Characterizing the Waste Streams from Alternative Solvent Dry Cleaners

Jessie Taylor

A thesis

submitted in partial fulfillment of the

requirements for the degree of

Master of Science

University of Washington

2012

Committee

Mike Yost

Steve Whittaker

Janice Camp

Program Authorized to Offer Degree

Department of Environmental and Occupational Health Sciences

Table of Contents

List of Figures

List of Tables

Introduction and Background

Introduction

The use of perchloroethylene (PERC) as a dry cleaning solvent has been associated with adverse health effects in workers and significant environmental contamination at current and former dry cleaning sites. The wastes generated by PERC dry cleaning machines are also extremely hazardous because they can contain percentage levels of PERC and other hazardous substances. Several solvent alternatives to PERC have been introduced over the last decade that are purported to be environmentally preferable. However, relatively little is known about the health or environmental impacts associated with these solvents. Previous studies have demonstrated the presence of PERC in the waste streams of dry cleaning operations that use the newer non-chlorinated, petroleum-based alternative hydrocarbon solvents. However, to date, neither the source of this contaminant nor the hazardous waste status of the still bottoms and separator water generated by these alternative machines has been adequately characterized. There is a lack of information concerning the type and composition of products used by alternative solvent cleaners. Characterization of the waste streams in comparison to the Washington State Department of Ecology's Dangerous Waste criteria has also not been conducted. This study seeks to chemically characterize the wastes generated by alternative solvent dry cleaning machines and evaluate any linkage to work practices and the composition of products used by the cleaners. This information will be beneficial for dry cleaning proprietors and King County Local Hazardous Waste Management Program (LHWMP) in providing recommendations for appropriate work practices, the selection of dry cleaning products, reevaluating current waste management policies, and evaluating the occupational health impacts of products and wastes.

History

Chemical solvents have been used to dry clean fabrics for many years. Beginning in the mid-19th century, kerosene and other low molecular weight hydrocarbons were used for cleaning. In 1925, Stoddard solvent was introduced; however, its flammability (flashpoint: 104˚ F) prompted the industry to switch to perchloroethylene (PERC) in the 1960s. PERC, also known as tetrachloroethylene, is essentially non-flammable, cleans efficiently, and was readily available, although the health effects were not well understood at the time. [2]. The use of "transfer" dry cleaning machines (in which PERC-laden fabrics were transferred manually from a washer to a separate dryer) resulted in high occupational exposures. Improvements in dry cleaning technology, including the advent of "dry-to-dry" machines, which eliminate handling of solvent-containing items, have decreased PERC exposures considerably [3].

The evolution of dry cleaning technology is defined by generations of machines as follows [1,4]:

- 1st Generation: Transfer Machine.
- 2nd Generation: Dry to Dry Vented, Water-cooled or Refrigerated.
    - Condense PERC from vapors, vent remainder to the atmosphere
- 2nd Generation Retrofitted: Self Contained Unit, Non-Vented and Refrigerated.
- 3rd Generation: Dry to Dry, Self-Contained, Non-Vented and Refrigerated.
    - Introduced in the 1970s[5]
    - Self-containment reduces occupational PERC exposure
- 4th Generation: Enclosed Machine with Refrigeration and Carbon Absorber.
    - Carbon absorber reduces environmental emissions
- 5th Generation: Enclosed Machine with Carbon Absorber and Vapor Sensor and Vapor Lock on Basket.
    - Vapor sensor and lock reduce occupational exposure

Although PERC is currently the most commonly used dry cleaning solvent in the United States, several alternative solvents are now available [1].

Dry Cleaning Solvents

PERC

Acute exposure to PERC can produce headaches, dizziness, eye irritation, and upper respiratory tract irritation [6]. The International Agency for Research on Cancer (IARC) has classified PERC as a probable human carcinogen. Because of these toxic effects, the Occupational Safety and Health Administration (OSHA) established a 100 parts per million (ppm) Personal Exposure Limit (PEL) for occupational exposures. Washington State's occupational exposure limits are 25 ppm, expressed as an 8-hour Time Weighted Average (TWA), and a 38 ppm Short Term Exposure Limit (STEL) (WAC 296-841-20025).

While improvements in engineering controls have reduced occupational exposures to PERC over time, exposure to this chlorinated hydrocarbon is still an occupational hazard for dry cleaners. Dermal and inhalation exposures may be experienced when opening the machine and handling the fabrics as well as when seals and gaskets fail [7]. According to Gold, et al[8], dry-to-dry machine exposures are in the 9.5 ppm range, while use of a transfer machine increased the personal exposure to 153 ppm. Another source of exposure is machine maintenance, such as disposing of the waste streams (primarily still bottoms and separator water). Occupational exposures can cause health effects such as possible human carcinogenicity. There is evidence of renal carcinogenicity among dry cleaners [2,9,10]. Cancer risks are associated with various levels of exposure, with occupational exposures being 10-100 times greater than the provisional reference concentration for chronic inhalation exposure (R_fC) (Figure 1). While PERC exposure in dry cleaners is relatively well documented, little is known about exposure to other solvents or to contaminants in the waste generated by dry cleaning machines.

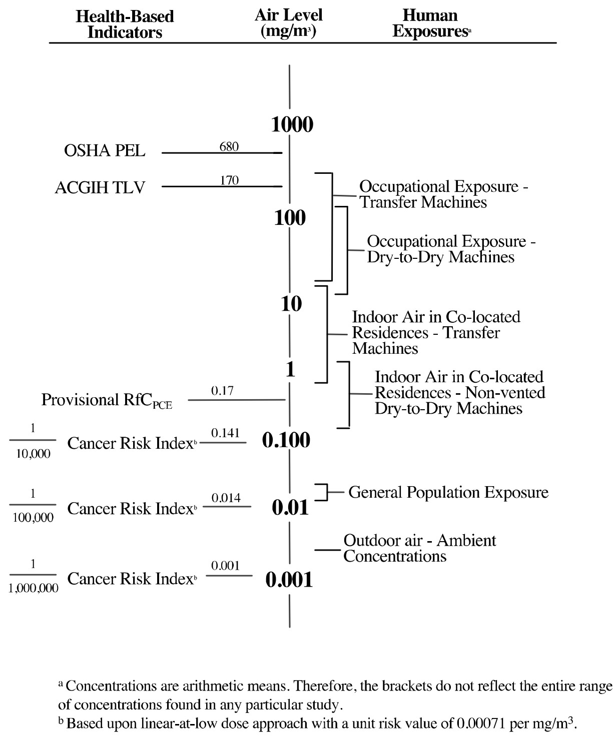


Figure 1. PERC exposure and associated health hazards. Co-located residences are homes in the same building as a dry cleaner. [1]

The data for long term health risks associated with environmental exposures to PERC are inconclusive [11]. Off-gassing from clothing that has been dry cleaned in PERC can be a source of environmental exposure; the amount that off-gasses depends on the fabric type [12]. Exposures may also occur through tap water originating from contaminated ground water via inhalation, ingestion, and dermal contact. A small study in New York showed decreased visual contrast sensitivity in non-dry cleaners with high PERC levels in their work places [13] and PERC has been found in apartments located over dry-cleaning establishments as well as in fatty foods in groceries co-located with dry cleaners[14,15]. As a result, many cities have enacted or are considering regulations for the types of businesses that may be co-located with a dry cleaner and the EPA specifies that residencies may not be co-located with PERC dry cleaners[16].

Spills of PERC can penetrate concrete slabs to become a persistent pollutant in groundwater. As a Dense Non-Aqueous Phase Liquid (DNAPL), PERC is very difficult to remove from contaminated groundwater. Many former dry cleaning business sites in King County are contaminated with PERC. As a drinking water contaminant, PERC has the potential to contribute to adverse birth outcomes such as low birth weight[17]. The EPA has set the maximum contaminant level for PERC at 5 parts per billion (ppb) for drinking water[18]. Thus, waste containing even low concentrations of PERC is treated as hazardous.

There are alternatives to PERC dry cleaning, which are becoming increasingly popular as jurisdictions place limits on PERC usage and incentivize the use of environmentally preferable solvents. King County offers incentives through the EnviroStars program that help the public identify and support environmentally friendly local businesses [4]. California is slowly phasing out PERC cleaners and promoting alternative cleaning methods[19]. Measures such as this, as well as wider dissemination of knowledge of the health hazards of PERC, have made many property owners reluctant to rent to PERC dry cleaners [20]. Alternative solvents to PERC include liquid carbon dioxide, glycol ethers, and petroleum-based hydrocarbons, among others[16].

Hydrocarbons

Following the recognition of PERC as a significant health and environmental hazard, new hydrocarbon solvents were developed. Modern petroleum-based hydrocarbon dry cleaning solvents include Shell DSC, Shell TK, Exxon DF2000, Exxon 3365D, and EcoSolv. The flashpoints of these solvents are high, relative to Stoddard solvent (104˚ F), and range from 131 to 149˚ F [21,22]. While the health effects associated with PERC have been well-characterized, relatively little is known about the long-term health effects of these alternative hydrocarbon solvents. Acute exposure can precipitate skin and eye irritation as well as central nervous system effects, such as drowsiness and dizziness. There is preliminary evidence that exposure to similar hydrocarbons such as those found in jet fuel (alkanes with similar molecular weight) may have adverse effects on the endocrine system[23]. The lack of knowledge of the environmental and human health effects of these solvents is a point of concern in promoting their use over PERC [24]. In addition, there are environmental consequences of these hydrocarbon solvents, which are regarded as volatile organic compounds (VOCs) and may contribute to ozone formation [25].

Carbon Dioxide

Liquid carbon dioxide (CO_2) can be used to remove a variety of stains to great effect and has several advantages. The cleaning cycle is relatively short and no hazardous waste is generated. However, the machines for liquid CO_2 cleaning are more expensive than conventional machines, as are the maintenance costs. There are few occupational health risks associated with CO_2 exposure; chiefly asphyxiation from leaking CO_2 displacing air in an enclosed space. Note that the CO_2 used in dry cleaning is an industrial by-product and thus does not add to the greenhouse gas inventory [25]

Wet Cleaning

Wet cleaning does not involve the use of organic solvents other than those necessary for spot cleaning. This method uses water, spot cleaners, detergents, and careful drying and tensioning of the cleaned items. While there a very few chemical exposure concerns associated with wet cleaning, there are drawbacks in the increased use of water and production of wastewater [20]. Additionally, the process is significantly more labor intensive than the other options, more time consuming, does not remove stains as efficiently, and is harder on fabrics [1].

