score). Subsequent examinations were made at 24, 48, and 72 hours. The untreated skin of each animal was used for comparison. Application of HFE-7100 to the skin of rabbits under 4-hour semioccluded conditions resulted in a very slight erythema reaction in two animals at the 4-hour observation. This irritation cleared by the 24-hour observation. No other dermal irritation was observed.

Huntingdon Life Sciences Ltd. (1996b) studied the potential dermal toxicity of HFE-7200 in New Zealand White rabbits. Three 13 to 15 week old rabbits (sex not specified) were used in the study. Use of a control group was not reported. The hair was clipped from the chemical application site on the back of each rabbit exposing an area of skin approximately 100 mm x 100 mm. A 0.5 ml amount of the test substance was applied under a 25 mm x 25 mm gauze pad to one intact skin site on each animal, then covered with a dressing for four hours. At the end of the exposure period, the dressing and gauze pad were removed and the treatment site was washed with warm water to remove any residual test substance. Examination of the treated skin was made on Day 1 (approximately 60 minutes after removal of the dressings) and on Days 2, 3, and 4 (equivalent to 24, 48, and 72 hours after exposure). There were no signs of toxicity or ill health in any rabbit during the observation period, and no dermal reactions were observed in any animal throughout the study.

Hazelton Wisconsin (1996) examined the ability of HFE-7100 to produce delayed contact hypersensitivity in male Crl:(HA)BR strain guinea pigs (age not specified). Study groups included an irritation screening group of two animals, a test group of 10 animals, a naive control group of 10 animals, and a positive control group of four animals. The positive control used was 2,4-dinitrochlorobenzene. An irritation screening study using two animals was conducted to determine the irritation threshold of the test material. The test material was administered undiluted with each animal receiving two applications of the undiluted test material. The 0.4 mL doses were applied to adhesive patches; the patches were then placed on two shaved sites (one on the right and one on the left anterior dorsal quadrants) on each animal, covered with an overlapping strip of dental dam, and overwrapped with tape. The patches remained in place for approximately 6 hours after which they were removed and the sites washed. The application sites were observed for dermal reactions at approximately 24 and 48 hours after test material application. No dermal irritation was observed when the undiluted test material was administered.

Based on the results of the irritation screening study, the test material was administered undiluted for the induction phase and for the challenge application. On the day of test material application, the hair was removed from the backs of each animal in the test and positive control groups with electric clippers. The undiluted test material was applied to each animal in the test group by placing 0.4 mL on an adhesive patch and placing the patch on the induction site along the dorsal anterior left quadrant. The patches remained in place for approximately 6 hours after which they were removed and the sites washed. The positive control material, 0.3% w/v 2,4-dinitrochlorobenzene (DNCB) in 80% v/v ethanol in deionized water, was administered as a 0.4-mL dose to the positive control animals in the same manner used for the test material. The animals in the test and positive control groups received one application per week for 3 weeks for a total of three applications. Due to the strong irritation present in the induction site of the positive control animals, the third induction dose for these animals was applied to an induction site slightly posterior to the initial site. The naive control animals were not treated during this phase of the study.

Two weeks following the administration of the third induction dose, a challenge dose of 0.4 mL of test material was administered along the dorsal anterior right quadrant of the test group animals in the same manner as during the induction phase of the study. At this time the 10 naive (previously untreated) control animals were also treated in the same manner with a challenge application of the test material. The positive control material was administered as a 0.4-mL dose at a concentration of 0.1% w/v in acetone. The method used for the positive control group was the same as that of the test group.

No dermal reactions were observed in the animals in the test group when administered the undiluted test material during the induction or challenge phases of the study. None of the naive control animals reacted to the challenge application of the test material. The positive control animals were considered to have been sensitized because of the moderate to strong dermal reactions they exhibited to the 0.1% w/v concentration of DNCB in acetone at challenge. The authors concluded that HFE-7100 is not a dermal sensitizer in guinea pigs when tested by the closed patch technique.

Male Dunkin/Hartley guinea pigs (6-7 weeks of age) were used to assess the ability of HFE-7200 to induce dermal sensitization (Huntingdon Life Sciences Ltd., 1997g). A group of 20 animals were exposed to HFE-7200; a control group of ten animals was included in the study. A positive control was not included in this study; however, the authors stated that the sensitivity of the guinea pig strain used was checked periodically using the known sensitizer, hexyl cinnamic aldehyde (HCA). Prior to each induction application, the skin on the left shoulder region of the guinea pig was clipped free of hair using electric clippers. A 20 × 20 mm patch of surgical gauze (three layers thick) was saturated with approximately 0.5 ml of HFE-7200; the patch was then placed on the skin and covered by impermeable plastic adhesive tape secured by an elastic adhesive bandage and fixed with impervious plastic adhesive tape. Contact with the skin was maintained for approximately 6 hours for each induction exposure. The dressings were then removed and the resulting dermal reactions assessed approximately 24 hours later. The control and test animals were challenged topically two weeks after the final induction application using HFE-7200. Hair was removed by clipping from a 50 × 50 mm area on the right flank of each guinea pig. A 20 × 20 mm gauze

patch (three layers thick) was saturated with approximately 0.5 ml of the test substance in a similar fashion to that used for the induction applications. The patch was sealed to the flank using the methodology described above. Dressings were left in place for approximately 6 hours after which time they were removed. The challenge sites were evaluated 24 and 48 hours after removal of the patches. No signs of ill health or systemic toxicity were noted in the treated animals. There were no dermal reactions seen in any of the test or control animals. The authors concluded that HFE-7200 did not produce evidence of skin sensitization (delayed contact hypersensitivity) in any of the twenty test animals.

Acute Toxicity: Ocular

Hazelton Wisconsin (1995c) studied the ability of HFE-7100 to induce eye irritation in male New Zealand White rabbits. Three animals weighing from 2,551 to 2,597 g were used. The test animals received 0.1 mL of the undiluted test material placed into the everted lower lid of the right eye, with the left eye serving as the untreated control. The upper and lower lids were gently held together for 1 second to prevent loss of material and then released. The eyes of the rabbits remained unflushed immediately after treatment. The treated eyes were observed for ocular irritation at 1, 24, 48, and 72 hours after treatment. Irritation was graded and scored according to the Draize technique using a penlight as the source of illumination. A sodium fluorescein examination was used to aid in revealing possible corneal injury at the observation conducted at 24 hours. The authors stated that HFE-7100 produced only slight conjunctival irritation at the 1-hour observation, and all treated eyes returned to a normal appearance by 24 hours after treatment.

HFE-7200-induced eye irritation in New Zealand White rabbits (sex unstated) was investigated by Huntingdon Life Sciences Ltd. (1996a). The animals weighed 3.1 to 3.7 kg and were approximately 13 to 16 weeks of age. The test procedure was essentially as used in the HFE-7100 ocular study by Hazleton Wisconsin (1995) as described above. All treated animals demonstrated slight conjunctival irritation at the 1-hour observation; treated eyes in two animals returned to a normal appearance by 24 hours after treatment. One animal exhibited slight conjunctival irritation up to 48 hours post-treatment.

Cardiac Sensitization

Huntingdon Life Sciences Ltd. (1996e) examined the ability of HFE-7100 to induce cardiac sensitization in male beagle dogs (7 - 15 months old). Nine animals were used in the first stage of the study, which established an adrenaline dose at which there was a clear but minimal effect on the ECG ideally with a few ectopic beats. Typically the response consists of a transient increase in heart rate followed by a reflex slowing of the heart rate and an increase in the height of the T-wave, with occasional multiple unifocal ventricular tachycardia. Six of the nine animals were selected for the second stage of the study, in which the animals were exposed to HFE-7200 vapor. The animals not used from the first stage were eliminated because of ECG or other cardiac function abnormalities, or because of poor

acceptance of the procedure. The animals were exposed to one exposure of 17 minutes/session. The test concentrations used were as follows:

Exposure session	Target test gas concentration (% volume in air)
1	Air only
2	1.0
3	2.0
4	5.0
5	10.0

The actual measured concentrations of HFE-7100 corresponding to the target concentrations of 1, 2, 5 and 10% were 1.0, 1.88 and 4.89 and 8.93%, respectively. At least one calendar day was allowed between each exposure session to allow the dogs to recover.

