



Final Report

Characterizing Alternative Solvent Dry Cleaning Processes

Stephen G. Whittaker, PhD

Local Hazardous Waste Management Program in King County
Research & Evaluation Services Team

Jessie Taylor, MS

Local Hazardous Waste Management Program in King County
Research & Evaluation Services Team and
University of Washington, Department of Environmental and
Occupational Health Sciences

Linda M. Van Hooser, MS

Local Hazardous Waste Management Program in King County
Business Field Services Team

This report was prepared by the Local Hazardous Waste Management Program in King County, Washington, a coalition of local governments. Our customers are residents, businesses and institutions with small quantities of hazardous wastes. The Program's mission is: to protect and enhance public health and environmental quality in King County by reducing the threat posed by the **production, use, storage** and **disposal** of hazardous materials.

For more information or to order additional copies of this report contact:

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Public Health 
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Management Program in King County**

401 Fifth Ave., Suite 1100

Seattle, WA 98104

Voice 206-263-8899 TTY Relay: 711

Fax 206-296-0189

www.lhwmp.org

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ACRONYMS AND ABBREVIATIONS

| | |
|---------|---|
| ATSDR | Agency for Toxic Substances Disease Registry |
| CAS | Chemical Abstract Service |
| DW | Dangerous Waste |
| EHW | Extremely Hazardous Waste |
| EPA | United States Environmental Protection Agency |
| Ecology | Washington State Department of Ecology |
| EIM | Environmental Information Management |
| EOX | Extractable Organic Halogens |
| °F | Degrees Fahrenheit |
| FOG | Fats, Oils & Grease |
| HDPE | High-density Polyethylene |
| HOCs | Halogenated Organic Compounds |
| KCEL | King County Environmental Laboratory |
| KCIW | King County Industrial Waste Program |
| L | Liter |
| LHWMP | Local Hazardous Waste Management Program in King County |
| mg/Kg | Milligrams per kilogram |
| mg/L | Milligrams per liter |
| MRL | Method Reporting Limit |
| MSDS | Material Safety Data Sheet |
| NFPA | National Fire Protection Association |
| NIOSH | National Institute for Occupational Safety and Health |
| OSHA | Occupational Safety and Health Administration |
| PAH | Polycyclic aromatic hydrocarbon |
| PCB | Polychlorinated biphenyl |
| PDF | Portable Document Format |
| PERC | Perchloroethylene |
| ppb | Parts per billion |
| ppm | Parts per million |
| RCRA | Resource Conservation and Recovery Act |
| SVOC | Semi-volatile Organic Compound |
| TCE | Trichloroethylene |
| TIC | Tentatively Identified Compound |
| TOX | Total Organic Halogens |
| µg/L | Micrograms per liter |
| VOA | Volatile Organic Analysis |
| VOC | Volatile Organic Compound |
| WTD | Wastewater Treatment Division |

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EXECUTIVE SUMMARY

In the last decade, many dry cleaners have transitioned from using perchloroethylene (“PERC”) as their cleaning solvent to several alternatives. In King County, Washington, the most frequently used alternative solvent is a hydrotreated petroleum hydrocarbon, referred to simply as “hydrocarbon” in the industry. However, another dry cleaning solvent, Solvon K4™, has recently emerged in King County and elsewhere in the United States. This solvent is part of a relatively new dry cleaning system developed in Europe, known as System K4™.

Relatively little toxicological information is available for these alternative solvents and the waste streams generated by these new dry cleaning processes have not been adequately characterized. In addition, the chemical composition of other process chemicals used in these new technologies has not been critically evaluated.

The objectives of this study were to: 1) determine the frequency of use of process chemicals and gather other operational information, 2) chemically-characterize the process chemicals, 3) characterize the still bottoms and separator water wastes according to dangerous waste and wastewater discharge regulations, and 4) identify any linkages between work practices, process chemicals, and the chemical composition of the waste streams. The study focused on 16 local businesses that used either hydrocarbon (13 shops) or Solvon K4™ (three shops). Data were gathered via a questionnaire and an extensive product- and waste- sampling campaign. This study was conducted between November 2011 and August 2012.

Many hydrocarbon dry cleaners used process chemicals that were originally designed for use in PERC operations. Three hydrocarbon businesses used a spot cleaner comprised of 100% trichloroethylene (TCE). In contrast, the System K4™ businesses used only products provided by the manufacturer, which did not contain chlorinated hydrocarbons.

Washington state’s dangerous waste regulations require that generators chemically characterize their waste streams before selecting a treatment or disposal method. However, very few of the shops had characterized their still bottoms or separator water. Separator water did not typically designate as dangerous waste or exceed waste water discharge thresholds. The single sample that failed regulatory benchmarks was visually distinct from all other samples and contained 13,000 µg/L TCE. This chlorinated hydrocarbon likely originated from a spot cleaner used at this hydrocarbon shop. In contrast, still bottoms from both hydrocarbon and System K4™ machines designated as dangerous waste.

We conclude that efforts should be directed towards replacing hazardous spot cleaning chemicals with safer alternatives and ensuring that wastes are disposed of appropriately. This could be achieved via regulatory intervention, education and outreach, and technical and financial assistance. However, it is vitally important that any intervention account for the unique financial and demographic characteristics of this industry.

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INTRODUCTION

Dry Cleaning History

Kerosene and other solvents have been used to dry clean fabrics since the mid-19th century. Stoddard solvent was introduced in 1925, but this petroleum distillate's flammability (flash point: 104 °F) prompted the industry to switch to perchloroethylene (PERC) in the 1960s. PERC (also known as tetrachloroethylene or "PCE") is essentially non-flammable and this chlorinated hydrocarbon is still regarded as one of the most efficient dry cleaning solvents.⁽¹⁾

In 2010, the Local Hazardous Waste Management Program in King County (LHWMP) conducted a survey of the dry cleaning industry, which revealed that PERC is still the most commonly-used solvent in King County.⁽²⁾ Sixty-nine percent of survey respondents reported that they used PERC, although this is substantially fewer than was observed during LHWMP field activities conducted in 1998-2000.⁽³⁾ Alternative solvents have been adopted over the last decade because of increased awareness of the consequences of PERC exposure to workers and releases to the environment. The King County survey revealed that the most common alternative solvent is "hydrocarbon", which was used in 21 percent of shops. Note that the term "hydrocarbon" is currently used to describe modern non-chlorinated solvents with relatively high flash points (see below). Subsequent to the survey, a new dry cleaning technology appeared in the United States, called "System K4TM". As of April 2013, four System K4TM dry cleaners are operating in King County.

Alternative Dry Cleaning Solvents

The solvent alternatives to PERC each have unique physico-chemical properties, cleaning abilities, health effects, and environmental impacts. Because of their dominance or recent emergence in the King County dry cleaning market, the following section will focus on the modern hydrocarbon solvents and Solvon K4TM. However, other solvents that are used less frequently include water (i.e., wet-cleaning), glycol ethers, liquid silicone, 1-bromopropane, and liquid carbon dioxide.⁽⁴⁾

Hydrocarbons

Modern petroleum-based "hydrocarbon" dry cleaning solvents include Shell HydrocleneTM, ExxonMobil DF2000TM, and Chevron-Phillips EcoSolvTM.⁽⁴⁾ The most frequently used hydrocarbon solvent in King County is DF2000TM, which is a hydrotreated aliphatic hydrocarbon. The Chemical Abstract Service (CAS) number for DF2000TM is 64742-48-9 and the flash point is 147 °F.⁽⁴⁾⁽⁵⁾

Although the flash points of these modern hydrocarbons are relatively high, they are more flammable than PERC and are generally classified as National Fire Protection Association (NFPA) Class IIIA solvents (i.e., flash points at or above 140 °F and below 200 °F). Consequently, businesses that replace their PERC machines with hydrocarbon

systems may be required to make structural modifications to their buildings, including installing fire suppression systems.

While the health effects associated with PERC have been well-characterized,⁽⁶⁾ relatively little is known about the modern hydrocarbon solvents. The CAS number associated with DF2000TM is typically assigned to “Naphtha, Hydrotreated Heavy (Heavy Aromatic Distillates)” or “Naphtha (petroleum), hydrotreated heavy; low boiling point hydrogen-treated naphtha”. According to the United States Environmental Protection Agency (EPA), the composition and physical properties of this substance can vary considerably, depending on the raw material and the production processes.⁽⁷⁾ Consequently, the toxicological and environmental data associated with substances identified as CAS number 64742-48-9 may not necessarily align with the properties of DF2000TM.