SystemK4

Kreussler, Inc. has recently introduced a new solvent to the United States. Developed in Germany, the SystemK4, using the solvent known as SolvonK4, is billed as an alternative to both PERC and other solvents, such as high flash point hydrocarbons. The principal component of SolvonK4 is the diether acetal, butylal (dibutoxymethane). Minor components of the solvent at <0.5% and <0.05% are n-butyl alcohol and formaldehyde, respectively. While the butylal is reportedly stable at pHs between 4 and 14, LHWMP discussions with the U.S. Environmental Protection Agency (EPA) and the National Institute for Occupational Safety and Health (NIOSH) have raised concern that the solvent may hydrolyze to formaldehyde (a carcinogen) in the presence of acid and heat. Occupational inhalation exposures to butylal are thought to be low due to the low vapor pressure of the solvent [27.] While the solvent is slightly biodegradable, there is little published information on the environmental fate and transport of butylal[27,28].

Similarly to many of the alternative solvents, the long-term health effects of SolvonK4 are not well understood.

Other solvents in limited use in King County include liquid silicone and glycol ethers.

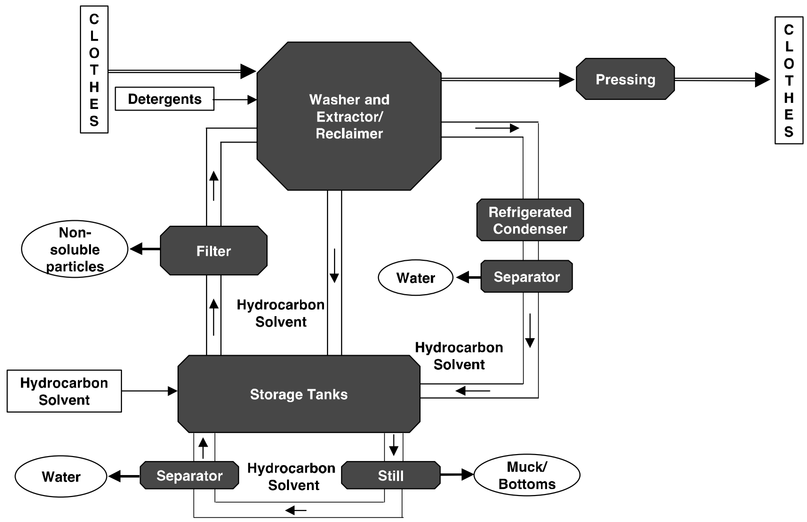
The Dry Cleaning Process

The dry cleaning process is similar for PERC and the alternative solvents. Exceptions to this are liquid carbon dioxide (CO_2), which cleans in a high pressure system, and wet cleaning, which uses water. This dry-to-dry process applies to all fabrics to be cleaned, including drapes, linens, sleeping bags, blankets, and clothing.

First, items to be cleaned are sorted according to color and fabric type, and spot-treated if necessary. Spot treatment products are formulated according to the type of stains to be removed. These spot cleaners may include organic solvents such as trichloroethylene, PERC, and methylene chloride, in addition to hazardous chemicals such as hydrochloric acid. Non-chlorinated spot treatments that are designed for use with alternative dry cleaning solvents are readily available. However, older chlorinated products designed for use with PERC machines are still used by many shops [1], including those who currently use non-chlorinated solvents.

Following spot treatment, the fabrics are placed in the dry cleaning machine where they are agitated with the solvent, detergent, and other additives, such as sizing agent. The solvent is then drained and the fabrics are placed under vacuum, dried, and tumbled to remove any remaining solvent.

The evaporated solvent passes through a refrigerated condenser and a separator, which removes any water that entered the system during the cleaning process. The solvent is distilled and filtered in a closed loop system for reuse. This process produces “separator water” and “still bottoms” (also known as “muck”). These wastes may contain the dry cleaning solvent, dirt, and soil removed from fabrics, spot treatment chemicals, and residual solvent from previous cleanings.



Sources: Adapted from OTEC, Swiss Clean Hydrocarbon Drycleaning Instruction Handbook.
With consultation from Hill Jr., 1998.

Figure 2. Simplified process flow diagram for dry-to-dry hydrocarbon solvent machinery. [1].

This process is illustrated in Figure 2. The still bottoms and separator water must be removed from the machine periodically. The separator water may be drained into another container directly from the machine, while the still bottoms are often heated or "cooked" before disposal to maximize solvent recovery. The still bottoms are scraped into a waste container using a rake; some cleaners wipe the inside of the still bottom compartment with paper towels. Gloves of some type are usually worn during the cleaning process.

Unpublished pilot study data from LHWMP found measurable quantities of PERC in the separator water and still bottoms from alternative hydrocarbon solvent dry cleaners (i.e., they do not use PERC as a dry cleaning solvent). Of 15 dry cleaning establishments using DF2000 hydrocarbon solvent, 10 had separator water PERC concentrations greater than 1.0 ppb; 11 of the still bottoms samples had concentrations of PERC greater than 1.0 ppb. A small study of dry cleaners using hydrocarbon solvent in California found PERC in the separator water in three of the four machines tested. PERC was also detected in the still bottoms in three of the four machines [1,19,29]. This preliminary data points to contamination of the waste stream in alternative solvent systems. Further characterization is needed to increase understanding of the sources of PERC and other contaminants.

Hazardous Waste

Several factors can cause a waste to be classified as hazardous or dangerous. “Hazardous” wastes are those regulated by federal hazardous waste regulations (40 C.F.R. Part 261). “Dangerous” wastes include hazardous wastes and those that are only considered dangerous under Washington State regulations (173-303-070 to 100). PERC is a listed waste under the Resource Conservation and Recovery Act (RCRA) (40 CFR 261.31). Sufficient PERC is present in the waste streams generated by PERC dry cleaning machines that it is always considered Dangerous Waste and must be removed and treated by a licensed hazardous waste collection company. Although little or no chlorinated chemicals should be present in the waste streams of alternative hydrocarbon machines, enough may be present such that they may also be considered hazardous waste under RCRA, or under the more stringent Washington State Dangerous Waste regulations (WAC 173-303).

In Washington State, the process of determining if a waste designates as Dangerous Waste involves evaluating several characteristics (presented in Table 1).

If any one characteristic exceeds the threshold set by Department of Ecology or RCRA, the waste designates as Dangerous Waste and must be labeled with the appropriate hazard codes. Listed wastes are those from certain chemicals, industrial processes, or unused chemicals contained in the F, K, P, and U lists in 40 CFR 261.31, 32, and 33. Wastes can be classified as characteristic wastes, which have flammable, corrosive, reactive, or toxic qualities. Washington State has additional classifications for Toxic Criteria wastes which contain a percentage of components with known toxic effects. Additional chemicals of concern are those that persist in the environment such as polyaromatic hydrocarbon (PAHs) and polychlorinated biphenyls (PCBs).

Table 1. Categories that may cause waste to designate as Dangerous Waste.

	Description	Examples	Code
Listed waste	Waste or process producing the waste is listed in this section	• F list • K list • P list • U list	• WAC 173-303-9904 • 40 CFR 261.31, 32, and 33
Characteristic Waste	Ignitability, corrosivity, reactivity, toxicity	• Flash Point • pH • contain cyanide or sulfide	• WAC 173-303-9904 (5-8) • 49 CFR 173-127 and 128
Toxicity Criteria	If information is known about toxicity of components or entire waste	Equivalent concentration calculation-takes individual constituents and their toxic category into account	• WAC 173-303-110 (3) (a) and (b)
Persistence criteria	Applies to compounds which do not rapidly degrade in the environment	• Total organic halogens • PAHs	• WAC 173-303-100 (5)

LHWMP has observed that dry cleaners using alternative solvents may not dispose of the separator water properly due to the mistaken belief that this waste stream does not designate as Dangerous Waste [30]. Further study of the contaminants present in separator water will better characterize this waste stream and provide information that can be used by the regulatory agencies to provide guidance for proper disposal and help the dry cleaning proprietors select appropriate waste management techniques.

Several factors may contribute to the designation of still bottoms and separator water as Dangerous Waste (summarized in Figure 2). In some cases, the concentration of trichloroethene (TCE) or PERC in the waste may cause the waste to designate as Dangerous Waste according to WAC 173-303-090(8). This code lists the Dangerous Waste threshold concentrations of various metals and compounds in waste. The Dangerous Waste threshold for TCE is 0.5 ppm by mass and for PERC is 0.7 ppm by mass. Other relevant Dangerous Waste thresholds are shown in Table 2. As previously discussed, these chemicals have been detected in still bottoms and separator water from hydrocarbon dry cleaners[1,19,29].

Table 2. Dangerous Waste criteria for select categories.

Chemical or Hazard	**Total Organic Halogens**	**Chromium**	**Trichloroethylene**	**Perchloroethylene**	**pH**	**Flash Point**
Dangerous Waste Threshold	0.01%	5 mg/L	0.5 mg/L	0.7 mg/L	<2 or >12.5	≤140 °F

Multiple factors contribute to the final composition of the still bottoms and separator water of alternative solvent dry cleaning machines. Inputs to the machine such as the solvent itself as well as spot treatment products and items to be cleaned are sources of chemicals in the waste. However, due to the complexity of the machine and the distillation process, not all components of the waste may be reflective of the inputs. The age, maintenance schedule, and use history may affect the waste streams. The current or former presence of a PERC machine on the premises could affect the PERC content of the waste.