The study was designed to provide information as to any dose level that gave rise to clear signs of test gas-related cardiac sensitization. The criterion for a positive effect was the appearance of a burst of multifocal ventricular ectopic activity (MVEA) or ventricular fibrillation (VF) at any time during exposure to the test gas. Ventricular tachycardia alone was not necessarily considered definitive evidence of a positive response.

The authors found no indications of cardiac sensitivity at concentrations of 1.0, 1.88, 4.89 and 8.93% HFE-7100. Adverse clinical signs were noted in the 2 dogs exposed to 8.93% HFE-7100, and included: Restlessness, cold extremities, limb rigidity, head and whole body tremors, head shaking, arched back, general state of agitation and salivation. Similar signs were seen in the dogs exposed to 4.89% v/v HFE-7100 but the signs were generally less severe. The authors did not explicitly note adverse clinical signs at the lower concentrations, but the study report indicates that similar adverse clinical signs were seen in the animals exposed to 1.88 % HFE-7100. This suggests that 1.0 % and 1.88% v/v (99.7 and 187 g/m^3, respectively) HFE-7200 are acute NOAEL and LOAEL values, respectively, for HFE-7100 acute toxicity in dogs in this study. The authors concluded that HFE-7100 does not cause cardiac sensitization in beagle dogs at concentrations of 8.93% or less.

The ability of HFE-7200 to induce cardiac sensitization in male beagle dogs (7 - 15 months old) was studied by Huntingdon Life Sciences Ltd. (1997e). The experimental design was generally the same as the HFE-7200 cardiac sensitization study described above. Nine animals were used in the first stage of the study, which established an adrenaline dose at which there was a clear but minimal effect on the ECG ideally with a few ectopic beats. Six of the nine animals was selected for the second stage of the study, in which the animals were exposed to HFE-7200 vapor. The animals not used from the first stage were eliminated because of ECG abnormalities, or to "maintain acceptable distribution of responders". The animals were exposed to one exposure of 17 minutes/session. The test concentrations used were as follows:

Exposure session	Target test gas concentration (% volume in air)
1	Air only
2	1.0
3	2.0
4	2.0
5	5.0

The actual measured concentrations of HFE-7200 corresponding to the target concentrations of 1, 2, and 5% were 0.97, 1.89, and 4.9%, respectively. At least one calendar day was allowed between each exposure session to allow the dogs to recover.

Cardiac sensitization was not observed in animals exposed to either 0.97 or 1.89% HFE-7200. At 4.90% HFE-7200 one dog responded within 20 seconds of the second adrenaline challenge with a series of ventricular premature complexes at approximately 130 beats per minute lasting approximately 30 seconds. Prior to this exposure the dog, which had been classified as a weak responder during the first study stage, had shown little or no abnormal cardiac activity with only 2 unifocal ectopic beats seen after adrenaline administration during exposure to 2% HFE-7200. While the ectopic beats were generally unifocal in nature, it is considered that in the absence of any previous activity, the response was indicative of cardiac sensitization.

Clinical signs were noted in the 2 dogs exposed to 4.90% HFE-7200, and included restlessness, limb and whole body tremors, limb and whole body rigidity, head shaking, arched back, coughing, licking muzzle, limb raising, redness of the eyes, general state of agitation and salivation. The severity of the signs was such that it was considered that exposures to higher concentrations of HFE-7200 could not be justified. Similar signs were seen in the dogs exposed at 1.89% v/v HFE-7200 in air but the signs were generally less severe. The authors concluded that the results of this study show that HFE-7200 has potential to cause cardiac sensitization in beagle dogs at concentrations in excess of 4.90%, and that the no effect level for cardiac sensitization was 1.89%. Additionally, the consistent adverse clinical signs beginning at 0.97% (hind limb tremors) which become progressively more severe with increasing dose (arched back, whole body tremors, limb rigidity, whole body rigidity),and which did not occur in animals challenged with adrenaline and exposed to air only, suggest that 0.97% v/v (96.7 g/m^3) HFE-7200 is an acute LOAEL for HFE-7200-induced acute toxicity in dogs in this study. A NOAEL was not available from this study.

Subchronic Toxicity: Inhalation

Huntingdon Life Sciences Ltd. (1996d) studied the effects of HFE-7100 on rats after a 4-week subchronic inhalation exposure. Male and female Sprague-Dawley rats (approximately 6 weeks of age) were exposed to target concentrations of 0, 1500, 3000, 9500 or 30,000 ppm (5 animals/sex/exposure group) for 6 hours/day, 5 days/week for four weeks; actual chamber concentrations were 1489, 2935, 9283 and 28,881 ppm, respectively.

The authors stated that no treatment-related clinical signs were observed during exposure. Liver weights were significantly increased (131% of control; $p < 0.01$) in the 30,000 ppm

male rat exposure group. Liver/body weight ratios were increased in male animals in a dose-dependent manner (108, 104, 115 and 126% of control in the 1500, 3000, 9500 and 30,000 ppm groups, respectively). The authors stated that this increase was not statistically significant; however, for reasons not explained, statistical analysis was performed using only the three animals selected for palmitoyl CoA oxidase activity analysis of the five animals in the exposure group. Centrilobular hepatocyte enlargement was observed in 2/5 and 4/5 of the animals in the male 9500 and 30,000 ppm exposure groups.

Increased urinary inorganic fluoride was evident at all levels of exposure, and the effect was dose related. The differences at all levels of exposure except those animals exposed to 1500 ppm were statistically significant compared to controls. Urinary fluoride concentration (μg/ml) and total output (μg) in the male 30,000 ppm group was 18-fold higher than controls. Urinary fluoride concentration and total output in the female 25000 ppm group was 8-fold and 5-fold higher, respectively, than controls. Urinary protein was also significantly increased in the male 9500 and 30,000 ppm group animals. Blood cholesterol was significantly lowered (68% of control; $p < 0.05$) in the 30,000 ppm male animals. Hepatic palmitoyl CoA oxidase activity was increased in the male 3000, 9500 and 30,000 ppm groups (190, 190 and 820% of control, respectively). This increase was not statistically significant; however, it should be noted that the authors chose to only assay three of the five animals in each treatment group.

HFE-7100 treatment resulted in increases in centrilobular hepatocyte hypertrophy (significant dose-response using Fisher's exact test; $p < 0.01$) and non-statistically significant increases in liver/body weight ratios and hepatic palmitoyl CoA oxidase activity in the 9500 and 30,000 ppm male rat exposure groups. Statistically significant increases in liver weight and decreases in blood cholesterol levels were also observed in the 3000 ppm male rat exposure group. These data suggest that HFE-7100 may be a peroxisome proliferator in male rats.

The effects of HFE-7100 on rats after a 13-week subchronic inhalation exposure were investigated by Huntingdon Life Sciences Ltd. (1996c). Male and female Sprague-Dawley rats (approximately 6 weeks of age) were exposed to target concentrations of 0, 1500, 4500, 7500 or 15,000 ppm (10 animals/sex/exposure group) for 6 hours/day, 5 days/week for 13 weeks; actual chamber concentrations were 1502, 4550, 7533 and 15,159 ppm, respectively.