According to the Material Safety Data Sheets (MSDSs) for these hydrocarbon dry cleaning solvents, acute exposure can precipitate skin and eye irritation as well as central nervous system effects, such as drowsiness and dizziness.^(5,8) Exposure to alkanes found in jet fuel with similar molecular weight may have adverse effects on the endocrine system.⁽⁹⁾ As volatile organic compounds (VOCs), these solvents may contribute to ozone formation.⁽¹⁰⁾ Although these non-chlorinated hydrocarbons are likely safer alternatives to PERC, uncertainties associated with their environmental and human health effects are preventing unreserved recommendation by government agencies and programs.

System K4TM

Developed in Germany by Kreussler GmbH, System K4TM has recently been introduced to the United States. The dry cleaning solvent, Solvon K4TM, is composed primarily of butylal, which is a diether acetal. Synonyms for butylal include dibutoxymethane, 1-(butoxymethoxy)butane, and formaldehyde dibutyl acetal. The CAS number is 2568-90-3.⁽¹¹⁾

According to Kreussler GmbH, n-butyl alcohol (1-butanol) and formaldehyde are present in Solvon K4TM at <0.5% and <0.05%, respectively.⁽¹¹⁾ While butylal is reportedly stable at pHs between 4 and 14, the solvent may theoretically hydrolyze in the dry cleaning machine to create formaldehyde 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.⁽¹¹⁾ However, the long-term health effects of butylal are also not well characterized. While the solvent is slightly biodegradable, there is also little published information concerning its environmental fate and transport.⁽¹¹⁾⁽¹²⁾

With a flash point of 143.6 °F,⁽¹¹⁾ Solvon K4TM is also regarded as a NFPA Class IIIA solvent.

The Dry Cleaning Process

The dry cleaning process is similar for PERC and the alternative solvents. Exceptions to this are liquid carbon dioxide, which cleans in a high pressure system, and wet cleaning, which uses water.

Cleaning procedures

Prior to being placed in the dry cleaning machine, stained fabrics may be pre-cleaned or “pre-spotted” with spot treatment products. These products are formulated according to the type of stains to be removed and are classified as either “wet-side” or “dry-side” agents. Wet-side spotting agents are generally aqueous products that are used to remove water soluble stains from clothing. Dry-side agents are generally based on non-aqueous solvents and alcohols, including PERC, TCE, methylene chloride, amyl acetate, acetone, ethanol, methanol, isopropyl alcohol, and petroleum solvents. These products are used to remove stains comprised of oils, fats, waxes, grease, cosmetics, paints, and plastics.⁽⁴⁾

Following spot treatment, the fabrics are placed in the dry cleaning machine where they are agitated with liquid solvent and a detergent. Additives may also be introduced to the machine during cleaning. The most frequently used additive is “sizing”, which may be injected into the machine during the cleaning process. Sizing is typically comprised of plastic-based hydrocarbon resins in a petroleum solvent carrier, and is used to restore shape, body, and texture to fabrics.⁽⁴⁾

When the cleaning cycle has completed, the solvent is drained and the fabrics placed under vacuum, heated, and tumbled to remove any remaining solvent.

Fabrics that are still stained or soiled after dry cleaning may be spot-cleaned using the same products used in pre-cleaning.

Waste stream generation

In modern dry cleaning machines, the heated solvent vapors generated during the drying cycle pass 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 generates “separator water” and “still bottoms”. An alternative process is available that employs a calcium bentonite/diatomaceous earth-based “tonsil” filtration system,⁽¹³⁾ rather than distillation. Although tonsil filtration was previously observed in a single hydrocarbon cleaner in King County, this shop is no longer operating.

The still bottoms are distilled or “cooked” before disposal to maximize solvent recovery and minimize waste volume. After the machine has cooled (usually overnight), the operator scrapes the still bottoms into a waste container using a specially-designed rake. Depending on the volume of dry cleaning processed in a shop, still bottoms are typically removed once every 1-2 weeks.

The separator water is either periodically drained from the machine’s storage tank or allowed to continuously fill an external container (typically a 5-gallon plastic bucket).

A preliminary study conducted by LHWMP in 2006 identified PERC contamination of the separator water and still bottoms from hydrocarbon solvent dry cleaners (unpublished data). Of 15 dry cleaning establishments using DF2000™, 10 had separator water PERC concentrations greater than 1 ppb and 11 of the still bottoms samples had PERC concentrations greater than 1 ppb. A small study of dry cleaners using the hydrocarbon solvent in California also found PERC in the separator water and still bottoms.⁽¹⁴⁾

Some shops treat their separator water in an attempt to reduce the concentration of hazardous chemicals prior to disposal. In PERC operations, charcoal filtration is relatively common, and Washington state's regulations allow evaporation of the filtered liquid waste to the outdoors.⁽¹⁵⁾ However, the efficacy of this treatment method for separator water derived from hydrocarbon and System K4™ machines has not been critically evaluated.

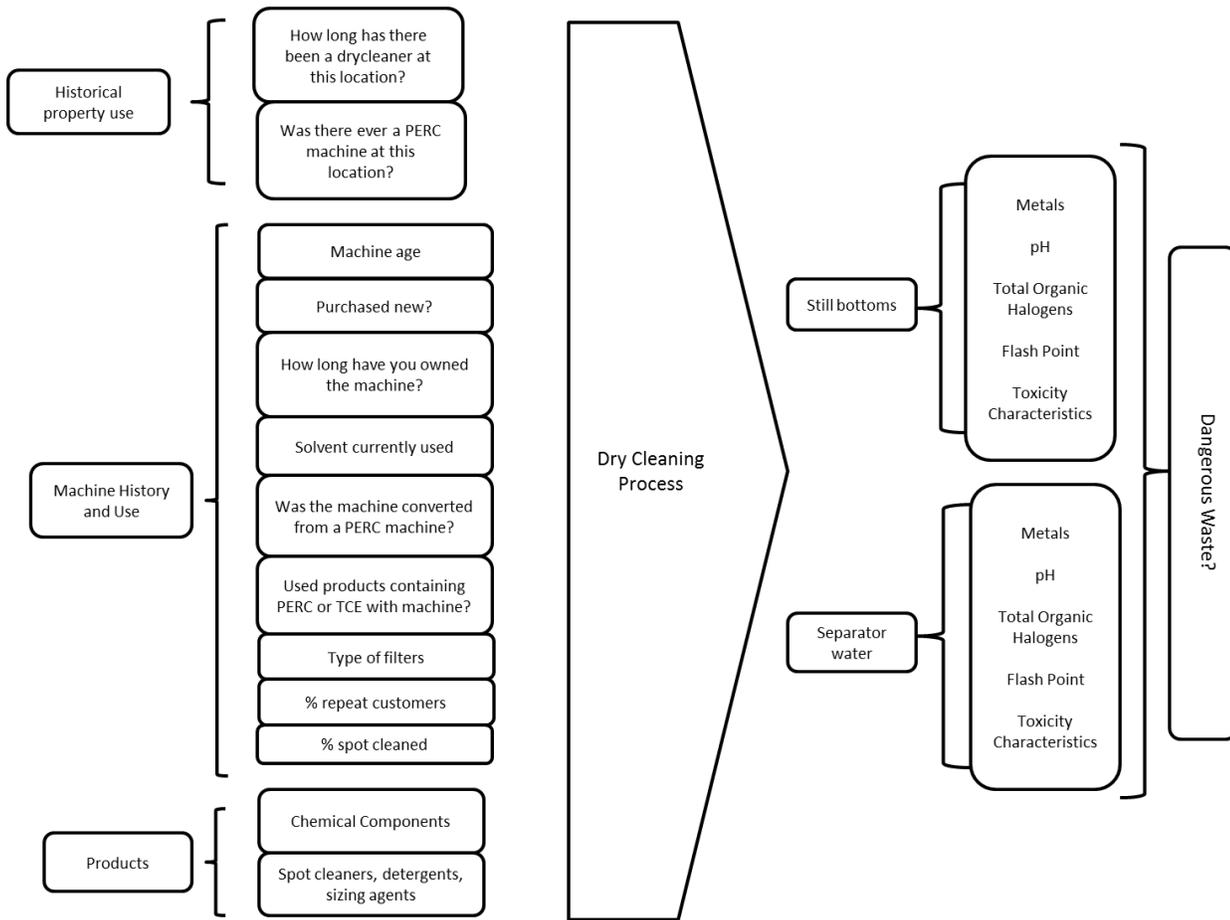
Waste Characterization and Disposal

Multiple factors contribute to the chemical composition of the waste streams (see Figure 1). Contributions may be expected from the dry cleaning solvent, detergent, sizing agent, spot treatment chemicals, residues removed from fabrics (stains, cosmetics, personal care products, body oils, etc.), and residual solvent from previous cleanings. The composition may also be influenced by machine characteristics such as age and usage history. Because PERC is such a persistent environmental contaminant, the current or historical presence of a PERC machine on the premises may also affect the PERC content of the waste.