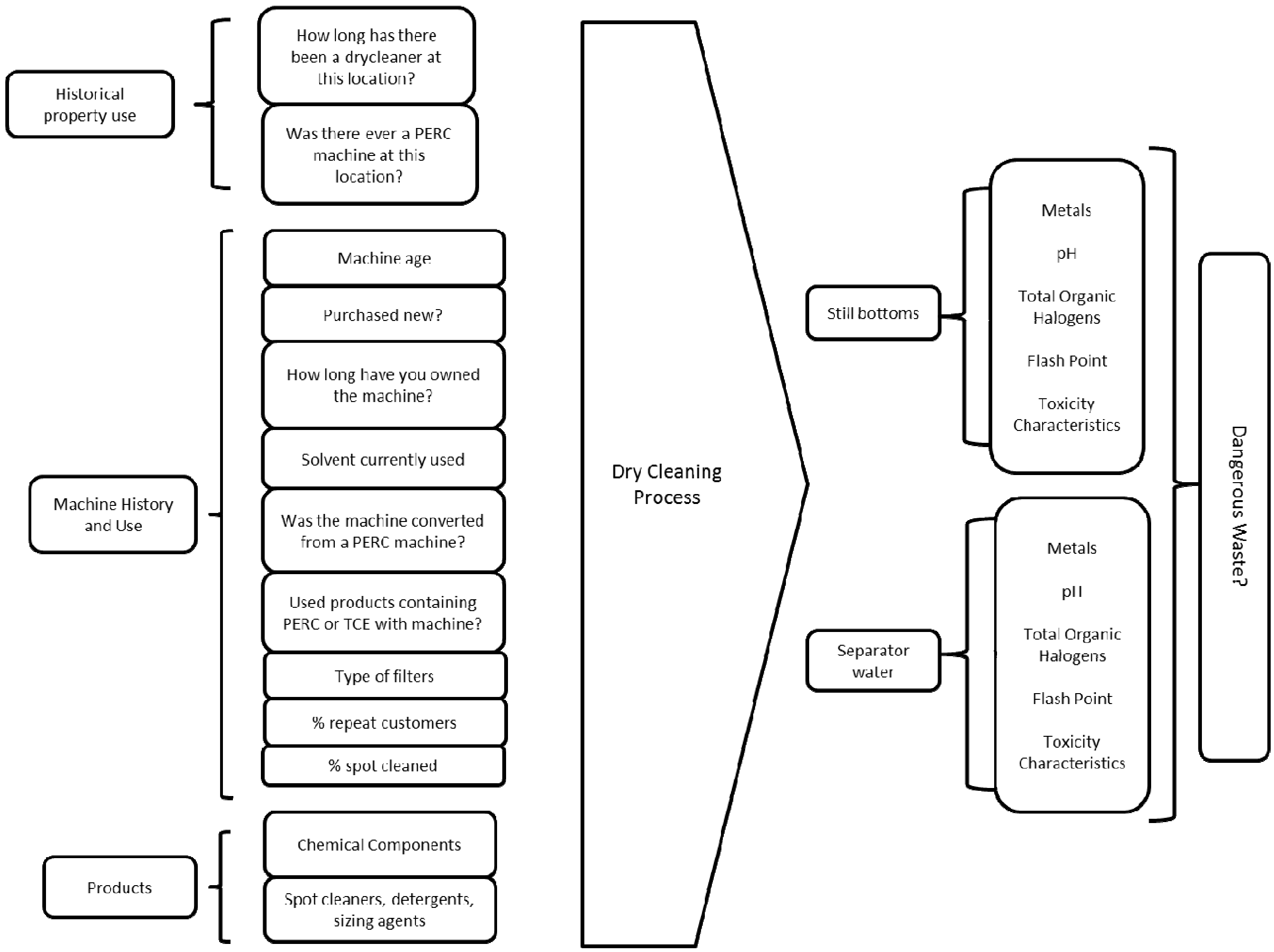


Figure 3. Factors contributing to dry cleaning waste designating as Dangerous Waste. Toxicity characteristics that can cause the waste to designate as Dangerous Waste are listed in WAC173-303-100.

A previous study conducted by LHWMP surveyed dry cleaners in King County to characterize the state of dry cleaning in the area. The results of the survey which are relevant to this study, include the following [4]:

- 69% of respondents use PERC in their primary machine
- 21% use hydrocarbon solvent in their primary machine
- 98% of all cleaners have still bottoms waste hauled by a licensed hazardous waste hauler.
- Of the PERC dry cleaners surveyed, the most commonly used type of gloves were reusable chemical resistant followed by disposable latex [4].

We do not currently know the chemical composition of the products used or the wastes generated by alternative solvent dry cleaners in King County, particularly SolvonK4. This study will seek to answer those questions and shed light on potentially overlooked occupational and environmental exposures at alternative solvent dry cleaners.

Specific Aims

1) Identify and chemically characterize the products used in dry cleaning operations that use solvent alternatives to PERC.

2) Using the Washington State Department of Ecology's Dangerous Waste designation methods, characterize the waste streams generated by dry cleaning operations that use solvent alternatives to PERC.

3) Administer a survey to determine the frequency of use of dry cleaning products and other operational information at dry cleaning establishments.

4) Identify any linkages between work practices, products used, and the chemical composition of the waste streams.

Methods

Study Design

The purpose of this study was 1) to determine whether and how the waste streams from dry-cleaning machines that use solvent alternatives to PERC exceed Dangerous Waste criteria and 2) identify the operational factors and products that may contribute to any exceedence. In order to accomplish this, data was collected on the chemical composition of dry cleaning products and waste streams (i.e., still bottoms and separator water). Fish bioassays were conducted on a subset of samples, according to Ecology's Dangerous Waste designation criteria. Surveys were used to collect information on the frequency of product use and other operational factors.

Study Population

The subjects in this study are the dry-cleaners in King County who operate alternative solvent dry cleaning machines and volunteered to participate. All but one shop used hydrocarbon solvent; this establishment used SolvonK4. The cleaners all had previous interactions with LHWMP because of enrollment in the EnviroStars program or previous field visits by LHWMP's Business Field Services team.

Study Setting

The waste and product samples were collected at the dry-cleaning establishments and analyzed at Friedman and Bruya, Inc., Seattle, Washington. Fish bioassays of select waste samples were conducted at the King County Environmental Laboratory, Seattle, Washington.

Questionnaire

The questionnaire was developed to determine whether dry cleaner's work practices may be responsible for the presence of PERC and other chlorinated hydrocarbons in the waste streams of alternative solvent machines. The questionnaire covered topics including establishment history, machine specifications and history, maintenance schedules, waste disposal, spot treatment information, and the fraction of repeat customers. Note that this questionnaire was developed by LHWMP prior to this current investigation and is typical of the data-gathering instruments used routinely by LHWMP in previous studies. This type of information gathering has not previously required Institutional Review Board (IRB) approval.

Product Sample Collection

Samples of products (spot cleaners, detergents, sizing agents) were collected during an initial site visit. The proprietor or machine operator was asked for the spot cleaners used with the alternative solvent dry cleaning machine. One 20 ml sample of each product was collected according to the Standard Operating Procedure (SOP) for Product Samples (Appendix A). On this site visit, the survey (Appendix B) was also administered to the proprietor or machine operator. The questionnaire was administered by verbally asking the questions, with further questions for clarification if necessary.

Waste Sample Collection

SOPs were developed for collecting still bottom and separator water samples. The SOPs contain an equipment list, safety and health information, sampling procedure, and labeling guidance (Appendices C and D). Samples were collected on a subsequent site visit. Sampling kits containing the appropriate containers and preservatives, as listed in

Table 3, were obtained from Friedman and Bruya, Inc. Immediately after sample collection, all samples were delivered to the laboratory for analysis.

Table 3. Number and type of waste sample collected

Number of containers	Type of container	Preservative	Analytes	Notes
Separator Water				
3	40 ml Volatile Organic Analyis (VOA) vial	none	Volatile Organic Compounds (VOCs)	
3	500 ml amber bottle	none	Semi-Volatile Organic Compounds (SVOCs), Total Organic Halogens (TOH)	Half-filled if there was limited separator water availability
1	500 ml HDPE bottle	HNO_3	Metals	Half-filled if there was limited separator water availability
1	250 ml I-CHEM jar	none	Acute static fish toxicity testing	For fish bioassay, not collected at all sites
Still Bottoms				
2	4 oz I-CHEM jar	none	VOCs, SVOCs, metals, TOH	
1	I-CHEM jar	none	Acute static fish toxicity testing	For fish bioassay, not collected at all sites

Sample Analysis

All chemical sample analysis was conducted by Friedman and Bruya, Inc. Analyses conducted are shown in Table 4. The waste samples were processed according the holding time specified in the method. A holding time was not used for the product samples due to their high concentration of analytes. Volatile organic compounds (VOCs) were identified using US EPA Method 8260C which utilizes gas chromatography/mass spectrometry (GCMS). Semi volatile organic compounds (SVOCs) were identified by a similar method, US EPA Method 8270 D. The metals content of the samples was analyzed using US EPA Method 200.8 which uses inductively coupled plasma mass spectrometry (ICP-MS) to detect trace elements. The mercury content was obtained using US EPA Method 1631 E by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry. The wastes' pH was measured using EPA Method 9045 D for soil and waste pH. Flash point was determined using the closed cup method ASTM D-93. Total organic halogens (TOHs) were measured by oxidative combustion and microcoulometry as required by RCRA Method SW 846 9076. Static Acute Fish Toxicity Tests were conducted by the King County Environmental Lab according to Method 80-12. These methods, with the limits of detection and applicable analytes are listed in Table 4 and Table 5.

Table 4. Methods used to analyze waste and product samples

Samples		Method	Analyte	Limit of Detection
Still bottoms, Separator water	Spot Cleaners, Detergent, Sizing Agent	EPA Method 8260C	VOCs	Depends on analyte
		EPA Method 8270D	SVOCs	Depends on analyte
		EPA 200.8	Metals	10 ppm
		EPA 1631 E	Mercury	0.1 ppm
		EPA 9045 D	pH	N/A
		ASTM D-93	Flash Point	Upper limit of 210˚F
		SW 846 9076	Total Organic Halogens	N/A
		80-12	Static Acute Fish Toxicity	N/A

The samples of separator water were prepared for analysis by typical laboratory procedures. Due to the complexity of the still bottoms, the samples had to be greatly diluted to avoid saturating the detector or damaging the laboratory instruments. This resulted in high detection limits and variable limits of detection between the samples.