The authors stated that no treatment-related clinical signs were observed during exposure. Liver (120% of control; $p < 0.01$), spleen (117% of control; $p < 0.05$) and kidney (112% of control; $p < 0.05$) weights were significantly increased in the 15,000 ppm male rat exposure group. Liver/body weight ratios were increased in male animals in a dose-dependent manner (103, 113, 106 and 117% of control in the 1500, 4500, 7500 and 15,000 ppm groups, respectively). The authors stated that the increase in liver/body weight ratios in the 15,000 ppm group was significant ($p < 0.05$); it should also be noted that this analysis was performed using only the three animals selected for palmitoyl CoA oxidase activity analysis of the ten animals in the exposure group. Significant centrilobular hepatocyte enlargement was observed in 9/10 males ($p < 0.01$) and 6/10 females ($p < 0.05$) in the 15,000 ppm exposure groups.

Increased urinary inorganic fluoride was evident at all levels of exposure, and the effect was dose related. The differences at all levels of exposure except those male animals exposed to 1500 ppm were statistically significant compared to controls. Urinary fluoride concentration (µg/ml) and total output (µg) in the male 15,000 ppm group was 27-fold and 34-fold higher than controls, respectively. Urinary fluoride concentration and total output in the female 15,000 ppm group was 15-fold and 14-fold higher, respectively, than controls.

Hepatic palmitoyl CoA oxidase activity was increased in the male 4500, 7500 and 15,000 ppm groups (220, 180 and 550% of control, respectively). This increase was statistically significant for the 15,000 ppm group; additionally, it should be noted that the authors chose to only assay three of the ten animals in each treatment group.

HFE-7100 treatment resulted in increases in centrilobular hepatocyte hypertrophy (significant dose-response using Fisher's exact test; $p < 0.01$) in male rats and statistically significant increases in liver weights, liver/body weight ratios and hepatic palmitoyl CoA oxidase activity in the 15,000 ppm male rat exposure groups. The authors stated these data indicate that HFE-7100 is a peroxisome proliferator in male rats. Peroxisome proliferators often cause increased liver tumor incidences in chronically exposed susceptible rodents (e.g., rats or mice). This suggests that HFE-7100 would be an appropriate candidate for a chronic toxicity/carcinogenicity bioassay. Any risk assessment for widespread use of HFE-7100 needs to include consideration of long-term toxicity endpoints in test animals and humans, for which data are currently unavailable.

The subchronic inhalation toxicity of HFE-7200 in rats was investigated by Huntingdon Life Sciences Ltd. (1997a). Male and female Sprague-Dawley rats (5/sex/exposure group; 180 – 191 g body weight) were exposed to target concentrations of 0, 1000, 3000, 9000 or 25,000 ppm (10.8, 32.4, 97.2 and 270 g/m^3, respectively) HFE-7200 for 6 hours/day, 5 days/week for four weeks. Actual chamber concentrations were found to be 1066, 3006, 8844 and 24,386 ppm.

The authors stated that no treatment-related clinical signs were observed during exposure. However, after four weeks of exposure to HFE-7200, a statistically significant increase in the number of animals for which assessment of gait was not possible was noted in the male 25,000 ppm exposure group. There was also the observation of slightly lower activity and rearing counts among males at 25,000 ppm, although this difference was not statistically significant. The authors stated that no treatment-related differences in biochemistry were seen, and that differences achieving statistical significance were considered not of toxicological significance. However, statistically significant increases in blood alkaline phosphatase levels were seen in the 9000 and 25,000 ppm male exposure groups (138 and 140% of controls; $p < 0.05$). Statistically significant decreases in blood cholesterol level were seen in the 9000 and 25,000 ppm male exposure groups (60 and 63% of controls; $p < 0.05$). Increased urinary inorganic fluoride was evident at all levels of exposure, and the effect was dose related. The differences at all levels of exposure were statistically significant compared to controls. Urinary fluoride concentration (µg/ml) and total output (µg) in the male 25,000 ppm group was 105-fold and 120-fold higher, respectively, than controls. Urinary fluoride

concentration and total output in the female 25,000 ppm group was 38-fold and 31-fold higher, respectively, than controls.

Gross pathological examination indicated that liver enlargement was present in 1 of 5 rats in the 9000 ppm group, and in 4 of 5 rats in the male 25,000 ppm group. Liver/body weight ratios were significantly increased in the male 9000 and 25,000 ppm groups (32 and 45% increases compared to controls, respectively). Centrilobular hepatocyte hypertrophy was observed in the male 3000, 9000 and 25,000 ppm groups; this change was statistically significant in the 9000 and 25,000 ppm groups. Statistically significant and treatment-related increases in palmitoyl CoA oxidase activity (a peroxisomal enzyme often used as a marker for peroxisome proliferation) were seen in male rats of the 3000, 9000 and 25,000 ppm treatment groups when compared with the control group. Maximum increases, of approximately 25-fold ($p < 0.01$), were measured in the high dose group.

Kidney enlargement was noted in 3 of 5 male rats and 1 of 5 female rats in the 25,000 ppm group, and in 1 of 5 male rats in the 9000 ppm group. Tubular basophilia with nuclear clustering in the inner cortex was seen in two males in each of the 25000 ppm and 9000 ppm groups.

HFE-7200 treatment resulted in increases in blood alkaline phosphatase activity, liver enlargement, liver/body weight ratios, centrilobular hepatocyte hypertrophy, and hepatic palmitoyl CoA oxidase activity in the 9000 and 25,000 ppm male rat exposure groups. Increases in centrilobular hepatocyte hypertrophy, and hepatic palmitoyl CoA oxidase activity were also observed in the 3000 ppm male rat exposure group. A decrease in blood cholesterol levels in exposed male rats was also observed in the 9000 and 25000 ppm male rat exposure groups. These data indicate that HFE-7200 is a peroxisome proliferator in male rats.

Kidney enlargement and tubular basophilia with nuclear clustering in the inner cortex was also seen in the 9000 ppm and 25000 ppm male rat exposure groups. Possible explanations for these effects could be that they are due either to the peroxisome proliferator effects of HFE-7200, or to regeneration of renal cortical tubules subsequent to tubule epithelial cell damage. Peroxisome proliferators have been shown to induce renal cortical tubule peroxisome proliferation (Hawkins *et al.*, 1987; Reddy and Lalwani, 1983) and increase renal DNA synthesis (Seifert and Mostecká, 1987) in rodents. Additionally, urinary fluoride resulting from fluorocarbon metabolism has been reported to be acutely toxic to renal cortical tubules. Statistically significant increases in blood alkaline phosphatase levels, a marker of renal tubule damage, were seen in the 9000 and 25000 ppm male exposure groups (138 and 140% of controls; $p < 0.05$). Increased creatinine excretion, which is also often used as an indicator of compromised renal function, was not noted in the HFE-7200-exposed animals. However, Usuda *et al.* (1999) noted that increased creatinine excretion does not correlate well with the induction of fluoride-induced acute renal damage. More data would be required to determine the toxicological significance of the renal effects described above.

Peroxisome proliferators often cause increased liver tumor incidences in chronically exposed susceptible rodents (e.g., rats or mice); as noted for HFE-7100, this suggests that HFE-7200 would be an appropriate candidate for a chronic toxicity/carcinogenicity bioassay. Any risk

assessment for widespread use of HFE-7200 also needs to include consideration of long-term toxicity endpoints in test animals and humans, for which data are currently unavailable."

Subchronic Toxicity: Oral

Mitsubishi Chemical Safety Institute Ltd. (1996d) studied the oral toxicity of HFE-7100 in rats. In a preliminary study, male and female Sprague-Dawley rats (3 animals/sex/dose; 5 weeks old) were exposed to 0, 8, 40, 200 or 1000 mg/kg bodyweight HFE-7100 by daily oral gavage for 14 days. The authors stated that no abnormalities were observed in clinical observation, body weight, hematology and necropsy, but a slight increase in liver weight in males and females was noted in the 1000 mg/kg group. The main study exposed male and female Sprague-Dawley rats (5 weeks old) to 0, 8, 40, 200, or 1000 mg/kg bodyweight HFE-7100 by daily oral gavage for 28 days. Six animals/sex/group were used for the 8 and 40 mg/kg bodyweight exposure groups; all animals in these groups were sacrificed and necropsied at the end of the exposure period. Twelve animals/sex/group were used for the 0 and 200 and 1000 mg/kg bodyweight exposure groups. Six animals in these groups were sacrificed and necropsied at the end of the exposure period; six animals were allowed a 14-day recovery period, then sacrificed and necropsied.