Dangerous waste designation

The term “dangerous waste” encompasses federally-regulated “hazardous wastes” and those identified as dangerous waste only by Washington state's regulations. Washington further divides all federal and state-only dangerous wastes into two categories: DW (Dangerous Waste) and EHW (Extremely Hazardous Waste). Several factors can cause a waste to “designate” as dangerous waste. The definition of hazardous waste, based on the Resource Conservation and Recovery Act (RCRA), is presented in Title 40 of the Code of Federal Regulations (CFR), Part 261. Federally-regulated hazardous wastes include “listed wastes” because they appear on one of four EPA lists, or designate because they exhibit one of four characteristics: ignitability, corrosivity, reactivity, or toxicity. In Washington state, generators must follow these federal rules and additional state-only rules that are specified in Chapter 173-303 WAC (173-303-070 to 100) of the dangerous waste regulations. Washington state's dangerous waste regulations are more stringent than the federal hazardous waste rules, and include one listed state source, in addition to “state-only” toxicity and persistence criteria. A summary of federal and state-only waste designation categories is presented in Table 1.

Figure 1. Factors contributing to designation of dry cleaning waste



Generators must determine whether their wastes designate based on all the designation categories. If the waste designates as dangerous waste, it is assigned an appropriate “waste code” and identified as either DW or EHW. Sufficient PERC is present in the waste streams generated by PERC dry cleaning machines that untreated waste always designates as dangerous waste. As the local regulatory authority, the Washington State Department of Ecology (Ecology) allows for treatment of separator water from PERC dry cleaning operations to reduce the concentration of hazardous chemicals (including PERC) below regulatory limits.⁽¹⁵⁾ Otherwise, PERC-containing wastes must be managed as hazardous waste.

Although the spot cleaners used in hydrocarbon and Solvon K4™ shops may contain F-listed solvents (such as trichloroethylene and methylene chloride), EPA has determined that incidental use of listed solvents for similar situations does not trigger F-listing of the resulting waste streams (personal communication, Robert Rieck, Washington State Department of Ecology, March 26, 2013).

| Table 1. Waste designation categories | |
|--|--|
| Category | Definition |
| Listed waste* | <ul style="list-style-type: none"> • F list: process-specific wastes (any industry) • K list: industry specific process wastes • P list: discarded chemical products • U list: discarded chemical products |
| Listed waste** | <ul style="list-style-type: none"> • State sources: certain PCB wastes |
| Characteristic waste* | <ul style="list-style-type: none"> • Ignitability • Corrosivity • Reactivity • Toxicity |
| Toxicity criteria** | <ul style="list-style-type: none"> • Book designation based on equivalent concentration calculation • Bioassay designation |
| Persistence criteria** | Applies to chemicals that do not rapidly degrade in the environment: <ul style="list-style-type: none"> • Halogenated organic compounds (HOCs) • Polycyclic aromatic hydrocarbons (PAHs) |
| * Federal regulation ** Washington state regulation | |

As shown in Figure 1, several factors may contribute to the designation of still bottoms and separator water as dangerous waste. In some cases, the concentration of TCE or PERC in the waste exceeds the Federal toxicity characteristic thresholds and may cause the waste to designate according to WAC 173-303-090(8). Subsection (c) lists the dangerous waste threshold concentrations of various metals and compounds in waste. The dangerous waste threshold for TCE is 0.5 ppm and for PERC is 0.7 ppm. Other relevant dangerous waste thresholds are shown in Table 2.

| Table 2. Dangerous waste designation thresholds for select endpoints | | | | | | |
|--|--------------|--------------|---------------|----------------------|-----------------------|-------------------------|
| Endpoint | HOCs* | TCE** | PERC** | Corrosivity** | Ignitability** | Fish toxicity*** |
| Threshold | 100 ppm | 0.5 mg/L | 0.7 mg/L | pH ≤2 or ≥12.5 | Flash point <140 °F | ≤100 mg/L |
| * Washington state persistence criteria ** Federal characteristic waste *** Washington state toxicity criteria | | | | | | |

King County Industrial Waste discharge limits

Discharge of industrial wastewater to the King County sewer system is regulated by the King County Industrial Waste Program (KCIW).⁽¹⁶⁾ KCIW sets numerical concentration limits to prevent businesses from discharging substances that can degrade the wastewater treatment process, harm workers or facilities, or impact water quality. The discharge limits for Fats Oils & Grease (FOG) and organic chemicals apply to separator water generated by King County dry cleaners located within the King County Wastewater Treatment Division (WTD) service area. Note that the WTD service area excludes the cities of Burien, SeaTac, Normandy Park, Des Moines, and Federal Way.

The regulatory limit for non-polar FOG (i.e., of petroleum or mineral origin) is 100 mg/L of discharged wastewater.⁽¹⁷⁾

KCIW has also developed screening levels for several VOCs that may be present in separator water, including PERC (0.24 mg/L) and TCE (0.5 mg/L).⁽¹⁸⁾ Note that the KCIW threshold for PERC (0.24 mg/L) is lower than the dangerous waste toxicity characteristic threshold (0.7 mg/L).

If the dry cleaner is connected to an on-site septic system, the business may not discharge separator water, even when KCIW's discharge limits are not exceeded.

Current Study

Recognizing the lack of information about process chemicals and the wastes generated by alternative solvent dry cleaning operations, this study involved administering a questionnaire and conducting an extensive product- and waste- sampling campaign to gather information about:

1. The frequency of use of process chemicals and other operational details,
2. The chemical characteristics of the process chemicals,
3. The composition of the still bottoms and separator water wastes, with reference to dangerous waste and wastewater discharge regulations, and
4. Linkages between work practices, process chemicals, and the chemical composition of the waste streams.

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METHODS

Business Recruitment

Recruitment of businesses for the study commenced in November 2011 and continued through July 2012. Participation in the study was voluntary. Most participants had previous interactions with LHWMP because of enrollment in the EnviroStars program⁽¹⁹⁾ or previous field visits by LHWMP's Business Field Services team. Two businesses were recruited with the assistance of a local dry cleaning equipment vendor. The study included 16 shops located in King County that used alternative solvent dry cleaning machines. Of these, 13 used hydrocarbon (DF2000TM) and three used Solvon K4TM. Initial contact was made with the businesses owner or manager via telephone. The purpose of the study was explained and arrangements were made to conduct the initial site visit.

Questionnaire Administration and Product Sampling

Questionnaires were administered and sampling was conducted between December 2011 and August 2012. At the initial site visit, contact was made either with the business owner/manager or an employee who had previously been designated as the point-of-contact. The purpose of the study was described and the interviewee was provided with the opportunity to ask questions.

The questionnaire was then administered verbally and covered the following topics: establishment history, machine specifications and history, waste disposal practices, fraction of repeat customers, and product usage. The questions were derived from a survey instrument that had been administered previously to dry cleaners.⁽²⁾ Additional questions were developed in cooperation with dry cleaning business owners at preliminary field visits. The questionnaire is presented in Appendix A.

An inventory was conducted of all products used in the dry cleaning operation, including the solvent used, spot cleaning chemicals, detergents, and sizing agents. Samples were collected whenever the product was first observed at a dry cleaner (resource limitations prevented sampling and analysis of the same product when it was found at subsequent dry cleaners). Samples of spot cleaners were collected only if they were used for "pre-spotting" (i.e., used before placing the fabrics in the dry cleaning machine, rather than for "finishing" cleaned fabrics).

Product samples were collected from original product containers, and the operator was asked to verify that the sampled container contained the original product. Customized spotting mixtures (i.e., containing multiple products) were sampled after receiving a description of their approximate composition from the operator.

The Product Sample data collection form is presented in Appendix B and the Standard Operating Procedure (SOP) for product sampling is presented in Appendix C. Sample collection was conducted using secondary containment to prevent spillage.

Approximately 12 ml of product sample was collected using a disposable 25 ml serological pipette equipped with a pipette bulb. The sample was deposited into a pre-labeled 15 ml-capacity screw-capped (with PTFE liner) amber glass vial (Supelco Analytical #27003).

Product samples were placed on ice in a cooler, a chain of custody form was completed, and then delivered to the analytical laboratory.

MSDSs for all products were retrieved, typically from the Internet and occasionally from the manufacturer or supplier.

Waste Sample Collection

The return visit to collect waste samples was scheduled at the conclusion of the initial site visit. Waste samples were collected when the operator typically removed the still bottoms from the machine. This process usually took place before the shop started production for the day, generally before 7 AM. Separator water samples were typically collected on the same day, after the still bottoms had been sampled. The goal was to minimize disruption of the dry cleaning production process and collect samples that were representative of the business's waste stream. Waste sample collection was also conducted using secondary containment.