The still bottoms analyses conducted in this study were for the total content of the samples of waste. However, the Washington State Department of Ecology regulations are based on Toxicity Characteristic Leaching Procedure (TCLP), which measures the amount of chemical that leaches from complex solid wastes into a slightly acidic solution over a period of time. Nonetheless, the totals analysis provided information on the actual content of the waste. Dividing the concentrations obtained from the totals analysis by a factor of 20 provides an estimate for comparison to the Ecology regulations.

Statistical Analysis

Stata 11 was used to calculate correlation and p-values for certain variables. Categorical variables were created to indicate if a shop utilized a product containing the compounds of interest. Categorical variables were also created to indicate if the waste streams contained those chemicals. Continuous variables were used for metals, isopropanol, and acetone. In the case of samples below the limit of detection, the limit of detection divided by $\sqrt{2}$ was substituted.

Table 5. Limits of detection- the bolded limits are above the Dangerous Waste criteria

	Products	**Still Bottoms**	**Separator Water**
Chromium	10 ppm	**10 ppm***	10 or 1 ppb
Arsenic	10 ppm	**10 ppm***	10 or 1 ppb
Selenium	10 ppm	**10 ppm***	10 or 1 ppb
Cadmium	10 ppm	**10 ppm***	10 or 1 ppb
Barium	10 ppm	10 ppm*	10 or 1 ppb
Lead	10 ppm	**10 ppm***	10 or 1 ppb
Hg: EPA 1631 E	0.1 ppm	0.1 ppm	0.1 ppm
Total Organic Halogens	-	-	5.0 ppm
TCE	200 ppm *	**200 ppm**	10, 100, 200, 1000 ppb
PERC	200 ppm *	**200 ppm**	10, 100, 1000 ppb
	*2000 ppm for Product #4	* 1 ppm for Solvon K4 still bottoms	

Data Analysis

Data analysis was performed with Microsoft Excel 2010™. The data obtained from the characterization of the still bottoms and separator water waste was organized and associated with the survey data from the same dry cleaner. Open-ended responses were coded into appropriate categories. Medians and ranges were calculated for categories with sufficient data.

Results

Survey Results:

Dry cleaning machine specifications

Of the ten hydrocarbon solvent dry cleaners surveyed, three used machines manufactured by Bowe Permac®, and three used machines produced by Union S.p.A.. The remaining manufacturers represented were Realstar USA, Firbimatic/Eco Dry of America, BioClean, and Satec USA, LLC. All of the machines were different models, except two of the Union S.p.A. machines, which were the HL835 model. The machines varied in capacity, from 26 to 80 lbs, with a median capacity of 40 lbs. The age of the hydrocarbon solvent machines ranged from 1 year to 10 years, with a median of 6.5 years.

Operation and management

The cleaners reported running between 7 and 24 loads of garments per week. Estimates of the percentage of cleaning derived from repeat customers ranged from 10% to 80%. The amount of clothing requiring spot cleaning ranged from "not many" to 50%.

Machine maintenance/waste disposal

The majority of cleaners reported cleaning the still bottoms from the machines weekly, although the range of replies was from daily to once per month. All cleaners reported disposing of the still bottoms in a waste drum for removal by a hazardous waste disposal company, except one which had obtained King County Public Health approval to mix the waste with absorbent and place in the municipalmunicipal waste container for collection. Separator water was removed weekly by two cleaners, continuously by two cleaners, less than weekly by two, and 10 times per month by one cleaner. Of the shops that drained the separator water continuously, one used a ZeroWaste HX machine, originally designed to remove contaminants from perchloroethylene separator water prior to disposal (http://www.zerowaste.net/). This technology uses carbon filters to remove contaminants. Seven of nine shops used a hazardous waste disposal company to remove the separator water while two evaporated the water in a back room of the dry cleaning shop.

Product Analyses

A total of 39 different products used at the hydrocarbon solvent dry cleaners were analyzed for VOCs, SVOCs, and metals. 26 of these were spot treatment products, seven were detergents, and the remaining samples were sizing agents. The chemical concentration of some products did not exceed the detection limits. Products with positively identified components are shown in Table 6, with the percentage content of each analyte as well as the IARC classification, if available. Several of the products were found to contain probable or possible human carcinogens at a level greater than 0.1% that were not listed in the MSDS. One detergent was found to contain an unlisted possible carcinogen content of >0.1%. Two of the products, in agreement with their MSDSs, were found to consist of almost 100% TCE. One of the spot cleaners and one of the detergents contained methylene chloride. Spot cleaner #8 contained 35% TCE, although the MSDS listed "Trade secrets" as ingredients with no information regarding carcinogenicity. There were discrepancies between the ingredients listed on the MSDSs and the concentrations detected in our samples. This could be a function of collecting samples from previously opened containers of the product or lack of adequate description of the composition on the MSDS.

All but one cleaner reported disposing of the still bottoms in a waste drum for removal by a hazardous waste disposal company. The single exception had obtained King County Public Health clearance to mix the waste with absorbent and place it in the trash. Of the shops that drained the separator water continuously, one used a ZeroWaste HX machine, a filtration device designed to remove contaminants prior to disposal (http://www.zerowaste.net/). Seven of nine shops used a hazardous waste disposal company to remove the separator water, and two evaporated the water in a back room of the dry cleaning shop.

Table 6. Chemical Composition of Dry Cleaning Products

Product	Analysis			MSDS Information
	Substance	Concentration (%)	IARC Classification*	
Spot cleaner #2	TCE	96	2A	Carcinogen information provided. TCE: 100%
Spot cleaner #3	Methyl Isobutyl Ketone	**2.3****	2B	No carcinogens listed. Aromatic hydrocarbons: <30%, isopropyl alcohol 10-30%
	o-Xylene	0.22	3	
	n-propylbenzene	1.1		
	isopropyl benzene	**0.2****	2B	
	1,3,5-trimethylbenzene	1.9		
	1,2,4-trimethylbenzene	6.4		
	sec-butylbenzene	0.1		
	p-isopropyltoluene	0.042		
	1,2-dichlorobenzene	1.9	3	
Spot cleaner #4	Acetic acid, pentyl ester	45		No carcinogens listed.
Spot cleaner #5	1,2,4-trimethylbenzene	0.15		No carcinogens listed. Butoxyethanol: 10-15%, pentyl acetate: 35-40%, alcohols (C12-15): 30-35%, odorless mineral spirits: 20-25%
	naphthalene	**0.56****	2B	
	trichloroethene	0.028	2A	
Spot cleaner #8	TCE	**35****	2A	No carcinogens listed. Trade secrets.
Spot cleaner #9	TCE	100	2A	Carcinogen information is given. TCE: 100%
Spot cleaner #11	Acetic acid, pentyl ester	40		No carcinogens listed. Amyl acetate: 99-100%
Spot cleaner #12	Methylene Chloride	51	2B	Carcinogen information provided. Methylene chloride: >75%, dimethoxymethane: 1-10%, hydrated amorphous silica: 1-10%, liquified petroleum gas: 20-25%
	PERC	**1.3****	2A	
Spot cleaner #17	PERC	0.033	2A	No carcinogens listed. 1,3 dimethylol-5,5-dimethylhydatoin
Spot cleaner #20	m,p-Xylene	0.13	3	No carcinogens listed. Potassium hydroxide: 1-5%, petroleum distillates: 30-40%, ethylene glycol monobutyl ether(EB solvent): 25-35%
	o-Xylene	1.8	3	
	isopropyl benzene	0.53**	2B	
	n-propylbenzene	1.8		

Product	Analysis			MSDS Information
	Substance	Concentration (%)	IARC Classification*	
	1,3,5-trimethylbenzene	2.6		
	1,2,4-trimethylbenzene	9		
	sec-butylbenzene	0.15		
	p-isopropyltoluene	0.071		
Spot cleaner #23	dimethyl phthalate	0.23		A trace contaminant (<0.01%) listed as a carcinogen. Ammonium hydroxide: <1%, potassium hydroxide: <2%
	2,6-dinitrotoluene	0.65**	2B	
Spot cleaner #25	1,2-dichlorobenzene	2.1	3	No carcinogens listed. Orthodichlorobenzene: 1-5%, pentyl acetate: 3-7%, n-butyl alcohol: 3-7%, MIBK: 1-5%, cyclohexanol: 3-7%, aromatic petroleum distillates: 10-30%
Detergent #35	Methylene chloride	0.11**	2B	No carcinogens listed. Hydrocarbon solvent: 23-30%

* IARC classifications - 2A: Probable human carcinogen. 2B: Possible human carcinogen. 3: Not classifiable.
**IARC 2A or 2B constituents at concentrations > 0.1%, where carcinogen information is not given on the MSDS.

Separator Water

VOCs, SVOCs, and metals analysis of the separator water from seven dry cleaners were completed by Friedman and Bruya, Inc. Three of the shops are not represented in this data. Because two of these shops use a Zero Waste machine to filter their separator water, the data would not be comparable to the other untreated samples. The third shop did not have any separator water available for sampling. Positively identified VOCs and SVOCs are listed in Table 7 along with the limit of detection in each sample. The results of metals analysis, pH, flash point, and total organic halogens analysis are shown in Table 8. Limits of detection for the different chemicals varied among samples.

All samples of separator water contained acetone in concentrations ranging from 140 to 20,000 ppb and four of the seven samples contained isopropyl alcohol in concentrations from 6100 to 17,000 ppb. The separator water from Shop 2 designated as Dangerous Waste based on its trichloroethylene (TCE) content and a flash point slightly below the regulatory limit of 140°F. This sample also contained the largest number of compounds of interest, including 1,2 dichlorobenzene, 1,2,4-trimethylbenzene, methyl isobutyl ketone (MIBK), naphthalene, and toluene. One other sample contained a measurable level of MIBK. Shop 2 uses one of the spot treatment products that consists of 100% TCE. No other sample of separator water designated as Dangerous Waste. Only the sample from Shop 7 was found to contain PERC at levels above the limit of detection.

All samples of separator water contained measurable levels of chromium and four of the seven contained lead in concentrations above 1.0 ppb. Two samples contained mercury above 0.1 ppb and two contained TOH levels above 5.0 ppb. As with the VOCs and SVOCs analysis, the separator water from Shop 2 had the largest number of compounds of concern. Shop 2's separator water contained chromium, mercury, lead, and TOHs at levels above the limit of detection.