No deaths occurred throughout the observation period although irregular respiration and salivation were observed in males in the 1000 mg/kg group. Body weight, food consumption, hematology, and urinalysis in the treatment groups were similar to the control group. Absolute and relative liver weights were significantly increased in males in the 1000 mg/kg group. Additionally, relative liver weights were significantly increased in females in the 1000 mg/kg group. The liver was macroscopically enlarged, and hypertrophy of the centrilobular hepatocytes was observed. The thyroid in one male in the 1000 mg/kg group was macroscopically enlarged, and hypertrophy of the follicular cells was observed histologically. The changes described above resolved by the end of the recovery period, and they were thus considered to be reversible. The authors considered the No Observable Effect Level (NOEL) for HFE-7100 to be 200 mg/kg for both males and females in this study. In light of the data on hepatic peroxisome proliferation after inhalation exposure to HFE-7100 (Huntingdon Life Sciences Ltd., 1996c; Huntingdon Life Sciences Ltd., 1996d), the increased relative liver weights suggest the possibility of hepatic peroxisome proliferation in the 1000 mg/kg exposure groups.

The potential oral toxicity of HFE-7200 in rats was studied by Mitsubishi Chemical Safety Institute Ltd. (1996c). The protocol and exposure groups used were essentially as described above for the HFE-7100 rat 28-day oral toxicity study performed by Mitsubishi Chemical Safety Institute Ltd. (1996d). No abnormalities were observed in clinical observation, body weight, hematology and necropsy in the 14-day preliminary study. However, there were increases in liver weight in males in the 200 and 1000 mg/kg group and in females in the 1000 mg/kg group. In the main study, no deaths occurred throughout the observation period although irregular respiration in males and females in the 1000 mg/kg group and salivation in males in the 1000 mg/kg group were observed during the treatment period. Absolute and relative liver weights were significantly increased in males in the 1000 mg/kg group.

Additionally, relative liver weights were significantly increased in males in the 200 mg/kg group. The liver was macroscopically enlarged, and centrilobular hepatocyte hypertrophy was observed. Absolute and relative kidney weights were also significantly increased in males in the 1000 mg/kg group. The changes described above resolved by the end of the recovery period, and they were thus considered by the authors to be reversible. The authors stated that these results indicate that the NOELs for HFE-7200 in this study are 40 mg/kg in male rats and 200 mg/kg in female rats. In light of the data on hepatic peroxisome proliferation after inhalation exposure to HFE-7200 (Huntingdon Life Sciences Ltd., 1997a), the increased relative liver weights suggest the possibility of hepatic peroxisome proliferation in the 200 and 1000 mg/kg male exposure groups.

Chronic Toxicity

No chronic toxicity data are available for either HFE-7100 or HFE-7200.

Metabolism

No metabolism data are available for either HFE-7100 or HFE-7200.

Developmental/Reproductive Toxicity

The potential developmental toxicity of HFE-7200 in rats was studied by Huntingdon Life Sciences Ltd. (1998). A total of 133 sexually mature Sprague-Dawley female rats which were time-mated to identified males of the same strain were used in the study. The first batch (A) consisted of 32 animals followed by a second batch (B) of 32 animals mated one day later, a third batch (C) of 32 animals mated one day later than batch B and a fourth batch (D) of 37 animals mated one day later than batch C. The day of mating, as judged by the presence of a vaginal plug, was considered as Day 0 of pregnancy. The female rats were exposed by inhalation through whole body exposure to target concentrations of 0, 3000, 9000 or 25,000 ppm HFE-7200 for 6 hours/day starting on Day 6 of pregnancy and continuing through Day 19 of pregnancy. Actual mean measured concentrations of HFE-7200 were 1012, 3074, 9000 and 24,082 ppm. The authors did not note any treatment-related clinical signs at any exposure level. A significant reduction in mean bodyweight gain in the 25,000 ppm group was observed between Days 6 to 8 ($p < 0.01$) of pregnancy compared with controls. This difference was maintained throughout the remainder of pregnancy ($p < 0.05$). Litter parameter data, sex ratio, skeletal and visceral malformations and variants did not indicate treatment-related effects. However, the percentage of fetuses with supernumerary ribs was increased in the 9000 ppm (19.6%) and 25000 ppm (27.9%; $p < 0.05$) groups compared to controls (12.8%). The authors stated that the NOEL for HFE-7200 developmental toxicity by inhalation in this study was 3000 ppm (32.4 g/m^3).

Huntingdon Life Sciences Ltd. (1997b) studied the developmental toxicity of HFE-7100 in rats exposed by inhalation. A total of 53 sexually mature Sprague-Dawley female rats which were time-mated to identified males of the same strain were used in the study. The first batch

(A) consisted of 32 animals followed by a second batch (B) of 21 animals mated one day later. The day of mating, as judged by the presence of a vaginal plug, was considered as Day 0 of pregnancy. The female rats were exposed by inhalation through whole body exposure to target concentrations of 0 or 30,000 ppm HFE-7100 for 6 hours/day starting on Day 6 of pregnancy and continuing through Day 19 of pregnancy. The mean measured chamber concentration of HFE-7100 was 29,774 ppm. The authors did not note any treatment-related clinical signs at any exposure level. A reduction in mean bodyweight gain between Days 10 to 12 of pregnancy was noted in the HFE-7100-exposed animals compared to controls ($p < 0.01$). Thereafter there was a degree of recovery; the bodyweights at Day 20 of pregnancy were essentially comparable for both groups. Litter parameter data, sex ratio, skeletal and visceral malformations and variants did not indicate treatment-related effects. The percentage of fetuses with supernumerary ribs was increased in the 30,000 ppm (25.8%) group compared to controls (15.1%); however, the increase was not statistically significant.

Genotoxicity

Mitsubishi Chemical Safety Institute Ltd. (1996a, b) investigated the potential genotoxicity of HFE-7100 and HFE-7200 in bacteria. The bacterial species/strains used were *Salmonella typhimurium* TA98, TA100, TA1535 and TA1537, and *Escherichia coli* WP2*uvrA*$^-$. The mutation assays were performed using a sealed preincubation (to prevent volatilization of the test agent) in the presence and absence of metabolic activation (phenobarbital/5,6-benzo-flavone-induced rat liver S9). Appropriate positive controls were used; the test solvent used was acetone. The authors stated that a preliminary assay at concentrations of 4.88, 19.5, 78.1, 313, 1250, 5000 and 20,000 µg/plate resulted in no appreciable toxicity and no increase in revertant colonies for both chemicals; however, the study data was not included with the report. A final assay was conducted twice, using concentrations of 1250, 2500, 5000, 10,000 and 20,000 µg/plate. No microbial toxicity was observed, and increases in revertant frequencies were less than 2-fold greater than controls for both chemicals. The authors concluded that HFE-7100 and HFE-7200 were not mutagenic to *S. typhimurium* or *E. coli* under the study conditions described above.

Huntingdon Life Sciences Ltd. (1996f, 1997f) studied the ability of HFE-7100 and HFE-7200 to induce micronuclei (suggestive of chromosomal damage) in mouse bone marrow cells. Male and female CD-1 mice (15/sex/group) were exposed to HFE-7100 or HFE-7200 at dose levels of 1250, 2500 and 5000 mg/kg bodyweight. A toxicity range-finding study had previously shown that a dose level of 5000 mg/kg (the standard limit dose for the micronucleus test) was tolerated; this dose was therefore selected for use as an appropriate maximum in the micronucleus test.