The original study design included sampling wastes from every dry cleaner on at least two separate occasions, in order to evaluate variability in chemical composition. However, this approach was modified because of resource constraints and the finding that the chemical composition of these waste streams was generally consistent between shops. More extensive sampling was conducted at Shop #01, which was the first to adopt System K4TM in King County. This business was sampled on multiple occasions to ensure adequate characterization of this new process.

After collection, all samples were placed on ice in a cooler, a chain of custody form was completed, and the samples were delivered to the appropriate laboratory for analysis.

The SOPs for sampling still bottoms and separator water are presented in Appendix D and E, respectively. The Waste Sample data collection form is presented in Appendix F.

Still bottom sampling

The machine operator was instructed to open the still and allow the contents to flow into the waste receptacle (typically a plastic bag that lined a collection tray located beneath the still door). As the waste began to flow, a sample of still bottoms was collected from the lip of the still opening using a 32 oz. capacity stainless steel pitcher (Polar Ware Company #T1063). This initial material was typically liquid, with semi-solid or more viscous material remaining in the still. To ensure that a representative sample was collected, the operator was instructed to scrape the remaining material to the front of the still, where additional sample was collected with a 4 oz. capacity stainless steel ladle (Polar Ware Company #T1604). This material was then deposited in the pitcher and mixed with the previously-collected liquid still bottoms by gently stirring with the ladle. The mixed sample was then distributed into pre-labeled 8 oz. capacity I-CHEMTM jars

(I-CHEM #220-0250). One I-CHEM™ jar was reserved for chemical analysis of the still bottoms and a second was occasionally collected for fish bioassay (see Table 3). No preservative was added to these samples.

| No. containers | Type of container | Analysis | Notes |
|---|-------------------|---|---|
| 1 | 8 oz. I-CHEM jar | TCLP* VOCs, TCLP SVOCs, TCLP metals, EOX**, pH, flash point | Full container required to conduct all analyses |
| 1 | 8 oz. I-CHEM jar | Acute static fish toxicity testing | Not collected at all shops |
| *Toxicity Characteristic Leaching Procedure **Extractable Organic Halogens | | | |

Separator water sampling

When separator water was stored in an external container, the sample was collected by dipping a stainless steel pitcher (Polar Ware Company #T1063) into the container and removing ~ 800 ml of liquid. When the separator water was contained within the machine's reservoir, the operator was asked to open the reservoir valve to allow liquid to flow into the pitcher. Sample was then distributed from the pitcher into pre-labeled containers, as described in Table 4. Because the total sample volume needed for analysis exceeded the capacity of a single pitcher, all sample containers were initially partially filled as evenly as possible. Additional separator water was then collected in the pitcher, and its contents used to fill the sample containers.

| No. containers | Type of container | Preservative | Analysis | Notes |
|--|---------------------------|---------------|------------------------------------|---|
| 3 | 40 ml VOA* vial | None | VOCs | Filled via 25 ml serological pipette |
| 3 | 500 ml amber glass bottle | None | SVOCs, TOX**, pH, flash point | Filled by decanting from pitcher into container via a glass filter funnel |
| 1 | 500 ml amber glass bottle | Sulfuric acid | Non-polar FOG | Filled by decanting from pitcher into container via a glass filter funnel |
| 1 | 500 ml HDPE*** bottle | Nitric acid | Metals | Filled by decanting from pitcher into container via a glass filter funnel |
| 1 | 8 oz. I-CHEM jar | None | Acute static fish toxicity testing | Filled by decanting from pitcher directly into container. Not collected at all shops |
| *Volatile Organic Analysis **Total Organic Halogens ***High-density polyethylene | | | | |

Two dry cleaners (Shop #01 and #06) treated their separator water with a Zerowaste™ filtration device, which is comprised of a particulate filter and two carbon filters.⁽²⁰⁾ At these two shops, samples of both unfiltered and filtered separator water were collected to evaluate the efficacy of the treatment unit. The separator water collected from all other shops was untreated/unfiltered.

Product Analysis

The test methods used to analyze the product samples are presented in Table 5. Analytical services were provided by Friedman & Bruya, Inc. (Seattle, WA).

| Table 5. Product test methods | |
|---|------------------|
| Analysis | Method |
| Volatile Organic Analysis (VOA), including TICs | EPA Method 8260C |
| Semi-volatile Organic Analysis (SVOA), including TICs | EPA Method 8270D |
| Total metals | EPA Method 200.8 |
| Total mercury | EPA Method 1631E |

Waste Analysis

The methods used to analyze the waste streams were developed after extensive discussions with chemists associated with Ecology, KCIW, the King County Environmental Laboratory (KCEL, Seattle, WA), OnSite Environmental, Inc. (Redmond, WA), and Friedman & Bruya, Inc. Pilot samples were analyzed before the final test methods were selected. Procedures conformed to Ecology’s *Chemical Test Methods for Designating Dangerous Waste*⁽²¹⁾ and *Biological Testing Methods for the Designation of Dangerous Waste*.⁽²²⁾

Still bottom analysis

The original intent was to conduct a “totals” analysis on virgin still bottom samples for comparison to dangerous waste thresholds. However, the resulting Method Reporting Limits (MRLs) for the VOC and SVOC analyses exceeded the dangerous waste thresholds by an order of magnitude or more. Note that the MRL is defined as the lowest amount of an analyte in a sample that can be quantitatively determined with stated, acceptable precision and accuracy under stated analytical conditions (i.e., the lower limit of quantitation). The relatively high MRLs associated with these samples reflects the chemical complexity of the still bottoms, which are viscous or semi-solid with a “greasy” consistency. Consequently, the analytical laboratory was obligated to dilute the samples to avoid damaging their instruments, resulting in elevated MRLs. Therefore, analyses for VOCs, SVOCs, and metals were performed on TCLP extracts of

the still bottom samples. Testing for pH, Extractable Organic Halogens (EOX), flash point, and fish toxicity was conducted on virgin samples (Table 6). The chemical analyses were conducted by OnSite Environmental, Inc. and fish toxicity testing was performed by KCEL.

| Table 6. Still bottom test methods | |
|--|-----------------------------|
| Analysis | Method |
| TCLP Volatile Organic Analysis (VOA), including TICs | EPA Method 1311/8260B |
| TCLP Semi-volatile Organic Analysis (SVOA), including TICs | EPA Method 1311/8270D |
| TCLP Metals | EPA Method 1311/6010B/7470A |
| pH | EPA Method 9045C |
| Flash point | ASTM D-93 |
| Extractable Organic Halogens | SW846 9023 |
| Fish toxicity | Ecology 80-12 / Part A |

Separator water analysis

Test methods for separator water are summarized in Table 7. Chemical analyses were conducted by Friedman & Bruya, Inc. and fish toxicity testing was performed by KCEL.

| Table 7. Separator water test methods | |
|---|------------------------|
| Analysis | Method |
| Volatile Organic Analysis (VOA), including TICs | EPA Method 8260C |
| Semi-volatile Organic Analysis (SVOA), including TICs | EPA Method 8270D |
| Metals (except mercury) | EPA Method 200.8 |
| Mercury | EPA Method 1631E |
| pH | EPA Method 9040C |
| Non-polar FOG | EPA Method 1664 |
| Flash point | ASTM D-93 |
| Total Organic Halogens | SW846 9020 (mod) |
| Fish toxicity | Ecology 80-12 / Part A |

Waste Designation

Waste codes were assigned to the sample data using Ecology's Washington Dangerous Waste Designation Tool⁽²³⁾ and the Dangerous Waste Regulations (173-303 WAC).⁽²⁴⁾ The assigned waste codes reflect designation according to both federal (i.e., EPA-RCRA) and Washington-specific (i.e., state-only) regulations.

KCIW Sewer Discharge Limits

The non-polar FOG concentrations in separator water were compared to the KCIW discharge limit of 100 mg/L. Concentrations of VOCs in separator water were compared to KCIW's screening levels.

Data Management and Analysis

All field data forms were electronically scanned and stored as Adobe Portable Document Format (PDF) files. Select data were key-entered into Microsoft Excel 2010TM worksheets.

The analytical laboratories provided electronic data as Microsoft ExcelTM extracts from their Environmental Information Management (EIM) databases. Summary tables and cross tabulations were prepared from these extracts in Microsoft Excel 2010TM.

The laboratories also provided case narratives and data tabulations in PDF format, which were used for data review.

Semi-quantitative analyses of questionnaire, product, and waste data were conducted in Microsoft Excel 2010TM.

Statistical analyses

Statistical analyses were conducted by The Mountain-Whisper-Light Statistics (Seattle, WA) using R (The R Foundation for Statistical Computing, Vienna, Austria), version 2.15.2. Function cor.test was used for Spearman correlation analysis. Functions chisq.test and fisher.test were used for the chi-squared test and the Fisher's Exact Test, respectively. Function prop.trend.test was used for the chi-squared test for trend. Function wilcox.test was used for the Mann-Whitney test. Functions survdiff and survfit of the package survival were used for the log-rank test and Kaplan-Meier estimates, respectively.