Table 7. Concentrations of VOCs and SVOCs in separator water (in ppb).

	CAS #	Shop 2	Shop 3	Shop 7	Shop 8	Shop 9	Shop 10	Shop 11
Uses Products:		2,3,4,5	8,9, 12			5		35
1,2 dichlorobenzene	95-50-1	140*	<100	<10	<1000	<100	<10	<10
1,2,4-Trimethylbenzene	95-63-6	200*	<100	<10	<10	<100	<10	<10
2-Butanone	78-93-3	<2000	<1000	<10	230*	<1000	<100	200*
Tertbutyl alcohol	75-65-0	<5000	<5000	<500	1000*	<5000	<500	980*
Acetone	67-64-1	7000*	2800*	140*	20,000*	5100*	1800*	2200*
Ethanol	64-17-5	480,000*	<100,000	<10,000	<10,000	<10000	<10000	-
Isopropyl alcohol	67-63-0	1,200,000*	42,000*	<1000	6100*	170,000*	<1000	-
Methyl isobutyl ketone	108-10-1	10,000*	<1000	<100	240*	<1000	<200	<100
Naphthalene	91-20-3	150*	<100	<10	<1000	<100	<10	<10
Toluene	108-88-3	240*	<100	<10	<10	<100	<10	<10
Trichloroethene	79-01-6	13,000*	<200	<10	<1000	<100	<10	<10
Tetrachloroethene	127-18-4	<100	<100	15*	<10	<100	<10	<10

*Values above the limit of detection.

Table 8. Analysis of hydrocarbon solvent separator water.

	Shop 2	Shop 3	Shop 7	Shop 8	Shop 9	Shop 10	Shop 11	Median	Range
Chromium (ppb)	101*	42*	21.7*	2.26*	27.9*	1.33*	2.38*	21.7	1.33-101
Lead (ppb)	873*	15.3*	79.3*	<1.0	367*	<1.0	<1.0	223	<1.0-873
Mercury (ppb)	1.3*	1.2*	<0.1	<0.1	<0.1	<0.1	<0.1	1.25	<1.0-1.3
pH	5.97*	7.44*	5.71*	6.12*	6.93*	6.71*	6.65*	6.65	5.71-7.44
Flash Point (F)	138*	>210	>210	>210	>210	>210	>210	-	-
Total Organic Halogens (ppm)	12*	<5.0	<5.0	6.1*	<5.0	<5.0	<5.0	9.05	<5.0-12

*Values above the limit of detection.

Table 9. Correlation of ingredients of products used by hydrocarbon cleaners and the compounds in separator water. R(p-value).

		Products						Separator Water								
		TCE	Perc	Methylene Chloride	Trimethyl benzene	Dichloro benzene	Total Chlorinated Compounds >1%	Chromium**	Lead**	Mercury**	TCE	Dichloro benzene	Trimethyl benzene	Perc	Acetone**	Isopropanol**
Products	Perc	0.22 (0.55)														
	Methylene Chloride	0.51 (0.13)	0.68* (0.04)													
	Trimethylbenzene	0.52 (0.12)	-0.33 (0.33)	-0.22 (0.55)												
	Dichlorobenzene	0.22 (0.55)	-0.25 (0.48)	-0.17 (0.65)	0.22 (0.55)											
	Total Chlorinated Compounds >1%	0.52 (0.12)	0.22 (0.55)	0.51 (0.13)	0.05 (0.90)	0.76* (0.01)										
Separator Water	Chromium**	0.75 (0.05)	0.17 (0.72)	0.17 (0.72)	0.69 (0.08)	0.90* (0.01)	0.83* (0.02)									
	Lead**	0.65 (0.12)	-0.24 (0.61)	-0.24 (0.61)	0.89* (0.01)	0.92* (0.00)	0.53 (0.23)	0.90* (0.01)								
	Mercury**	0.73 (0.63)	0.61 (0.15)	0.61 (0.15)	0.33 (0.47)	0.68 (0.09)	0.99* (0.00)	0.85* (0.02)	0.56 (0.19)							
	TCE	0.47 (0.29)	-0.17 (0.72)	-0.17 (0.72)	0.65 (0.12)	1*	0.65 (0.12)	0.90* (0.01)	0.92* (0.00)	0.68 (0.09)						
	Dichlorobenzene	0.47 (0.29)	-0.17 (0.72)	-0.17 (0.72)	0.65 (0.12)	1*	0.65 (0.12)	0.90* (0.01)	0.92* (0.00)	0.68 (0.09)	1*					
	Trimethylbenzene	0.47 (0.29)	-0.17 (0.72)	-0.17 (0.72)	0.65 (0.12)	1*	0.65 (0.12)	0.90* (0.01)	0.92* (0.00)	0.68 (0.09)	1*	1*				
	Perc	-0.35 (0.44)	-0.17 (0.72)	-0.17 (0.72)	-0.26 (0.58)	-0.17 (0.72)	-0.26 (0.57)	-0.08 (0.86)	-0.15 (0.75)	-0.26 (0.58)	-0.17 (0.72)	-0.17 (0.72)	-0.17 (0.72)			
	Acetone**	-0.09 (0.56)	-0.18 (0.70)	-0.18 (0.70)	0.05 (0.92)	0.09 (0.84)	-0.07 (0.88)	-0.06 (0.90)	0.05 (0.92)	-0.06 (0.90)	0.09 (0.84)	0.09 (0.84)	0.09 (0.84)	-0.36 (0.43)		
	Isopropanol**	0.564 (0.19)	-0.16 (0.73)	-0.16 (0.73)	0.74 (0.06)	0.99* (0.00)	0.64 (0.12)	0.92* (0.00)	0.96* (0.00)	0.68 (0.09)	0.99* (0.00)	0.99* (0.00)	0.99* (0.00)	-0.20 (0.67)	0.09 (0.85)	
	TOH	0.09 (0.85)	-0.26 (0.58)	-0.26 (0.58)	0.30 (0.51)	0.65 (0.12)	0.30 (0.51)	0.45(0.32)	0.51 (0.24)	0.33 (0.47)	0.65 (0.12)	0.65 (0.12)	0.65 (0.12)	-0.26 (0.58)	0.80* (0.03)	0.62 (0.14)

*p-value <0.05

**Continuous variables. All other variables are categorical: 1= yes, 0=no.

The contents of spot cleaners used were analyzed with respect to the contents of the separator water samples. As shown in the correlation matrix in Table 9, the concentrations of chromium and lead are correlated to the presence of TCE, trimethylbenzene, dichlorobenzene, and the concentration of isopropanol. This analysis was hampered by the large number of samples below the limit of detection.

Still Bottoms

Still bottoms samples from the same ten dry cleaners were collected and analyzed.

As was seen in the separator water samples, the metals analysis of the still bottoms revealed chromium in all samples. Additionally, as shown in Table 10, six of the ten samples had lead levels above 10 ppm and mercury levels above 0.1 ppm. The concentrations of the metals are totals rather than TCLP values, which may be estimated by dividing the concentrations by 20. The flash points of the still bottoms ranged from 110˚F to 230˚F with 5 being ≤ 140˚F. The flash point of the still bottoms was correlated (R=0.5603, p-value=0.0921) with whether the cleaning solvent was DF2000 (categorical variable=0) or not known (categorical variable =1). All still bottoms had TOH concentrations above 100 ppm. No patterns were observed in the different concentrations of analytes between the still bottoms samples. The lead concentration in the still bottoms was correlated with whether the shop used a product containing PERC (R= 09407, p-value= 0.0052).

Table 10. Analysis of hydrocarbon solvent still bottoms. The concentrations of metals are totals rather than TCLP.

	Shop 2	Shop 3	Shop 4	Shop 5	Shop 6	Shop 7	Shop 8	Shop 9	Shop 10	Shop 11	Median	Range
Chromium (ppm)	68.3*	36.3*	19.8*	221*	64.2*	88.5*	148*	61.9*	18.1*	62.1*	63.2	18.1-221
Lead (ppm)	15.6*	<10	94.1*	<10	22.6*	34.2*	10.3*	37*	<10	<10	28.4	10.3-94.1
Mercury (ppm)	<0.1	0.11*	<0.1	0.3*	0.21*	0.38*	0.18*	<0.1	<0.1	0.26*	0.24	0.11-0.38
pH	4.96*	5.77*	6.09*	5.32*	6.34*	6.28*	6.75*	5.86*	5.96*	6.22*	6.03	4.96-6.75
Flash Point (F)	159*	140*	230*	110*	132*	133*	149*	155*	120*	120*	137	110-230
Total Organic Halogens (ppm)	150*	220*	210*	210*	680*	620*	270*	250*	320*	820*	260	150-820

*Values above the limit of detection

Solvon K4 waste streams

The results of analyses of still bottoms and separator water from a Solvon K4 machine are shown in Table 11 and Table 12. One sample of still bottoms designated as Dangerous Waste on the basis of flash point while all the samples designated as Dangerous Waste on the basis of Total Organic Halogens. Neither of the separator water samples designated as Dangerous Waste. The ranges and medians of the still bottom analytes were similar to those of the petroleum-based hydrocarbon solvent still bottoms. The boxplots shown in Figure 4 illustrate that the distributions of total organic halogens for the two types of solvent are very similar, as are the concentrations of lead and chromium. The median flash point of the four samples of Solvon K4 still bottoms was greater than the upper quartile of the hydrocarbon still bottoms.