The test substance and negative control (aqueous 1% methyl cellulose with 0.5% Tween 80) were administered by intraperitoneal injection. A positive control group (5 animals/sex) was dosed orally, by intragastric gavage, with mitomycin C at 12 mg/kg bodyweight. Bone marrow smears were obtained from five male and five female animals in the negative control and test substance groups at each of three sampling times (24, 48 or 72 hours post- dosing). Bone marrow smears were obtained from the positive control group 24 hours after dosing.

One smear from each animal was examined for the presence of micronuclei in 1000 immature erythrocytes. The proportion of immature erythrocytes was assessed by examination of at least 1000 erythrocytes from each animal. A record of the incidence of micronucleated immature erythrocytes was also kept.

At all three sampling times, mice treated with the test substance did not show any significant increase in the frequency of micronucleated immature erythrocytes. The positive control compound, mitomycin C, produced large, highly significant increases in the frequency of micronucleated immature erythrocytes. The authors concluded that exposure to either HFE-7100 or HFE-7200 did not result in micronucleus induction under the study conditions described above.

The ability of HFE-7100 to induce chromosomal aberrations *in vitro* in Chinese hamster lung fibroblast (CHL) cells was studied by the Japan Bioassay Research Center (1996a). CHL cells were exposed to HFE-7100 in the presence and absence of phenobarbital/5,6-benzoflavone-induced rat liver S9. The HFE-7100 was diluted using a 1% solution of carboxymethyl cellulose sodium salt; the final solvent concentration in the culture medium was 10%. Because of the volatility of HFE-7100, the cells were grown and exposed in sealed cell culture roller bottles. Treatment times were 24 and 48 hours without metabolic activation, and 6 hours with metabolic activation. Benzo[*a*]pyrene and mitomycin C were used as positive controls in the presence and absence of metabolic activation, respectively. An initial cytotoxicity assay was performed using HFE-7100 concentrations of 0.63, 1.3, 2.5, 5 and 10 mg/ml. A dose-response for cytotoxicity was not noted in cells treated for 24 hours in the absence of metabolic activation. Cytotoxicity was noted in the 2.5, 5 and 10 mg/ml exposure groups treated for 48 hours in the absence of metabolic activation, with maximum cytotoxicity occurring in the high dose group (64% survival compared to controls). Cytotoxicity was also noted in the 5 and 10 mg/ml exposure groups after 6 hours exposure in the presence of metabolic activation (69 and 84% survival, respectively). The same HFE-7100 concentrations were used in the chromosomal aberration assay; no increase in chromosomal aberrations was noted at any concentration tested in the presence or absence of metabolic activation.

The Japan Bioassay Research Center (1996b) also evaluated the potential of HFE-7200 to induce chromosomal aberrations *in vitro* in CHL cells. The protocol used, including exposure concentrations, was the same as that described above for HFE-7100. Cytotoxicity was noted in the 10 mg/ml group after 24 and 48 hours exposure in the absence of metabolic activation (78 and 59% survival, respectively), and in the 5 and 10 mg/ml groups after 6 hours exposure in the presence of metabolic activation (64 and 66% survival, respectively). The same HFE-7200 concentrations were used in the chromosomal aberration assay; no increase in chromosomal aberrations was noted at any concentration tested in the presence or absence of metabolic activation.

Carcinogenicity

No carcinogenicity data is available for either HFE-7100 or HFE-7200.

Interim inhalation chronic REL estimate for Hydrofluoroether HFE-7200

A chronic REL is a concentration at or below which adverse health effects are not likely to occur in the general population, even sensitive individuals. An interim chronic REL was estimated for HFE-7200 (a hydrofluoroether compound in PureDry) based on changes in blood (increases in blood alkaline phosphatase, decreases in blood cholesterol), and liver (increased liver/body weight ratios) in rats in a 28 day study.

Study	Huntingdon Life Sciences, 1997a
Study population	Male and female Sprague-Dawley rats
Exposure method	Inhalation of 0, 1000, 3000, 9000, or 25,000 ppm
Critical effects	Blood and liver changes
LOAEL	9000 ppm
NOAEL	3000 ppm
Exposure continuity	6 hours/day, 5 days/week
Exposure duration	4 weeks
Average experimental exposure	536 ppm
Human equivalent concentration	536 ppm
LOAEL uncertainty factor	1
Subchronic uncertainty factor	10 (study was only 4 weeks)
Interspecies uncertainty factor	3 (see below)
Intraspecies uncertainty factor	10
Cumulative uncertainty factor	300
Interim Reference Exposure Level	1.8 ppm (19 mg/m^3)

Huntingdon Life Sciences (1997a) conducted a 4-week inhalation study of HFE-7200 in male and female Sprague-Dawley rats at 0, 1000, 3000, 9000, or 25,000 ppm. OEHHA staff determined that 3000 ppm was a subchronic NOAEL in rats. The next higher level of 9000 ppm was a LOAEL, since various adverse effects were noted there (increases in blood alkaline phosphatase, decreases in blood cholesterol, increased liver/body weight ratios, etc.). The NOAEL was time adjusted from the 6 hours/day, 5 days/week exposure to an equivalent continuous 24-hour exposure of 536 ppm. Use of OEHHA's methodology for developing a chronic Reference Exposure Level (REL) (division by a subchronic uncertainty factor (UF) of 10, an interspecies UF of 3 to account for residual susceptibility differences in rats not accounted for by U.S. EPA Human Equivalent Concentration (HEC) approach, and an intraspecies UF of 10) results in a chronic inhalation REL of 1.8 ppm (19 mg/m^3). This is an estimate based on our approved procedure (OEHHA, 2000). However, it has not been reviewed by the Scientific Review Panel. (Staff note that HFE-7200 comprises only 3.6% of PureDry by weight.)

Conclusions

Limited acute rat inhalation toxicity data indicates that HFE-7200 is lethal at high concentrations (917 g/m^3). No rat acute inhalation toxicity data is available for HFE-7100. Neither HFE-7100 nor HFE-7200 caused cardiac sensitization in dogs. However, adverse clinical signs were noted (restlessness, cold extremities, limb rigidity, head and whole body tremors, head shaking, arched back, general state of agitation and salivation) in dogs exposed to either HFE-7100 or HFE-7200 at high concentrations. LOAELs for acute inhalation exposure in dogs based on clinical signs were 187 and 96.7 g/m^3 for HFE-7100 and HFE-7200, respectively. Additionally, the NOAEL for HFE-7100 was 99.7 g/m^3. Acute rat oral toxicity data suggests that the acute lethal oral dose for HFE-7100 and HFE-7200 in rats is greater than 5000 and 2000 mg/kg-day, respectively. Neither HFE-7100 nor HFE-7200 induced skin sensitization (delayed contact hypersensitivity) in guinea-pigs. HFE-7200 did not cause acute skin irritation in rabbits; HFE-7100 caused slight acute skin irritation in rabbits. Both HFE-7100 and HFE-7200 caused slight acute eye irritation in rabbits.