Comparison of chemical composition of waste streams

The chemical composition of System K4TM separator water vs. hydrocarbon separator water and System K4TM still bottoms vs. hydrocarbon still bottoms was compared using the Kaplan-Meier method.⁽²⁵⁾ This technique yields estimates of the proportion of samples expected to fall at or below any specified analyte concentration. A plot of these proportions vs. the analyte concentrations provides a visual comparison of the System K4TM vs. hydrocarbon results. Non-detected values (i.e., those that fell below MRLs) were either treated as censored at the MRL (if there was a single value for a shop) or

replaced by one-half of their respective MRLs (when there were multiple values per shop). When multiple values were available for a shop, the adjusted MRLs were averaged prior to analysis.

Due to the small sample size, the statistical significance of the differences between System K4™ and hydrocarbon concentration distributions for each analyte was determined using a permutation test. The test statistic for the permutation test was the logrank chi-squared value. This chi-squared value is commonly used to assess statistical significance when comparing Kaplan-Meier curves for larger sample sizes. For the permutation test, hydrocarbon/System K4™ labels were randomly permuted among shops. The logrank chi-squared statistic was computed for each of 4999 random permutations, and the statistical significance of the test hydrocarbon/System K4™ difference was computed as $(N+1)/5000$, where N is the number of chi-squared values falling at or above the observed chi-squared value for the original (non-permuted) data. Under the null hypothesis that the hydrocarbon and System K4™ shops have the same distribution of concentrations, the observed (non-permuted) chi-squared value would fall approximately in the middle of the 4999 chi-squared values from random permutations. Such a finding would indicate no statistically significant difference between System K4™ and hydrocarbon shops.

As an additional comparison of SystemK4™ vs. hydrocarbon waste streams, concentration bins were created for each analyte (e.g., barium concentration ≤ 0.33 mg/L vs. >0.33 mg/L). The proportion of hydrocarbon shops in each concentration bin was then calculated. The lower concentration bins would be expected to have a higher proportion of hydrocarbon shops if their waste streams contained lower analyte concentrations, and vice-versa. The bin boundaries were specified following visual inspection of concentration plots, but the designation was blinded to the hydrocarbon or System K4™ identity of all observed concentrations and non-detected values.

For this analysis of proportions, a shop with non-detected values would be placed in the lowest concentration bin if all observed concentrations and all MRLs for the facility fell into the lowest bin; otherwise the shop would be excluded from the proportion analysis for the specific analyte. (The bin boundaries for each substance or type of measurement were created to minimize exclusion of shops.) The proportion of hydrocarbon shops was compared between concentration bins using Fishers Exact Test. If there were three or more concentration bins, the chi-squared test for an increasing or decreasing trend of proportion of hydrocarbon results across bins was used. For the few analytes with no values below MRLs, all concentrations within a shop were averaged and the Mann-Whitney test was used to compare distributions between hydrocarbon and System K4™ shops. The distributions were visually displayed in a boxplot. In general the Mann-Whitney test and the boxplot were also used for an analyte which had at least one observed concentration above MRLs for each shop.

Correlations between process parameters and waste stream composition

Correlations between process parameters (i.e., work practices and process chemicals) and the chemical composition of the waste streams were evaluated only for hydrocarbon shops. Insufficient System K4™ shops were available for analysis.

The concentrations of an analyte that included values below MRLs were binned as described above. The associations between survey questions and the concentrations that were binned into two categories were analyzed using the Mann-Whitney test. The survey question was the response in this analysis and the concentration category was the predictor variable. The associations between survey questions and the concentrations binned into three (or more) categories were analyzed using the Spearman correlation coefficient. The survey variable, “machine purchase new” (yes/no) was a dichotomous variable and was analyzed with the chi-squared test for trend.

For analytes without any values below MRLs, no binning was performed and the association between concentrations and answers to survey questions was analyzed using the Spearman correlation coefficient. However, for the dichotomous survey variable, “machine purchased new”, the Mann-Whitney test was used in place of the Spearman correlation to test its association with concentrations when a substance or measurement had no values below MRLs.

RESULTS

Questionnaire Results

The questionnaire was administered at all 16 businesses; the results are summarized in Table 8.

| Table 8. Questionnaire results | | |
|--|-------------------------------------|---------------------------------------|
| Question | Hydrocarbon Shops (n=13) | System K4™ Shops (n=3) |
| Machine manufacturer | | |
| Bioclean | 1 (8%) | 0 (0%) |
| Bowe | 6 (46%) | 0 (0%) |
| Firbimatic | 1 (8%) | 0 (0%) |
| Multimatic | 0 (0%) | 2 (66%) |
| Realstar | 1 (8%) | 0 (0%) |
| Satec | 1 (8%) | 0 (0%) |
| Union | 3 (23%) | 1 (33%) |
| Machine capacity (pounds) | | |
| Range | 26 - 80 | 50 - 60 |
| Median | 40 | 50 |
| Loads run per week | | |
| Range | 8 - 24 | 25 - 40 |
| Median | 17 | 30 |
| Length of time any dry cleaner at this location (years) | | |
| Range | 5 - 63 | 4 - 40 |
| Median | 12 | 20 |
| Age of dry cleaning machine (years) | | |
| Range | 1 - 10 | <1 - 12 |
| Median | 7 | <1 |
| Dry cleaning machine purchased new | | |
| Yes | 12 (92%) | 2 (66%) |
| No | 1 (8%) | 1 (33%) |
| Length of time current dry cleaning machine owned (years) | | |
| Range | 1 - 10 | <1 |
| Median | 6 | <1 |

| Table 8. Questionnaire results | | |
|--|---------------------------------|-------------------------------|
| Question | Hydrocarbon Shops (n=13) | System K4™ Shops (n=3) |
| Machine ever converted from PERC | | |
| Yes | 0 (0%) | 0 (0%) |
| No | 13 (100%) | 3 (100%) |
| Use products containing PERC or PCE | | |
| Yes | 2 (15%) | 0 (0%) |
| No | 11 (85%) | 3 (100%) |
| Ever a PERC machine at location | | |
| Yes | 5 (38%) | 2 (66%) |
| No | 8 (62%) | 1 (33%) |
| Who cleans out still bottoms | | |
| Owner | 9 (69%) | 2 (66%) |
| Employee | 4 (31%) | 1 (33%) |
| Frequency of still bottom clean-out (times per month) | | |
| Range | 1.5 - 30 | 2 - 8 |
| Median | 4 | 4 |
| How still bottoms are disposed of | | |
| Placed in waste drum and hauled | 12 (92%) | 3 (100%) |
| Treated and placed in trash | 1 (8%) | 0 (0%) |
| How separator water is disposed of | | |
| Placed in waste drum and hauled | 9 (69%) | 2 (66%) |
| Filtered and evaporated in shop | 0 (0%) | 1 (33%) |
| Filtered and discharged to sewer | 1 (8%) | 0 (0%) |
| Evaporated in shop (no treatment) | 2 (15%) | 0 (0%) |
| Added to cooling tower water | 1 (8%) | 0 (0%) |
| EnviroStar Status | | |
| Not enrolled | 7 (54%) | 2 (66%) |
| Two-stars | 0 (0%) | 0 (0%) |
| Three-stars | 0 (0%) | 0 (0%) |
| Four-stars | 1 (8%) | 0 (0%) |
| Five-stars | 5 (38%) | 1 (33%) |
| Percentage of dry cleaning from repeat customers | | |
| Range | 10 - 95 | 80 - 90 |
| Median | 75 | 80 |
| Percentage of items requiring pre-spotting | | |
| Range | 0 - 50 | 5 - 15 |
| Median | 10 | 10 |

Four of the hydrocarbon shops and one of the System K4™ shops were potentially disposing of their separator water improperly. As stated previously, a waste stream must be chemically characterized prior to the selection of a treatment method. Consequently, it is inappropriate to filter and then discharge to the sewer without first testing the separator water. It is also inappropriate to evaporate separator water to an interior workspace (with or without treatment) or add it to a cooling tower. The hydrocarbon shop that was disposing of their still bottoms in the municipal solid waste stream had received permission to do so from the local waste characterization program. However, upon review, the analytical data was not sufficiently comprehensive to adequately characterize the waste (i.e., the still bottoms were analyzed only for TCE and PERC).

Rigorous comparison of the questionnaire results from hydrocarbon vs. System K4™ shops was not possible because only three System K4™ business owners were interviewed. The only major difference was in the duration of machine ownership; the machines in System K4™ shops were installed less than one year ago, whereas the hydrocarbon machines were installed between one and ten years ago (median of six years). These findings are consistent with the relatively recent appearance of System K4™ dry cleaning. However, one shop that recently adopted System K4™ installed a 12-year old machine that had been converted from using hydrocarbon.