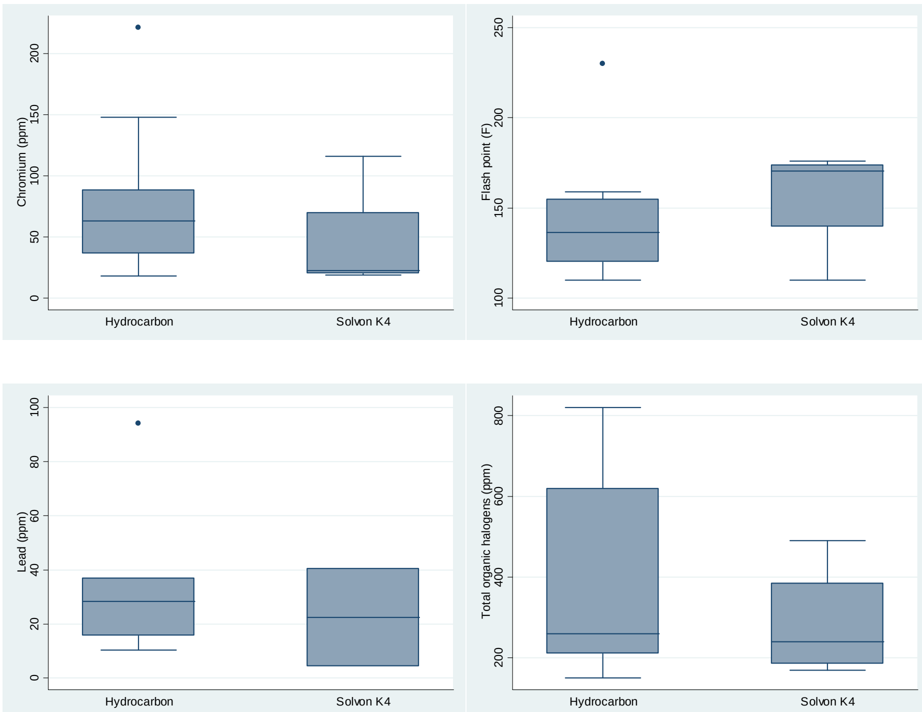
Table 11. Analyses performed on samples (n=4) of still bottoms from a SolvonK4 machine.

	Range	**Median**
Chromium (ppm)	19-116	22.5
Barium (ppm)	<10-23	14.1
Lead (ppm)	<10-40.5	22.4
Mercury (ppm)	<0.1-0.44	0.44
pH	5.46-6.68	5.98
Flash Point (˚F)	110-176	170.5
Total Organic Halogens (ppm)	170-280	240

Table 12. Analyses performed on samples (n=2) of separator water from a SolvonK4 machine.

	Range
Chromium (ppb)	17.5-25.5
Lead (ppb)	<10-25.22
Mercury (ppb)	0.13-0.15
pH	6.82- 6.99
Flash Point (˚F)	>210
Total Organic Halogens (ppm)	<5.0 ppm

Figure 4. Box plots of chromium, lead, flash point, and total organic halogens in hydrocarbon solvent still bottoms and Solvon K4 still bottoms.



No compounds of interest were identified in the analysis of other productsthe Kreussler products designed for use with Solvon K4this machine.

Fish Toxicity

Both SolvonK4 wasteswaste and the dry cleaning solvent as well as hydrocarbon waste were subjected to acute fish toxicity testing at the King County Environmental Laboratory.

The separator water sample from the hydrocarbon solvent dry cleaning machine elicited 100% survival at both the 10 mg/L and 100mg/L test concentrations, while the still bottoms caused 100% survival at 10mg/L but 0% survival at 100mg/L.

The SolvonK4 solvent produced a survival rate of 3% at the 100 mg/L test concentration while there was 100% survival at 10mg/L test concentration. Although this method is not strictly applicable for products, this result suggests a Dangerous Waste classification for the solvent.

Two samples each of SolvonK4 still bottoms and separator water were subjected to the same tests. As shown in Table 13, both samples of separator water had 100% survival at both 10 and 100 mg/L test concentrations. Thus the separator water does not designate as Dangerous Waste. Both samples of SolvonK4 still bottoms had 0% survival at 100 mg/L, which causes designation as Dangerous Waste. One of the still bottom samples also had 0% survival at 10 mg/L test concentration which classifies that sample as Extremely Hazardous Waste. The fact that the second sample of still bottoms had 100 % survival at this test level indicates variability in the contents of the waste stream. This could be an effect of the amount and type of fabrics cleaned, amount of spot cleaner use, or the maintenance schedule of the machine.

Table 13. Acute Fish Bioassays of SolvonK4 still bottoms, and separator water.

	Test Concentration (mg/L)	Percent Survival	Dangerous Waste	Extremely Hazardous Waste
Solvon K4 Still Bottoms #1	10	0	--	**Yes**
	100	0	**Yes**	--
Solvon K4 Still Bottoms #2	10	100	--	No
	100	0	**Yes**	--
Solvon K4 separator water #1	10	100	--	No
	100	100	No	--
Solvon K4 separator water #2	10	100	--	No
	100	100	No	--

Discussion

The results of this study confirm that the wastes derived from dry cleaning machines that use non-chlorinated alternative solvents may designate as Dangerous Waste. Although preliminary information has been described previously for hydrocarbon solvents like DF-2000, this is the first time that such a study has been conducted for machines that use the relatively new solvent, SolvonK4. The analysis of spot cleaners and other products has implications for the occupational health of dry cleaners. The results of this investigation will help environmental professionals and dry cleaners make informed decisions about appropriate selection of products and dry cleaning technology.

Products

This study identified a number of products used by alternative solvent cleaners in the King County area. It was found that only a few products were used by more than one business. Of the 39 products sampled, 13 contained chemicals of interest. Of these 13 products, 7 contained possible or probable human carcinogens at >0.1%, which is the reporting threshold for MSDSs. The composition of the spot cleaners may be reflected in the waste streams under certain circumstances as seen in the TCE content of the separator water from Shop 2. Four of the shops used products that did not contain any of the compounds of interest. These shops use spot cleaners and other products that are less hazardous, yet are effective. While the cleaners in this study use alternative solvents rather than perchloroethylene dry cleaning machines, many are still using the spot treatment products designed for use with PERC machines. Many of the spot treatment products and detergents analyzed in this study did not contain hazardous compounds and can thus be recommended as having lower occupational health risks than the others. Encouraging the exclusive use of these products rather than those traditionally used with PERC machines would likely reduce concentration of harmful constituents in the waste of alternative solvents.

Still bottoms

Despite the observed variability in chemical composition, all still bottom samples collected from both hydrocarbon and Solvon K4 machines designated as Dangerous Waste. The ten hydrocarbon solvent still bottom samples are well above the 100 ppm TOH Dangerous Waste criteria level, with the lowest TOH concentration being 150 ppm. In addition, all but three still bottom samples designated as Dangerous Waste on the basis of flash point. The still bottoms from both the hydrocarbon solvent and Solvon K4 machines also designate as Dangerous Waste on the basis of the acute fish toxicity test. Variability among samples from the same machine, as seen in the Solvon K4 data, could be due to different load sizes, amount of spot treatment needed, whether the still bottoms were "cooked", time from the last machine maintenance, or other factors. Our results differed from the previously discussed studies in California and King County in that PERC was not detected in our still bottom samples while it was found in 3 out of 4 samples in the California study and the majority of still bottoms samples in the previous King County study. The analyses in the previous King County study were conducted on a TCLP extract; this method had a limit of detection of 1.0 ppb for PERC. This limit is lower than achieved attempting to measure the total amount of PERC in still bottoms, as was done in this study. The TCLP values may be estimated by dividing the concentrations by 20. This may explain why this study found fewer samples containing PERC and TCE. The California study found in aquatic toxicity tests that the still bottoms have a lethal concentration (LC)-50 of less than 500 mg/L, in agreement with our findings of 100% mortality at 100mg/L. The source of the metals such as chromium and lead in the still bottoms and separator water is unclear, but may be due to leaching from machine parts or the metals may be components of dirt removed from soiled fabrics.

These results reinforce the need for licensed hazardous waste removal companies to dispose of the still bottoms from alternative solvent dry cleaning machines.

Separator Water

The concentrations of metals, TOHs, and other chemical constituents were very similar in all separator water samples, whether they were derived from machines that used hydrocarbon or Solvon K4. The observed variability between samples may be due to a number of factors, including type and number of items being cleaned or amount of spot treatment needed. Specific management and maintenance practices could affect the contaminant level of the separator water.

As with the still bottoms, previous studies found proportionally more samples with PERC and TCE than this study. This could be a result of the lower detection limits; the previous King County study had a limit of detection of 1 ppb for PERC, while this study had detection limits that varied from 10 ppb to 100 ppb. The California study of hydrocarbon dry cleaners also found acetone in all separator water samples, as did this study.

Only one sample of hydrocarbon solvent separator water designated as Dangerous Waste. This sample was visually different from other separator water samples, having a distinct, immiscible layer of liquid on top of the bulk of the liquid. The unique appearance was reflected in the chemical analysis. For example, of the seven shops sampled, the concentrations of chromium, lead, mercury, and TOHs were the highest in the separator water from this shop. Additionally, this separator water was the only sample that had a flash point that exceeded the Dangerous Waste limit of 140˚F. This shop also had a relatively high concentration of TCE in the separator water, at 13,000 ppb. While several factors contribute to the composition of separator water, it is notable that this shop used a spot cleaner that contained 100% TCE. The separator for this hydrocarbon solvent machine is likely malfunctioning, which could prevent the proper separation of the solvent and other substances from the waste separator water. Additional compounds present above the limit of detection in only this sample were naphthalene, toluene, 1,2-dichlorobenzene, and 1,2,4-trimethylbenzene. The distinct appearance of this sample could be the most reliable indicator that the separator water may designate as Dangerous Waste and could be used as a tool to prompt the further evaluation of dry cleaning machines.

The fact that two of the shops evaporate the separator without any vapor controls or testing of the water is concerning in light of the possibility of having probable carcinogens in the separator water.

Implications for the industry

The results of this study have implications for the dry cleaning industry in the disposal of waste from dry cleaning machines as well as the selection and use of spot treatment products, detergents, and sizing agents. All but one of the hydrocarbon solvent cleaners sampled dispose of their still bottoms with a licensed hazardous waste disposal company. Based on our results, all the cleaners should do so. Separator water should be disposed of in a similar manner until a simple and quick method of determining the Dangerous Waste status may be validated. While ZeroWaste machines may be and effective solution to reducing amounts of dangerous waste, their use may be considered treatment by the separator water or disposingDepartment of Ecology. This classification would force the cleaners to change their waste generator status with resultant increase in reporting and waste management requirements. The guidance on these regulations is being clarified. In the future, it might be beneficial for cleaners, manufacturers, and agencies for the manufacturers to integrate an absorbent system similar to ZeroWaste into new models of the cleaning machine to reduce dangerous waste production. Evaporation of the separator water or pouring the waste into the sanitary sewer should be avoided to prevent worker exposure and environmental contamination. The cleaners should use adequate PPE when cleaning the separator water and still bottoms to avoid skin contact with the solvents and other compounds in the waste. The analysis of SolvonK4 indicates that it should be treated similarly to the petroleum-based hydrocarbon solvents, with similar waste disposal techniques.