Subchronic inhalation exposure (4 or 13 weeks) of rats to either HFE-7100 or HFE-7200 produced substantially increased urinary inorganic fluoride output, indicating that rats are capable of metabolizing both compounds. Urinary inorganic fluoride output was approximately 5-fold greater in rats exposed to HFE-7200 compared to HFE-7100-exposed rats, suggesting that HFE-7200 may be metabolized to a greater degree than HFE-7100. Both HFE-7100 and HFE-7200 induced hepatic peroxisome proliferation in male rats but not female rats, as indicated by increased liver weights, liver/body weight ratios and palmitoyl CoA oxidase activity. HFE-7200 caused peroxisome proliferation at lower doses and shorter exposure periods than HFE-7100, suggesting that it is the more potent peroxisome proliferator of the two compounds. This may be due to differences in compound metabolism. HFE-7200 exposure results in higher urinary inorganic fluoride output in both male and female rats than HFE-7100 exposure, and urinary inorganic fluoride output is higher in male rats (which demonstrate peroxisome proliferation) than female rats (which do not demonstrate peroxisome proliferation) after comparable exposures to either HFE-7100 or HFE-7200. Kidney enlargement and tubular basophilia with nuclear clustering in the inner cortex was also seen in male rats exposed to high concentrations (9000 and 25000 ppm; 97.2 and 270 g/m^3, respectively) of HFE-7200. Possible explanations for these effects could be that they are due either to the peroxisome proliferator effects of HFE-7200, or to regeneration of renal cortical tubules subsequent to tubule epithelial cell damage. Peroxisome proliferators have been shown to induce renal cortical tubule peroxisome proliferation (Hawkins *et al.*, 1987; Reddy and Lalwani, 1983) and increase renal DNA synthesis (Seifert and Mostecká, 1987) in rodents. Additionally, urinary fluoride resulting from fluorocarbon metabolism has been reported to be acutely toxic to renal cortical tubules (Lochhead *et al.*, 1997).

HFE-7100 and HFE-7200 have tested negative in bacterial gene mutation and mammalian chromosomal damage assays (*in vivo* micronucleus and *in vitro* chromosomal aberration), but have not been tested in mammalian gene mutation or oxidative DNA damage assays. Additionally, no carcinogenicity data exists for these compounds. However, peroxisome proliferators often cause increased liver tumor incidences in chronically exposed susceptible rodents (rats or mice). The structurally related chlorofluorocarbon perfluorooctanoic acid has been demonstrated to induce hepatic peroxisome proliferation and oxidative DNA damage (Takagi *et al.*, 1991) and cause increased incidences of liver, pancreatic acinar cell and Leydig

cell adenomas in rats (Olsen *et al.*, 2000; Rao MS and Reddy JK, 1997). This suggests that HFE-7100 and HFE-7200 would be appropriate candidates for chronic toxicity/carcinogenicity bioassays, since data on long-term toxicity data are currently unavailable for these chemicals.

OEHHA staff are concerned about the environmental persistence of perfluorinated chemicals. Determination of the lipid/water partition coefficients for HFE-7200 (and of the other fluorocarbons in PureDry) is important. In addition information is needed on the fate of the fluorocarbons in the environment.

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Appendix H

Laboratory Evaluation of Leak Detectors

Air Resources Board

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Arnold Schwarzenegger
Governor

MEMORANDUM

TO: Richard Boyd, Manager
Emissions Evaluation Section
Stationary Source Division

FROM: Dennis Goodenow, Manager
Source Testing Section
Monitoring and Laboratory Division

DATE: October 3, 2005

SUBJECT: Portable VOC Analyzer Evaluations

At the request of the Emissions Evaluation Section (EES), the Monitoring and Laboratory Division Source Testing Section (STS) is engaged in ongoing evaluations of portable VOC analyzers. The evaluations are intended to compare responses from analyzers of varying cost and detection principles to perchloroethylene (PERC) gas calibration standards. Stationary Source Division is considering amendment of the vapor leak threshold in the ATCM for PERC emissions from dry cleaning operations.

An initial, qualitative evaluation of two low cost analyzers was performed October 4, 2004 at the Source Testing Section facility at 1301 V Street in Sacramento. Results for this evaluation were reported to the Emissions Evaluation Section in an October 28, 2004 memorandum. However, the results are of questionable validity because they were produced using a non-traceable PERC standard with an assumed concentration of 50 ppmv. STS has since procured certified, traceable dry calibration standards of 25 ppmv PERC, 50 ppmv PERC and 100 ppmv isobutylene. EES has also identified eight additional portable analyzers and presented them to STS for evaluation. The analyzers range in sophistication from semiconductor sensors with audible alarms costing approximately $200.00 to photoionization detectors with LCD displays costing in excess of $3,000.00. The ten analyzers and their respective principles of operation are identified in Table 1.

The h·nu Systems HW-101 was the designated reference analyzer for this survey based on its availability and photoionization detector (PID). The other PID analyzers used in the survey were available to EES on a temporary basis. The HW-101 analog display is also motion sensitive, making it impractical for field use as a leak detection tool. Although the HW-101 display is a relatively unsophisticated analog potentiometer, it

produced repeatable PERC concentration values in the 0 – 200 ppmv range when calibrated against the 100 ppmv isobutylene standard. HW-101 calibration was examined, and adjusted if necessary, before beginning each evaluation session.

Table 1
Portable VOC Analyzers Evaluated for PERC Response

Model and (Manufacturer)	Detection Principle	Sample Delivery	Display
Gas Alert Micro 5 (BW Technologies)	PID	diffusion	LCD w/ audio & visual alarms
Phocheck (Ion Solutions)	PID	internal pump	LCD
Mini Rae 2000 (Rae Systems)	PID	internal pump	LCD w/ visual alarm
Aeroqual 200 (Aeroqual)	semiconductor	diffusion	LCD
Aeroqual 500 (Aeroqual)	semiconductor	diffusion	LCD w/ audio alarm
C-21 (Eco Sensors, Inc.)	semiconductor	diffusion	LED bar w/ audible alarm
D-Tek (Inficon)	infrared cell	internal pump	audible w/ LED bar
Tek-Mate (Inficon)	semiconductor	internal pump	audible
tif - 5100 (tif Instruments)	semiconductor	diffusion	audible
Drager CMS (Drager)	colometric	internal pump	LCD
HW 101 reference analyzer (h·nu Systems)	PID	internal pump	analog potentiometer

Candidate analyzers were evaluated by exposing the analyzer probe a minimum of three times to both 25 ppmv and 50 ppmv PERC calibration standards contained in Tedlar bags. Gas was discharged by slowly depressing the bags by hand, no metering devices were used to control the rate of discharge. The stable response registered by each analyzer was recorded along with an approximation of the time necessary to attain the response. Standards were derived immediately prior to analyzer evaluation by transferring 25 ppmv and 50 ppmv PERC calibration standards directly into dedicated 3 liter Tedlar bags from certified, traceable cylinders. The PERC concentration in each bag was then determined using the HW-101.

Results for the portable VOC analyzer evaluations are reported in Table 2. The results include PERC standard concentrations, the number of exposures to each standard, the average response for each analyzer, and the average response time. Please note that the response times reported in Table 2 are the approximate time needed for the analyzer to display a stable concentration. Therefore, these values are inflated compared to the traditional definition of response time as the time required for the analyzer to register 50% (T50) or 90% (T90) of the standard concentration.

The results indicate that portable PID analyzers with internal sample pumps (PhoCheck, MiniRae 2000) provide the best combination of accuracy and response time. Since PID analyzers are calibrated to isobutylene, its response to a PERC standard must be multiplied by a correction factor to obtain an equivalent response as PERC. The correction factor applied to PID analyzers in this survey is defined as the photoionization sensitivity ratio of PERC (8.6 eV) to isobutylene (5.5 eV) or 1.56.

The Micro 5 diffusive PID analyzer also registered concentrations consistent with the calibration gas standards, though its response time was slightly longer than analyzers with an integral pump. The Micro 5 was evaluated versus the calibration gases using a manufacturer supplied faceplate which channels calibration gases directly to the detector. The faceplate is removed from the analyzer during field use. Since diffusive analyzers lack an integral sample pump, gas must be discharged from the Tedlar bag to the sensor by depressing the bag. Therefore, the time necessary for a diffusive analyzer to attain a stable response can be influenced by the rate of discharge from the bag, meaning response time can be affected by the magnitude of a leak.

A variety of results were observed for diffusive analyzers incorporating semiconductor sensors. Analyzers producing an audible response, such as the tif – 5100 and Inficon Tek – Mate, demonstrated the ability to quickly detect the PERC standard. However, there is no discernible correlation between standard concentration and the audible frequency produced by these instruments. The tif – 5100 can also be induced into registering a positive response by blowing air across its sensor.