Product Inventory and Analysis

Hydrocarbon shops

The products used by the 13 hydrocarbon businesses varied considerably between shops (see Table G-1, Appendix G).

Eight different types of detergent were used, although six shops used Street's Pinnacle™ detergent, manufactured by R.R. Street & Co. Inc. (Naperville, IL). Only two shops used a sizing agent.

Twenty-five different spot cleaning products were identified. The number of spot cleaners used by a single shop ranged from zero (two shops) to five (three shops). The median number of spot cleaners used by a shop was two.

Spot cleaners were manufactured by nine different companies. The most frequently represented manufacturer was R.R. Street & Co. Inc., with seven spot cleaning products; followed by Adco Products, LLC (Albany, GA), with six products; and A.L. Wilson Chemical Co., Inc. (Kearny, NJ), with five products.

The most frequently used spot cleaner was Street's Picrin™, which was used by three shops. According to the MSDS, this product is “~100%” TCE.⁽²⁶⁾

Chemical analysis was conducted on all but three of the products (see Table G-1). Only the VOC analyses yielded useful data, and the results for chlorinated hydrocarbons (i.e., PERC, TCE, and methylene chloride) were the most informative (SVOCs and metals were rarely detected above MRLs). The highest concentration of chlorinated hydrocarbon was detected in Street's Picrin™, which was confirmed to contain almost 100% TCE.

One or more chlorinated hydrocarbons were also detected in samples of the following products at concentrations exceeding MRLs (typically 200 ppm): Adco-Laidlaw Pull-Out Premium-V™, Street's MultiSpot™, and Street's Spotless™. While the MSDS for Adco-Laidlaw Pull-Out Premium-V™ listed methylene chloride as an ingredient at ">75%",⁽²⁷⁾ the Street's MSDSs referred to their products' compositions as "Trade Secret".^(28,29) These findings indicate that unused spot cleaning products may designate as U-listed wastes and should be disposed of as hazardous waste.

System K4™ shops

The products used by the three System K4™ shops were less variable than those used by the hydrocarbon businesses (see Table G-2, Appendix G). All shops used Kreussler's Clip K4™ detergent and none used a sizing agent. All three shops used Kreussler's Prenett K4™ as their spotting product. Two shops used a custom-mixture of Prenett K4™, Solvon K4™, and water as their primary spotting agent. One shop also used several Kreussler "Desprit™" products to remove specific stains.

None of the Kreussler products, including the custom-prepared mixtures, contained detectable concentrations of chlorinated hydrocarbons.

Still Bottom Analysis and Designation

Hydrocarbon shops

A total of 17 still bottom samples were collected from the 13 hydrocarbon shops. However, a full suite of analytical data is available only for 14 samples because of technical difficulties with preparing the TCLP extract in three samples. Only VOC data are available for two shops because of insufficient sample volume. Still bottoms were collected from four hydrocarbon shops on two separate occasions and the remaining shops were sampled once.

Summary data for TCLP VOCs, TCLP SVOCs, and TCLP metals are presented in Table 9 and complete sample-by-sample results are provided in Appendix H. Data are presented for any target analyte that was detected above MRLs in one or more still bottom samples collected from a hydrocarbon machine. Note that for all analytical data presented in this study, the MRLs varied by analyte and sample, reflecting issues such as matrix interference and dilution of samples by the analytical laboratory. The TIC data for still bottoms were not informative and are not presented.

The most frequently detected chemical classes were PAHs (e.g., benzo[a]anthracene and benzo[a]pyrene) and phthalates (e.g., diethylphthalate and bis(2-ethylhexyl)phthalate)). Note that the PAH concentrations detected in these samples did not exceed the thresholds for designation according to Washington state's persistence criteria.

It is noteworthy that 26 µg/L TCE was detected in a sample from Shop #02; this concentration exceeded the MRLs achieved in all other samples (i.e., 2.0 - 20 µg/L).

Chromium was the only metal detected in all samples, with a maximum concentration 0.26 mg/L in still bottoms from Shop #09. However, the chromium concentration detected in a second sample from this shop (collected 75 days later) was 0.072 mg/L.

None of the detected concentrations of any analyte in any shop exceeded waste designation thresholds for the federal toxicity characteristic.

| Table 9. Still bottom analytical data from hydrocarbon machines | | | | |
|--|-----------------------------------|----------------------------------|----------------------|--|
| Analyte | Number of Samples Analyzed | Number of Samples >MRL | Range of MRLs | Range of Concentrations >MRL |
| TCLP metals (mg/L) | | | | |
| Barium | 14 | 2 (14%) | 0.20 | 0.29 - 0.34 |
| Cadmium | 14 | 3 (21%) | 0.02 | 0.023 - 0.089 |
| Chromium | 14 | 14 (100%) | | 0.024 - 0.26 |
| Lead | 14 | 2 (14%) | 0.20 | 0.27 - 0.74 |
| TCLP SVOCs (µg/L) | | | | |
| 1-Methylnaphthalene | 14 | 1 (7%) | 1.0 - 170 | 1.0 |
| 2-Methylnaphthalene | 14 | 2 (14%) | 1.0 - 170 | 1.2 - 1.5 B |
| 4-Nitroaniline | 14 | 2 (14%) | 10 - 830 | 62 - 140 |
| Acenaphthylene | 14 | 5 (36%) | 1.0 - 42 | 8.1 - 16 |
| Benzo[a]anthracene | 14 | 9 (64%) | 0.1 - 5.0 | 0.15 - 9.0 |
| Benzo[a]pyrene | 14 | 9 (64%) | 0.1 - 1.0 | 0.18 - 22 |
| Benzo[b]fluoranthene | 14 | 4 (29%) | 0.1 - 0.5 | 1.3 - 33 |
| Benzo[g,h,i]perylene | 14 | 1 (7%) | 0.1 - 4.2 | 0.9 |
| Benzo[j,k]fluoranthene | 14 | 3 (21%) | 0.1 - 1.0 | 0.41 - 38 |
| bis(2-Ethylhexyl)phthalate | 14 | 12 (86%) | 10 - 100 | 67 - 18,000 |
| Butylbenzylphthalate | 14 | 2 (14%) | 10 - 830 | 11 - 110 |
| Chrysene | 14 | 7 (50%) | 0.1 - 4.2 | 0.1 - 2.0 |
| Dibenz[a,h]anthracene | 14 | 1 (7%) | 0.1 - 4.2 | 1.1 |
| Diethylphthalate | 14 | 13 (93%) | 830 | 86 - 2200 |
| Dimethylphthalate | 14 | 1 (7%) | 10 - 830 | 12 |
| Di-n-butylphthalate | 14 | 8 (57%) | 10 - 100 | 24 - 2100 |
| Fluoranthene | 14 | 2 (14%) | 1.0 - 42 | 1.3 - 3.4 |
| Indeno[1,2,3-cd]pyrene | 14 | 1 (7%) | 0.1 - 4.2 | 1.3 |
| Naphthalene | 14 | 4 (29%) | 1.0 - 10 | 2.3 - 210 |
| Phenol | 14 | 1 (7%) | 10 - 830 | 28 |
| TCLP VOCs (µg/L) | | | | |
| Acetone | 16 | 1 (6%) | 500 - 2500 | 77 |
| Chloromethane | 16 | 3 (19%) | 100 - 500 | 60 - 250 |
| Trichloroethene (TCE) | 16 | 1 (6%) | 2.0 - 20 | 26 |
| B: also detected in blank | | | | |

The pH of the still bottoms ranged from 4.96 to 6.9. Therefore, no sample designated for corrosivity.

However, when complete data were available, all still bottoms from hydrocarbon machines designated as dangerous waste according to at least one of the following endpoints: acute fish toxicity, persistence (EOX), and ignitability (flash point) (see Table 10). The test results responsible for designating the sample are underlined in the table.