The implications of the hazardous ingredients of spot cleaners include potential adverse health effects and the presence of the chemicals in the waste. Using effective and carcinogen-free products, as is the case for over half the hydrocarbon dry cleaners in this study, reduces occupational exposure to potential and possible carcinogens. Dry cleaning proprietors should be aware of the contents of the products they use. While this can be accomplished to some degree by reading the MSDSs provided with the products, as this study shows, the MSDSs are often misleading and incomplete.

Implications for agencies

The findings of this study can inform guidance LHWMP and King County Public Health offer to dry cleaners in the area. The disposal of still bottoms as Dangerous Waste should be enforced and it should be strongly suggested that separator water be disposed of in the same manner. Waste management policies should be reevaluated in light of this new information. The information on product ingredients can be utilized to develop a list of spot treatment and detergent products that do not contain hazardous ingredients. This list could be used as a recommendation to alternative solvent dry cleaners. While such recommendations would be valuable, there are barriers to naming specific products, including inability to disclose proprietary information. The fact that several of the products contained possible or potential carcinogens at concentrations greater than 0.1% without having carcinogen warnings listed on the MSDS is concerning and the agencies involved with dry cleaning may wish to pursue this issue.

Limitations

The small sample size of ten hydrocarbon solvent dry cleaners is the largest limitation of this study. While sufficient samples were collected to provide useful information on the constituents of separator water and still bottoms from these machines, it is not large enough to draw definitive conclusions about the causal relationship between individual constituents and other variables.

Although all the still bottom samples designated as Dangerous Waste, the chemical analyses presented an analytical challenge because of their complex composition and tar-like consistency. While the total concentrations of the analytes were obtained, the necessary dilution of these samples resulted in detection limits above the Dangerous Waste criteria levels for some of the analytes. Additionally, the analysis protocol for still bottoms varied from the Department of Ecology (Ecology) criteria which requires toxicity characteristic leaching procedure (TCLP). Future analysis should use TCLP for VOCs, SVOCS, and metals to facilitate comparison with Ecology criteria.

The dry cleaning shops that participated in this study did so voluntarily through a previous relationship with King County LHWMP and thus present a biased sample. These shops may have different work practices than those that do not have a good relationship with LHWMP, and thus have waste streams and products that differ from other shops. It is noteworthy that the one shop with separator water that designated as Dangerous Waste (Shop #2), subsequently dropped out of the study and is lost to follow-up.

The survey questions were answered by the most knowledgeable person available when sampling was taking place. Several of the questions were difficult to convey or for the dry cleaners to answer accurately. This was especially a consideration because the majority of shop owners are of Korean ancestry with occasionally limited English language skills.

Conclusions and Recommendations

While limited by small sample size and other factors, this study indicates several characteristics of products and waste that have implications for occupational health and waste disposal. The still bottoms of hydrocarbon solvent and Solvon K4 machines designate as Dangerous Waste by several criteria. Separator water did not typically designate as Dangerous Waste, although visible solvent in the separator water may indicate that the waste will designate. The spot treatment, detergent, and other products used in the cleaning process may contain harmful chemicals that are not reflected on the MSDS. Spot treatment products that contain probable or possible human carcinogens should be avoided. Analyzing the contents of unopened containers of the same products would provide information on the original ingredients of the products as well as on the effects of using opened containers of products for spot treatment over time.

Additional work could be conducted to further characterize the wastes generated by alternative solvent dry cleaners, including:

- Recruit more dry cleaning establishments
- Collect waste samples on multiple occasions to characterize temporal variability and compare with information on machine maintenance schedule
- Investigate source of metals in waste: sample soiled clothing brought to dry cleaners, investigate materials used in the components of dry cleaning machines
- Analyze samples for Fats, Oils, and Greases

From a regulatory standpoint, non-polar Fats, Oils, and Greases are regulated by the King County Industrial Waste program for when discharge to the sewer.

Additionally, PPE use during still cleaning and maintenance should be investigated and appropriate glove and clothing selections made in light of these results. Future study of dry cleaning machines, maintenance schedules, and separator water could investigate the link between appearance of separator water and the concentration of its components. It may be beneficial for the dry cleaning proprietors to treat all waste as Dangerous Waste and dispose of it in the waste drum with the still bottoms. A study of alternative dry cleaner waste before and after switching from products containing these compounds to products that do not contain these hazardous constituents could be performed to determine the effect of product constituents on the status of the waste streams.

While further study will clarify questions raised by this research, important knowledge was gained about the nature of alternative solvent dry cleaner waste as well as the products such cleaners use. The survey administered to the cleaners provided useful information on waste disposal and machine cleaning. Analyzing the data from this study showed gaps in the survey which can be filled by adding questions on machine maintenance and seeking to clarify spot treatment use. A number of products used by hydrocarbon dry cleaners in King County were identified and a third were found to contain probable or possible carcinogens. While this raises regulatory and occupational health concerns, the majority of the products did not contain such compounds and are used effectively by cleaners. Samples of waste from hydrocarbon and Solvon K4 dry cleaning machines were analyzed for a range of organic compounds and metals. One sample of separator water and all the still bottoms samples were found to designate as dangerous waste on the basis of one or more criteria. The waste streams from the Solvon K4 machine were not found to have markedly different characteristics than the waste from hydrocarbon solvent machines. Combining the survey data with information on the products and the analyses of the waste indicates a few factors that could influence the contents of the waste streams. In addition, maintenance schedules may affect the contents of the waste and how well the still and separator function. Metals were identified in all samples of waste, but not in the products, leaving their source unknown. Overall, this study succeeded in characterizing the still bottoms and separator water from hydrocarbon and Solvon K4 dry cleaning machines and identifying potential links between work practices, products used, and the contents of the wastes.

Bibliography

1. United States Environmental Protection Agency [US EPA]. Cleaner technologies substitutes assessment: Professional fabricare processes. . 1998;EPA 744-B-98-001.

2. Agency for Toxic Substances and Disease Registry. ATSDR - toxicological profile: Stoddard solvent. http://www.atsdr.cdc.gov/ToxProfiles/TP.asp?id=416&tid=73. Accessed January 21, 2011.

3. Occupational Safety and Health Administration [OSHA]. Reducing worker exposure to perchloroethylene (PERC) in dry cleaning. . 2005;OSHA 3253-05N.

4. Whittaker SG, Johanson CA. A profile of the dry cleaning industry in king county, washington. . 2011;LHWMP 0048.

5. State Coalition for Remediation of Drycleaners (SCRD). A chronology of historical developments in drycleaning. http://www.drycleancoalition.org/reference.cfm. Accessed December 30, 2010.

6. Agency for Toxic Substances and Disease Registry [ATSDR]. ATSDR - toxicological profile: Tetrachloroethylene (PERC). http://www.atsdr.cdc.gov/ToxProfiles/TP.asp?id=265&tid=48. Updated 1997. Accessed January 4th, 2011.

7. Tetrachloroethylene (CASRN 127-18-4) | IRIS | US EPA. http://www.epa.gov/iris/subst/0106.htm. Accessed April 7, 2010.

8. Gold LS, De Roos AJ, Waters M, Stewart P. Systematic literature review of uses and levels of occupational exposure to tetrachloroethylene. *J Occup Environ Hyg*. 2008;5(12):807-839. doi: 10.1080/15459620802510866.

9. Ma J, Lessner L, Schreiber J, Carpenter DO. Association between residential proximity to PERC dry cleaning establishments and kidney cancer in new york city. *J Environ Public Healt*h. 2009;2009:183920. doi: 10.1155/2009/183920.

10. Calvert GM, Ruder AM, Petersen MR. Mortality and end-stage renal disease incidence among dry cleaning workers. *Occup Environ Me*d. 2010. doi: 10.1136/oem.2010.060665.

11. Bukowski JA. Review of the epidemiologic literature on residential exposure to perchloroethylene. *Crit Rev Toxico*l. 2011. doi: 10.3109/10408444.2011.581649.

12. Sherlach KS, Gorka AP, Dantzler A, Roepe PD. Quantification of perchloroethylene (PCE) residues in dry cleaned fabrics. *Environmental Toxicology and Chemistr*y. 2011:n/a-n/a. doi: 10.1002/etc.665.

13. Schreiber JS, Hudnell HK, Geller AM, et al. Apartment residents' and day care workers' exposures to tetrachloroethylene and deficits in visual contrast sensitivity. *Environ Health Perspec*t. 2002;110(7):655-664.

14. McDermott MJ, Mazor KA, Shost SJ, Narang RS, Aldous KM, Storm JE. Tetrachloroethylene (PCE, perc) levels in residential dry cleaner buildings in diverse communities in new york city. *Environ Health Perspec*t. 2005;113(10):1336-1343.

15. Miller LJ, Uhler AD. Volatile halocarbons in butter: Elevated tetrachloroethylene levels in samples obtained in close proximity to dry-cleaning establishments *Bull Environ Contam Toxico*l. 1988;41(3):469-474.

16. California Air Resources Board [CARB]. Final california dry cleaning industry technical assessment report. http://www.arb.ca.gov/toxics/dryclean/finaldrycleantechreport.pdf. Updated 2006. Accessed May 20, 2011.

17. Sonnenfeld N, Hertz-Picciotto I, Kaye WE. Tetrachloroethylene in drinking water and birth outcomes at the US marine corps base at camp lejeune, north carolina *Am J Epidemio*l. 2001;154(10):902-908.

18. Agency for Toxic Substances and Disease Registry. ToxFAQs: Tetrachloroethylene. . 1997. http://www.atsdr.cdc.gov/tfacts18.pdf.

19. Institute for Research and Technical Assistance [IRTA]. Hydrocarbon technology alternatives to perchloroethylene for dry cleaning. . 2005.