The Aeroqual Series 200 and Series 500 analyzers were initially evaluated with the 25 ppmv and 50 ppmv PERC standards August 12, 2005. At that time, the response from both analyzers to the calibration gases was a negative shift from the baseline concentration towards zero. Subsequent conversations with Aeroqual staff revealed that Aeroqual PERC analyzers are designed for optimum performance when the sample gas is between 30% and 80% relative humidity (RH). For calibration, or sample gases below 30% RH, the magnitude of negative shift increases with decreasing RH. The calibration gases used by STS are dry (0% RH), explaining the initial results. The Series 500 also displayed baseline concentrations of 7 ppmv to 11 ppmv, compared to the zero to 2 ppmv baseline concentrations registered by other analyzers. Replacing the Series 500 sensor head resulted in acceptable baseline concentrations.

The Aeroqual Series 200 and Series 500 evaluations were repeated with humidified gas standards on August 23, and August 25, 2005. PERC standards were humidified to approximately 50% RH by injecting 30 microliters of distilled water into the 3 liter Tedlar bag and allowing the contents to equilibrate for 3 hours at 72 degrees Fahrenheit. Analysis of the humidified standards using the HW-101 indicates the humidifying process reduces the standard concentration by approximately one-third.

Exposing the Aeroqual analyzers to the humidified standards produced a LCD response consistent with the concentration determined using the HW-101. However, there is increased potential for these analyzers to produce biased results when sample gas relative humidity is outside the range of 30% to 80%. Both the series 200 and Series 500 demonstrated response times in the range of 20 to 30 seconds, which is significantly longer than the other diffusion analyzers.

The Drager Chip Measurement System (CMS) uses an internal pump to draw sample through a gas-specific, reagent filled, capillary chip. The response times demonstrated by this analyzer (>100 sec.) indicate it is better suited for occupational safety applications rather than leak detection. This analyzer appears to be especially sensitive to sample pump inlet pressure and power supply (battery) voltage. Therefore, we are unsure if the poor results (29.6 ppmv) reported by the CMS for the 50 ppmv PERC standard represent typical instrument performance.

The Eco Sensors C-21 and Inficon D – Tek analyzers did not produce any noticeable response to the PERC calibration standards. The lack of response by the D – Tek is understandable since its sensor is tuned to detect refrigerant compounds. The performance of the C-21 is confusing since a PERC calibration chart is supplied with the instrument and placing a felt tip marker near the C-21 sensor produces a full scale (140 ppmv) response on the LED display. We believe the C-21 may also require a humidified gas sample to achieve a representative response. However, we are not currently in possession of a C-21 to test this theory and attempts by EES to obtain a replacement have, to this date, been unsuccessful.

We hope the results presented in this memorandum are of assistance to the PERC ATCM amendment process. Please direct questions regarding the portable analyzer evaluation results to Angus MacPherson at 445-4686 or amacpher@arb.ca.gov.

Table 2

Portable VOC Analyzer Response to 25 ppmv and 50 ppmv PERC Calibration Gas Standards

Date	Analyzer (display, detection, delivery)	PERC standard conc.	# Trials	Average Response as PERC	Response Time (sec)	Notes (see text for discussion)
28 Jan 05	tif – 5100 (audible, semi conductor, diffusion)	50 ppmv	4	rapid beep	< 5	beep frequency can be influenced by flow past sensor
31 Jan 05		25 ppmv	3			
28 Jan 05	Eco Sensors C-21 (LED, semiconductor, diffusion)	50 ppmv	4	no response	na	responds to felt tip pen. may require humidified sample.
31 Jan 05		25 ppmv	3			
23 May 05	PhoCheck (LCD,PID, internal pump)	50 ppmv	3	49.5 ppmv	< 5	
		25 ppmv	3	26.8 ppmv	< 5	
23 May 05	Tek-Mate (audible, semi conductor, diffusion)	50 ppmv	3	constant tone	< 5	constant tone produced in both high and low ranges.
		25 ppmv	3	constant tone	< 5	
23 May 05	D-Tek (audible/LED, infrared, diffusion)	50 ppmv	3	no response	na	primary analyzer application is refrigerant leak detection.
		25 ppmv	3			
10 Aug 05	Micro 5 (LCD,PID, diffusion)	50 ppmv	3	58.0 ppmv	5 – 10	gas flow and pressure may affect analyzer response.
		25 ppmv	3	26.4 ppmv	5 – 10	
10 Aug 05	Drager (LCD, chem. cell internal pump)	50 ppmv	4	29.6 ppmv	110	excessive response time. poor results for 50 ppmv standard.
		25 ppmv	3	20.7 ppmv	110	
23 Aug 05	Aeroqual 200 (LCD, semi conductor, diffusion)	32 ppmv	2	30 ppmv	20 – 30	analyzers require humidified sample for proper response.
		16 ppmv	2	15 ppmv	20 – 30	
25 Aug 05	Aeroqual 500 (LCD, semi conductor, diffusion)	36 ppmv	1	31 ppmv	20 – 30	
06 Sep 05	MiniRae2000 (LCD, PID internal pump)	50 ppmv	3	50.7	< 5	
		25 ppmv	3	24.2	< 5	
All Dates	HW – 101 (analog, PID, internal pump)	50 ppmv	8	48 ppmv	< 5	reference analyzer.
		25 ppmv	8	26 ppmv	< 5	

Appendix I

Contact Information for Alternative Solvents

Contact Information for Alternative Solvents

Solvent	Company	Address	City	State	ZipCode	Phone
DF-2000™	ExxonMobil Chemical Co.	13501 Katy Freeway	Houston	TX	77079	(281) 870-6000
PureDry®	3M Global Headquarters	3M Corporate Headquarters, 3M Center	St. Paul	MN	55144	(800) 364-3577
EcoSolv®	Chevron Phillips Chemical Company, LLC	10001 6 Pine Drive	Woodlands	TX	77380	(832) 813-4100
Shell Sol 140 HT	Shell Chemical LP	7594 Highway 75	Geismar	LA	70734	(225) 201-6222
GreenEarth®(D5)	Dow Corning Corporation	2200 W. Salzburg Road	Midland	MI	48686	(989) 496-4400
Rynex®	Rynex Cleaning Solutions	7600 Jericho Turnpike	Woodbury	NY	11787	(516) 364-0800
Stoddard	Qualitek International	315 Fairbank Street	Addison	IL	60101	(630) 628-8083
Resolve™	R. R. Street & Co. Inc.	184 Shuman Blvd.	Naperville	IL	60563	(800) 478-7338
Impress™	Lyondell Chemical Co.	1221 Mckinney St., One Houston Center, Suite 100	Houston	TX	77252	(713) 652-7200
Hydroclene	Caled Chemical	26 Hanes Drive	Wayne	NJ	07470	(800) 652-2533

Appendix J

Electricity Cost Calculations

Electricity Cost Calculation

Equation 1 was used in combination with the information provided to us from the Machine Manufacturer Survey to calculate maximum operating load in kW for each machine.

(1) Maximum Operating Load = (V)(A)(Power Factor)(Square Root of Phase)/1000

Where:

V	=	machine voltage
A	=	amperage of machine
Power Factor	=	power factor in percent, usually about 0.8 for single phase and 0.9 for three phase.

Assuming a typical load draws a 30 percent average of the maximum operating load then Equation 2 was used to determine the kW that a typical load would draw. (JE, 2003)

(2) Typical Load kW = (Maximum Operating Load)(30 percent)

To calculate the hours that the machine runs Equation 3 was used.

(3) Hours Ran = (cycles/day)(minutes/cycle)(60 minutes/hour)

Where:

Hours Ran	=	the hours that the machine runs for one day
Cycles/day	=	6 cycles per day for a typical dry cleaner
Minutes/ cycle	=	the time each machine takes to run one cycle

Equation 4 was used to determine what the cost per day would be to run the dry cleaning machine.