Note that the sample numbering scheme presented in Table 10 (and subsequent tables) provides detailed information about the sample. For example, SW021712-03-HC was collected by “SW” on 02/17/12 at Shop #03, which has a hydrocarbon machine. The abbreviation “NA” in the tables denotes “Not Analyzed” (i.e., the sample was not submitted for testing or technical difficulties prevented analysis).

| Sample Number | Endpoint | | | Waste Designation Codes | | Waste Designation Summary |
|----------------|------------------|-----------------|----------------------|-------------------------|---------|---------------------------|
| | Flash point (°F) | EOX Conc. (ppm) | Fish Toxicity (mg/L) | Washington-specific | Federal | |
| SW021312-02-HC | 159 | <u>150</u> | NA | WP02 | No | WA only |
| SW021712-03-HC | 140 | <u>220</u> | NA | WP02 | No | WA only |
| SW050812-03-HC | <u>125</u> | <u>150</u> | <u>100</u> | WP02 WT02 | D001 | WA & Fed |
| JT021912-04-HC | 230 | <u>210</u> | NA | WP02 | No | WA only |
| SW022712-05-HC | <u>110</u> | <u>210</u> | NA | WP02 | D001 | WA & Fed |
| SW022712-06-HC | <u>132</u> | <u>680</u> | NA | WP02 | D001 | WA & Fed |
| SW050712-06-HC | 157 | <u>130</u> | NA | WP02 | No | WA only |
| SW030412-07-HC | <u>133</u> | <u>620</u> | NA | WP02 | D001 | WA & Fed |
| SW030512-08-HC | 149 | <u>270</u> | <u>100</u> | WP02 WT02 | No | WA only |
| SW021112-09-HC | 155 | <u>250</u> | NA | WP02 | No | WA only |
| SW042612-09-HC | NA | 80 | NA | No | -- | -- |
| SW021612-10-HC | <u>120</u> | <u>320</u> | NA | WP02 | D001 | WA & Fed |
| SW052412-10-HC | 145 | 33 | <u>100</u> | WT02 | No | WA only |
| SW022312-11-HC | <u>120</u> | <u>820</u> | NA | WP02 | D001 | WA & Fed |
| SW062512-16-HC | <u>75</u> | 22 | <u>100</u> | WT02 | D001 | WA & Fed |
| SW062912-17-HC | <u>107</u> | 41 | <u>100</u> | WT02 | D001 | WA & Fed |
| SW070612-18-HC | <u>107</u> | 36 | >100 | No | D001 | Fed |

Fed: Federally regulated hazardous waste
 WA: Washington-only dangerous waste
 Test results responsible for designating the sample underlined

The waste designation of sample SW042612-09-HC was indeterminate because of missing flash point data. This sample was also not tested for fish toxicity and the EOX concentration (80 ppm) did not exceed the regulatory benchmark of 0.01% (100 ppm). However, a sample collected from this shop (#09) on a previous occasion (SW021112-09-HC) designated according to Washington state regulations (code WP02, DW); the EOX concentration was 250 ppm.

Of the 16 samples with complete data, seven (44%) designated solely on the basis of Washington state regulations, eight (50%) for both federal and Washington state regulation, and one (6%) for federal regulations only.

Of the 15 samples that designated for Washington state regulations, 12 (80%) designated for persistence (code WP02, DW). Of the six samples tested for fish toxicity, five (83%) designated as dangerous waste (code WT02, DW). One of the six samples tested (17%) designated solely on the basis of fish toxicity.

All 10 samples that designated as federal regulated hazardous waste did so on the basis of ignitability (i.e., flash point <140 °F; code D001, DW).

System K4™ shops

A total of eight still bottom samples were collected from three System K4™ shops. Analysis for TCLP metals, TCLP SVOCs, and TCLP VOCs was not conducted on sample SW031612-01-K4 because insufficient sample volume was collected for analysis. Samples were collected from one shop on five separate occasions, one shop was sampled twice, and one shop was sampled only once.

Summary data for TCLP SVOCs and TCLP metals are presented in Table 11 and sample-by-sample results are provided in Appendix I. Data are presented for any target analyte that was detected above MRLs in one or more still bottom samples collected from a System K4™ machine. No TCLP VOCs were detected above MRLs, so these data are not presented. (The MRLs for VOCs did not exceed regulatory benchmarks.)

The most frequently detected chemical classes were PAHs (e.g., benzo[a]anthracene and benzo[a]pyrene) and phthalates (e.g., diethylphthalate and bis(2-ethylhexyl)phthalate)). The plasticizer, bis-2-ethylhexyladipate, was also detected at relatively high concentrations in two shops (i.e., 30,000 and 46,000 µg/L). None of the PAH concentrations exceeded the threshold for designation according to Washington state's persistence criteria.

Chromium was the only metal detected in all samples, with a maximum concentration of 0.61 mg/L in Shop #01. However, the chromium concentrations in other samples collected from this shop ranged from 0.068 to 0.28 mg/L.

None of the detected concentrations for any analyte in any shop exceeded waste designation thresholds for the federal toxicity characteristic. In addition, no System K4™ sample designated for corrosivity; pH ranged from 5.46 to 6.9.

| Table 11. Still bottom analytical data from System K4™ machines | | | | |
|--|-----------------------------------|----------------------------------|----------------------|--|
| Analyte | Number of Samples Analyzed | Number of Samples >MRL | Range of MRLs | Range of Concentrations >MRL |
| TCLP metals (mg/L) | | | | |
| Barium | 7 | 6 (86%) | 0.2 | 0.2 – 0.69 |
| Cadmium | 7 | 1 (14%) | 0.02 | 0.032 |
| Chromium | 7 | 7 (100%) | | 0.068 - 0.61 |
| Lead | 7 | 2 (29%) | 0.2 | 0.41 - 1.4 |
| TCLP SVOCs (µg/L) | | | | |
| 4-Nitroaniline | 7 | 1 (14%) | 100 - 1000 | 2300 |
| Acenaphthene | 7 | 5 (71%) | 10 - 750 | 100 - 290 |
| Acenaphthylene | 7 | 2 (29%) | 10 - 150 | 33 - 61 |
| Benzo[a]anthracene | 7 | 4 (57%) | 10 - 75 | 4.5 - 19 |
| Benzo[a]pyrene | 7 | 5 (71%) | 1.0 - 10 | 14 - 43 |
| Benzo[b]fluoranthene | 7 | 6 (86%) | 1.0 | 15 - 180 |
| Benzo[j,k]fluoranthene | 7 | 5 (71%) | 1.0 - 15 | 5.2 - 120 |
| bis(2-Ethylhexyl)phthalate | 7 | 7 (100%) | | 12,000 - 91,000 |
| bis-2-Ethylhexyladipate | 7 | 2 (29%) | 1000 - 5000 | 30,000 - 46,000 |
| Butylbenzylphthalate | 7 | 4 (57%) | 200 - 600 | 1000 - 3000 |
| Chrysene | 7 | 5 (71%) | 1.0 - 15 | 4.3 - 49 |
| Dibenz[a,h]anthracene | 7 | 1 (14%) | 1.0 - 15 | 4.3 |
| Diethylphthalate | 7 | 5 (71%) | 1000 | 450 - 1900 |
| Di-n-butylphthalate | 7 | 7 (100%) | | 1300 - 7400 |
| Fluoranthene | 7 | 1 (14%) | 10 - 150 | 290 |
| Phenanthrene | 7 | 1 (14%) | 10 - 150 | 170 |
| Pyrene | 7 | 1 (14%) | 10 - 150 | 150 |

All System K4™ still bottoms designated as dangerous waste according to at least one of the following endpoints: acute fish toxicity, persistence (EOX), and ignitability (flash point) (see Table 12). The test results responsible for designating the sample are underlined in the table.

Six of the eight samples (75%) designated solely on the basis of Washington state regulations and two (25%) failed both federal and Washington state regulations.

Of the eight samples that failed the Washington state regulations, six (75%) designated for persistence (code WP02, DW). Of the six samples tested for fish toxicity, five (83%) designated as Extremely Hazardous Waste (code WT01, EHW) and one designated as Dangerous Waste (code WT02, DW). Two of the six samples tested (33%) designated solely on the basis of fish toxicity.

The two samples that failed the federal regulations did so on the basis of ignitability (i.e., flash point).

| Table 12. Waste designation of still bottoms from System K4™ machines | | | | | | |
|--|------------------|-----------------|----------------------|-------------------------|---------|---------------------------|
| Sample Number | Endpoint | | | Waste Designation Codes | | Waste Designation Summary |
| | Flash point (°F) | EOX Conc. (ppm) | Fish Toxicity (mg/L) | Washington-specific | Federal | |
| SW121611-01-K4 | 172 | <u>280</u> | NA | WP02 | No | WA only |
| SW021012-01-K4 | 176 | <u>490</u> | NA | WP02 | No | WA only |
| SW030212-01-K4 | <u>110</u> | <u>170</u> | <u>100</u> | WP02 WT02 | D001 | WA & Fed |
| SW031612-01-K4 | 169 | <u>200</u> | <u>10</u> | WP02 WT01 | No | WA only |
| SW042712-01-K4 | 150 | <u>130</u> | <u>10</u> | WP02 WT01 | No | WA only |
| SW042012-14-K4 | 175 | 76 | <u>10</u> | WT01 | No | WA only |
| SW052512-14-K4 | 150 | 28 | <u>10</u> | WT01 | No | WA only |
| SW080212-19-K4 | <u>134</u> | <u>1830</u> | <u>10</u> | WP02 WT01 | D001 | WA & Fed |
| Fed: Federally regulated hazardous waste WA: Washington-only dangerous waste Test results responsible for designating the sample <u>underlined</u> | | | | | | |

Separator Water Analysis and Designation

Hydrocarbon shops

A total of 16 separator water samples were collected from 11 hydrocarbon shops. Data for ethanol and isopropyl alcohol are missing for one shop (#06) because the contract laboratory failed to provide analytical results. One shop (#06) filtered their separator water using a Zerowaste™ filtration device. Consequently, one sample of pre-treatment, unfiltered separator water was collected in addition to two filtered samples (“filtered” data are reported separately below). For the remaining shops, two samples were collected at three shops and a single sample was collected at seven shops.