20. Onasch J, Improving the Health of the Public,Workers and the Environment:Twenty Years of Toxics Use Reduction. A feasibility and cost comparison of perchloroethylene dry cleaning to professional wet cleaning: Case study of silver hanger cleaners, bellingham, massachusetts. *J Clean Pro*d. 2011;19(5):477-482.

21. Exxon Mobil Chemical Company. MSDS: DF-2000 fluid. . 2001;92842583.

22. Chevron Phillips Chemical Company LP. Material safety data sheet: ECOSOLV® dry cleaning fluid. . 2008;711230.

23. Reutman SR, LeMasters GK, Knecht EA, et al. Evidence of reproductive endocrine effects in women with occupational fuel and solvent exposures. *Environ Health Perspec*t. 2002;110(8):805-811.

24. NIOSH, ed. *Control of fire hazards in commercial dry cleaning shops using petroleum-based solvents.* CDC; 1997Hazard Controls.

25. California Air Resources Board. Dry cleaning alternative solvents: Health and environmental impacts. . 2008.

26. New cleaning solvent with related detergent and machines. *National Clothesslin*e. 2010.

27. Kruessler USA. What landlords need to know about SystemK4. . 2010.

28. NYSDEC, Division of Air Resources. Draft memorandum: Toxic contaminant review of the butylal dry-cleanin solvent (currently marketed under the trade name SolvonK4 by kruessler, inc.). . 2011.

29. Famurew R, Chapman A, Balogh C, Perry W. Alternative dry cleaner sampling project: Final report. *LHWMP, King Count*y. unpublished.

30. Johanson CA. *Characterizing the health and safety needs of the dry cleaning industry in king county.* [Master of Science]. University of Washington; 2011.

Appendix A

Standard Operating Procedure: **Drycleaner product sample collection**

Revised: 15 December 2011

Preparation:

Print out latest versions of “Sample_tracking.xlsx” and “Sample_tracking.xlsx”.

Print out maps to locations or program GPS/iPhone

Equipment:

Lab coat

Safety glasses

Nitrile gloves

Clipboard

Sample info sheets

Pen

Sharpie

Sample labels

Ziploc bags

Paper towels/pads

Sample vials- Amber glass vials from Friedman and Bruya

Pipettes- disposable glass 25ml

Scissors

Questionnaire

Cooler

Ice packs

5-gallon bucket containing trash bags

Camera

Wheeled cart (if room in vehicle)

Safety:

1. See Health and Safety Plan

Procedure:

1. Put on all PPE
2. Label sample vials
3. Place vials on a horizontal surface, protected with paper towels or lab bench lining material. Use the wheeled cart if sufficient room in the vehicle and in the shop. Otherwise use a spotting table or other relatively clean surface.
4. Collect liquid samples with pipette
    a. When sampling viscous or dense materials, use paper towels to capture drips from the pipette and clean any spillage
    b. Fill vials by ejecting the liquid from the pipette gently down the side of the vial to reduce introduction of air into the sample
    c. Fill the sample vial to the very top- reduce volume of air in vial as much as possible
        i. Spilling a small amount of liquid when the cap is screwed on is acceptable
    d. Use a new pipette for each sample
    e. Firmly screw on the vial caps and place in a Ziploc bag
    f. Clean any residual on outside of vial with a paper towel
    g. Place the samples in the cooler with the ice
    h. Handle with care- avoid shaking/turning upside down, etc.
5. Place all waste materials in the trash bag located in the 5-gallon bucket.
6. Administer questionnaire to manager/owner

Labeling:

1. Label each sample vial individually with the date, number assigned to the drycleaner, and sample number
    a. XXMMDDYY_##_PSS
        i. XX= initials
        ii. ##= drycleaner site designation number
        iii. P= product
        iv. SS= Sample number
2. Label the Ziploc bag with initials and the date

Analysis

3. VOCs-
    a. Volume: 1-2ml

2. SVOCs

    b. Volume: 1-2ml

3. Metals

    c. Volume: 5ml

Appendix B

DRY CLEANING SAMPLING QUESTIONNAIRE

Interview date: __________ Interviewed by: _____________________

Business name / City: _______________________________________

Interviewee name: _______________ Job position: ____________________

Manufacturer of machine: _____________ Model of machine: ____________

What is the capacity of the machine? ___________ pounds

How many loads do you run per week? ________ per week

How long has there been a dry cleaner at this location? __________ years

How old is the dry cleaning machine? ____________ years

Did you buy the machine new? Y / N

How long have you had the machine? ______________ years

What solvent does the machine currently use? ____________________________

Was the machine ever converted from being a PERC machine? Y / N

Have you ever used any products (dry cleaning solvent or spot cleaners) that contain PERC or TCE with this machine? Y / N

Was there ever a PERC machine at this location? Y / N

If yes, how long ago? __________ years

Does your machine have a still? Y / N

If yes:

Who cleans out the still bottoms? ________________________________

How often do you clean out the still bottoms? ___________times per month

What day and time are the still bottoms cleaned out?__________________

How do you dispose of the still bottoms? __________________________

If no:

Does your machine have "tonsil" filters? Y / N

How often do you dispose of the tonsil filters? _______________ times per month

How do you dispose of the tonsil filters? _________________________________

How often do you dispose of the separator water? _________________________

How do you dispose of the separator water? _____________________________

What type of filters do you used in your machine? ______________________

Are you an EnviroStar? Y / N

If yes, how many stars? ______________

Approximately how much of the cleaning is from repeat customers? _________%

Approximately what percentage of items requires spot cleaning? ____________%

What spot cleaners do you have at the location? [see Product Sheet to record data]

Which do you use the most?

1. ________________________________

2. ________________________________

Appendix C

Standard Operating Procedure: **Separator Water sample collection**

Revised: 3 October 2011

Equipment:

Lab coat

Safety glasses

Nitrile gloves

Clipboard

Sample info sheets

Pen

Sharpie

Labels

Ziploc bags

Paper towels/pads

Sampling kit from Friedman and Bruya:

Sample vials-

3- 40 ml VOA vials

3- 500 ml amber bottles for SVOC and Halogen analysis

250ml HDPE bottles- for metals analysis, with HNO_3 for preservation

Glass funnel

Pipettes- disposable glass 25ml

Scissors

Questionnaire

Cooler

Ice packs

Stainless steel pitcher

Safety:

1. See Health and Safety Plan

Procedure:

7. Obtain sampling kit from Friedman and Bruya
8. Put on PPE
9. Label sample vials
10. Collect liquid samples with glass pipette
    a. Fill vials by ejecting the liquid from the pipette gently down the side of the vial to reduce introduction of air into the sample
    b. Fill the sample vial to the very top- reduce volume of air in vial as much as possible
        i. Spilling a small amount of liquid when the cap is screwed on is acceptable
    c. Use a new pipette for each sample
11. Collect large volume (250-500 ml) samples with the stainless steel pitcher and glass funnel
    a. HDPE bottles do not have to be completely full
12. Firmly screw on the sample vial caps and place in a Ziploc bag
13. Place the samples in the cooler with the ice
14. Handle with care- avoid shaking/turning upside down, etc.
15. Questions for manager/owner

Labeling:

4. Label each sample vial individually with the date, number assigned to the drycleaner, and sample number
    a. XXMMDDYY_##_WSS
        i. XX= initials
        ii. ##= drycleaner site designation number
        iii. W= separator water
        iv. SS= Sample number
5. Label the Ziploc bag with initials and the date

Appendix D

Standard Operating Procedure: **Still Bottoms sample collection**

Revised: 3 October 2011

Equipment:

Lab coat

Safety glasses

Nitrile gloves

Clipboard

Sample info sheets

Pen

Sharpie

Labels

Ziploc bags

Paper towels/pads

Sampling kit from Friedman and Bruya:

2- 4 oz widemouth jars

For OnSite Environment: 1-4 oz jar

For KC lab: 1-4oz jar

Scissors

Questionnaire

Cooler

Ice packs

Stainless steel ladle

Stainless steel pitcher

Safety:

1. See Health and Safety Plan

Procedure:

16. Obtain sampling kit from Friedman and Bruya
17. Put on all PPE
18. Label sample jars
19. Collect 1-3 oz samples of still bottoms with the stainless steel ladle and pour into pitcher
    a. Still Bottoms are not homogenous- stir the sample or pour back an forth between two vessels to ensure that all jars have similar consistency.
20. Firmly screw on the sample jar caps and place in a Ziploc bag
21. Place the samples in the cooler with the ice
22. Handle with care- avoid shaking/turning upside down, etc.
23. Wipe the dipper with a paper towel and place in the container with other waste.

Labeling:

6. Label each sample jar individually with the date, number assigned to the drycleaner, and sample number
    a. XXMMDDYY_##_BSS
        i. XX= initials
        ii. ##= drycleaner site designation number
        iii. B= still bottoms
        iv. SS= Sample number
7. Label the Ziploc bag with initials and the date

Appendix E

Drycleaner Product and Waste Sampling

Health and Safety Plan

Revised: December 15, 2011

Steve Whittaker &Jessie Taylor

PPE:

- Nitrile gloves
- Tyvek lab coat
- Long pants
- Safety glasses
- Closed-toe shoes

Procedures:

- Inform Steve, Terri Jenkins-Mclean and Alice Chapman of sampling locations and safe return via phone or email
- Notify manager/owner of drycleaner of arrival
- Walk away from business if a hostile reaction
- PPE shall be worn during sampling
- Wash hands after sampling
- Avoid spilling while sampling and clean area thoroughly before leaving – use paper towels to capture drips and wipe up any material immediately
- Place all waste, including used pipettes and paper towels/pads, in a trash bag placed in a 5-gal. bucket. Place waste bag in the cooler with the samples to be disposed of as solid waste.

General Safety considerations:

- Driving – print maps or use GPS so locations are known before leaving. Drive defensively. Call 911 if involved in an accident, then Terri Jenkins-Mclean at 206-941-4358 or Charles Wu at 206-484-1960.
- Slip hazards: liquid spills on floor
- Low rails and carts for transporting clothes
- Heat stress near boilers
- Cold temperatures when outdoors