(4) Cost Per Day = (typical load)(hours ran)(cost per kW)

Where:

Typical Load	=	kilowatts that a typical load draws, see Equation (2).
Hours ran	=	the hours ran, see Equation (3).
Cost per kW	=	the current cost for kWh, which is $0.10.

Typically a facility will dry clean 5 days a week. Equation 5 was used to determine the annual electricity cost for a facility to run their machine.

(4) Cost Per Year = (cost per day)(5 days/week)(52 weeks/year)

Appendix K

Glossary and Acronyms

Glossary

Acute Exposure:	One or a series of short-term exposures generally lasting less than 24 hours.
Agency Shop:	Same as drop off shop. Facility with no dry cleaning machine on-site.
Airborne Toxic Control Measure:	Section 39655 of the Health and Safety Code, defines an "Airborne Toxic Control Measure" means either of the following: 1) Recommended methods, and, where appropriate, a range of methods, that reduce, avoid, or eliminate the emissions of a toxic air contaminant. Airborne toxic control measures include, but are not limited to, emission limitations, control technologies, the use of operational and maintenance conditions, closed system engineering, design equipment, or work practice standards, and the reduction, avoidance, or elimination of emissions through process changes, substitution of materials, or other modifications. 2) Emission standards adopted by the U.S. Environmental Protection Agency pursuant to section 112 of the federal act (42 U.S.C. Sec. 7412).
Air Dispersion Model:	A mathematical model or computer simulation used to estimate the concentration of toxic air pollutants at specific locations as a result of mixing in the atmosphere.
Chronic Exposure:	Long-term exposure usually lasting from one year to a lifetime.
Drop off Shop:	Same as agency shop. Facility with no dry cleaning machine on-site.
Flash Point:	The lowest temperature at which a liquid can form an ignitable mixture in air near the surface of the liquid. The lower the flash point, the easier it is to ignite the material.
Hazardous Air Pollutant (HAP):	A substance that the U.S. Environmental Protection Agency has listed in, or pursuant to, section 112 subsection (b) of the federal Clean Air Act Amendments of 1990 (42 U.S. Code, section 7412(b)).
Mixed Shop:	A dry cleaning facility that employs more than one type of dry cleaning process.

Permissible Exposure Limit (PEL):	The maximum amount or concentration of a chemical that a worker may be exposed to under the Occupational Safety and Health Administration (OSHA) regulations.
Risk:	The possibility of injury or disease, which may result from exposure to toxic air contaminants.
Scientific Review Panel on Toxic Air Contaminants (SRP):	A nine-member panel appointed to advise the Air Resources Board and the Department of Pesticide Regulation in their evaluation of the adverse health effects toxicity of substances being evaluated as Toxic Air Contaminants.
TIF Detector	Halogen leak detector made by TIF™ Instruments, Inc.
Toxic Air Contaminant (TAC):	Section 39655 of the Health and Safety Code, defines a TAC as an air pollutant which may cause or contribute to an increase in mortality or an increase in serious illness, or which may pose a present or potential hazard to human health. A substance that is listed as a hazardous air pollutant pursuant to subsection (b) of section 112 of the federal act (42 U.S.C. Sec. 7412(b)) is a TAC. TACs that are pesticides are regulated in their pesticidal use by the Department of Pesticide Regulation.
Volatile Organic Compound (VOC)	Means any compound containing at least one atom of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, and excluding the following: (A) methane, methylene chloride (dichloromethane), 1,1,1-trichloroethane (methyl chloroform), trichlorofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-13), 1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-14), chloropentafluoroethane (CFC-115), chlorodifluoromethane (HCFC-22), 1,1,1-trifluoro-2,2-dichloroethane (HCFC-123), 1,1-dichloro-1-fluoroethane (HCFC-141b), 1-chloro-1,1-difluoroethane (HCFC-142b), 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124), trifluoromethane (HFC-23), 1,1,2,2-tetrafluoroethane (HFC-134), 1,1,1,2-tetrafluoroethane (HFC-134a), pentafluoroethane (HFC-125), 1,1,1-trifluoroethane (HFC-143a), 1,1-difluoroethane (HFC-152a), cyclic,

branched, or linear completely methylated siloxanes, the following classes of perfluorocarbons:

1. cyclic, branched, or linear, completely fluorinated alkanes;
2. cyclic, branched, or linear, completely fluorinated ethers with no unsaturations;
3. cyclic, branched, or linear completely fluorinated tertiary amines with no unsaturations; and
4. sulfur-containing perfluorocarbons with no unsaturations and with the sulfur bonds to carbon and fluorine, and

(B) the following low-reactive organic compounds which have been exempted by the U.S. EPA: acetone, ethane, methyl acetate, parachlorobenzotrifluoride (1-chloro-4-trifluoromethyl benzene), perchloroethylene (tetrachloroethylene).

ACRONYMS

APCD	Air Pollution Control District
APCO	Air Pollution Control Officer
AQMD	Air Quality Management District
ARB	California Air Resources Board
ATCM	Airborne Toxic Control Measure
BACT	Best Available Control Technology
Cal/EPA	California Environmental Protection Agency
Cal/OSHA	California Occupational Safety and Health Administration
CAPB	Cocamidopropyl betaine
CAPCOA	California Air Pollution Control Officers Association
CAS	Chemical Abstract Service
CG	Cellulose gum
CEQA	California Environmental Quality Act
CO_2	Carbon Dioxide
CTSI	U.S. EPA's Cleaner Technologies Substitute Assessment : Professional Fabricare Processes
D_5	Decamethylcyclopentasiloxane
DfE	Design for the Environment
DHS	California Department of Health Services
Districts	Local Air Pollution Control and Air Quality Management Districts
DOF	California Department of Finance
DPNB	Dipropylene Glycol Normal Butyl Ether
DTSC	California Department of Toxics Substances Control
°F	Degrees Fahrenheit
HAP	Hazardous Air Pollutant
HHD	Halogenated Hydrocarbon Detector
H&SC	Health and Safety Code
HSIA	Halogenated Solvent Industry Alliance
IARC	International Agency for Research on Cancer
IFI	International Fabricare Institute
IRTA	Institute for Research and Technical Assistance
KB	Kauri Butanol
Kg	Kilogram
kWh	Kilowatt-hour
Lauramide DEA	lauric acid diethanolamide
LOC	Local ventilation system

m^3	Cubic meter
MDL	Minimum Detection Limit
$\mu g/m^3$	Microgram per cubic meter
MSDS	Material Safety Data Sheets
NESHAP	National Emissions Standards for Hazardous Air Pollutants
NIOSH	National Institute for Occupational Safety and Health
NTP	National Toxicology Program
OEHHA	Office of Environmental Health Hazard Assessment
OSHA	Occupational Safety and Health Administration
P-20	Ethoxylated sorbitan monodecanoate
PBR	Partial vapor barrier room
PEL	Permissible Exposure Limit
Perc	Perchloroethylene
pH	A logarithmic measure of hydrogen ion concentration
PID	Photoionization Detector
POTW	Publicly Owned Treatment Works
PPERC	Pollution Prevention Education and Research Center
ppm	Parts per Million
ppmv	Parts per Million by Volume
psi	Pound Per Square Inch
PVR	Partial Vapor Room
REL	Reference exposure level
SEHSC	Silicones Environmental, Health & Safety Council of North America
SLI	Sodium lauryl isethionate
SLS	Sodium laureth sulfate
SRP	Scientific Review Panel on Toxic Air Contaminants
TAC	Toxic Air Contaminant
TLV	Threshold Limit Value
TSCA	Toxic Substances Control Act of 1976
TWA	Time-weighted average
UCLA	University of California, Los Angeles
URF	Unit risk factor
U.S.	United States
U.S. EPA	United States Environmental Protection Agency
VBR	Vapor Barrier Room
VOC	Volatile Organic Compound