Unfiltered samples

Summary data for VOCs in unfiltered separator water, including TICs, are presented in Table 13 and complete sample-by-sample results are provided in Appendix J. Data are presented for any target analyte that was detected above MRLs in one or more separator water samples collected from a hydrocarbon machine.

TICs were evaluated against an analytical library “match”. Because some samples contained numerous TICs at relatively low concentrations, TICs are presented in the tables only if they were present at $\geq 10,000$ $\mu\text{g/L}$ in one or more samples. The abbreviation “ND” in the tables denotes that the TIC was “Not Detected” (i.e., it was not listed on the analytical report for that sample).

Although samples were also analyzed for SVOCs at the beginning of the study, this analysis was discontinued because the target analytes were never positively detected (i.e., the SVOCs never exceeded their respective MRLs). The SVOC MRLs never

exceeded regulatory thresholds. Similarly, metals analysis was also discontinued because no samples exceeded regulatory thresholds.

| Table 13. Unfiltered separator water analytical data from hydrocarbon machines | | | | |
|---|-----------------------------------|----------------------------------|----------------------|--|
| Analyte | Number of Samples Analyzed | Number of Samples >MRL | Range of MRLs | Range of Concentrations >MRL |
| VOCs (µg/L) | | | | |
| 1,2,4-Trimethylbenzene | 14 | 2 (14%) | 10 - 200 | 74 - 200 |
| 1,2-Dichlorobenzene | 14 | 1 (7%) | 10 - 200 | 140 |
| 2-Butanone | 14 | 3 (21%) | 100 - 2000 | 100 E - 230 |
| 2-Propanol, 2-methyl- | 14 | 3 (21%) | 500 - 5000 | 690 - 1000 |
| Acetone | 14 | 13 (93%) | 1000 | 140 - 18,000 E |
| Ethanol | 13 | 1 (8%) | 10,000 - 100,000 | 480,000 |
| Isopropyl alcohol | 13 | 8 (62%) | 1000 - 10,000 | 520 - 1,700,000 E |
| Methyl isobutyl ketone | 14 | 2 (14%) | 100 - 2000 | 240 - 10,000 |
| Naphthalene | 14 | 1 (7%) | 10 - 100 | 150 |
| Tetrachloroethene (PERC) | 14 | 1 (7%) | 10 - 200 | 15 |
| Toluene | 14 | 1 (7%) | 10 - 200 | 240 |
| Trichloroethene (TCE) | 14 | 2 (14%) | 10 - 200 | 33 - 13,000 |
| VOC TICs (µg/L) ≥10,000 µg/L in one or more samples | | | | |
| 1-Hexanol, 2-ethyl- | 14 | 4 (29%) | -- | 460 - 37,000 |
| Acetic acid, pentyl ester | 14 | 1 (7%) | -- | 23,000 |
| Heptadecane | 14 | 1 (7%) | -- | 16,000 |
| Hexane, 2,2,5-trimethyl- | 14 | 1 (7%) | -- | 12,000 |
| Nonane, 2,3-dimethyl | 14 | 2 (14%) | -- | 631 - 11,000 |
| Nonane, 3-methyl-5-propyl | 14 | 2 (14%) | -- | 1300 - 20,000 |
| Octane, 2,4,6-trimethyl- | 14 | 1 (7%) | -- | 12,000 |
| Unknown | 14 | 2 (14%) | -- | 14,000 - 22,000 |
| E: Estimated concentration | | | | |
| --: MRLs not applicable for TICs | | | | |

Fish toxicity testing was conducted on a subset of the samples because of resource constraints. No samples designated as dangerous waste using the fish toxicity test (see Table 14).

Although samples were not collected for FOG analysis at the beginning of the study, this test was conducted on later samples. At first, the analytical laboratory provided data erroneously for Total FOG, rather than the non-polar fraction. In the data tables, the results from Total FOG analysis are labeled “(Total)”. Samples that were not tested for FOG (non-polar or Total) are labeled “NA”. No samples exceeded the 100 mg/L KCIW wastewater discharge limit for non-polar FOG.

Table 14. Waste designation of separator water (unfiltered) from hydrocarbon machines

| Sample Number | Criteria | | | | KCIW Wastewater Discharge | Waste Designation Codes | | Waste Designation Summary |
|----------------|------------------|----------------------------|------------------|----------------------|---------------------------|-------------------------|-----------|---------------------------|
| | TCE Conc. (µg/L) | Non-polar FOG Conc. (mg/L) | Flash point (°F) | Fish Toxicity (mg/L) | | Washington-specific | Federal | |
| SW021312-02-HC | <u>13,000</u> | NA | <u>138</u> | NA | Fail (TCE) | No | D001 D040 | Fed |
| SW021712-03-HC | <200 | NA | >210 | NA | -- | No | No | No |
| SW050812-03-HC | <100 | <6 | >210 | NA | No | No | No | No |
| SW051412-06-HC | 33 | 7.8 | >210 | NA | No | No | No | No |
| SW030412-07-HC | <10 | 49 (Total) | >210 | NA | No | No | No | No |
| SW030512-08-HC | <10 | <6 (Total) | >210 | >100 | No | No | No | No |
| SW021112-09-HC | <100 | NA | >210 | NA | -- | No | No | No |
| SW042612-09-HC | <100 | <6 | >210 | NA | No | No | No | No |
| SW021612-10-HC | <10 | NA | >210 | NA | -- | No | No | No |
| SW052412-10-HC | <10 | <6 | >210 | NA | No | No | No | No |
| SW022312-11-HC | <10 | NA | >210 | NA | -- | No | No | No |
| SW062512-16-HC | <10 | <6 | >210 | >100 | No | No | No | No |
| SW070612-17-HC | <100 | 81 | >210 | >100 | No | No | No | No |
| SW071112-18-HC | <100 | <6 | >210 | >100 | No | No | No | No |

Fed: Federally designated waste
(Total): Sample analyzed for Total FOG
NA: Sample not analyzed for specific test
--: Indeterminate result
Test results responsible for designating the sample underlined

The pH of the unfiltered hydrocarbon separator water ranged from 5.71 to 7.61 and the TOX concentrations ranged from <1.0 to 15 mg/L. Consequently, no samples designated for corrosivity or persistence.

Only one sample (SW030412-07-HC) contained PERC above MRLs, although the detected concentration (15 µg/L) was lower than the MRL achieved in many other samples. PERC was not detected at concentrations approaching levels of concern for dangerous waste designation or wastewater discharge.

SW021312-02-HC was the only sample to designate as dangerous waste; the TCE concentration (13,000 µg/L) exceeded the maximum concentration for the federal toxicity characteristic and the KCIW screening level (500 µg/L). Consequently, this sample was assigned a federal dangerous waste code of “D040” and DW. With a flash point of 138 °F, this sample also designated for the federal characteristic of ignitability (code D001, DW).

Sample SW021312-02-HC was also unique in that it contained several other target VOCs above MRLs, including 1,2-dichlorobenzene (140 µg/L), toluene (240 µg/L), and naphthalene (150 µg/L). The VOC TIC, acetic acid-pentyl ester, was detected at 23,000 µg/L, and likely originated from the amyl acetate spot cleaner used at this shop (acetic acid-pentyl ester is a synonym for amyl acetate). This sample also contained the highest detected concentrations of 1,2,4-trimethylbenzene (200 µg/L), methyl isobutyl ketone (10,000 µg/L), isopropyl alcohol (1,200,000 µg/L), and ethanol (480,000 µg/L).

Filtered samples

Neither of the filtered samples from Shop #06 designated for federal or Washington state waste characterization regulations. These samples also did not exceed KCIW’s screening levels for VOCs or the regulatory threshold for non-polar FOG (see Appendix J).

System K4™ shops

A total of nine separator water samples were collected from three System K4™ shops. One shop (#01) filtered their separator water using a Zerowaste™ filtration device. Consequently, four samples of pre-treatment, unfiltered separator water were collected in addition to two filtered samples (“filtered” data are reported separately below). For the remaining shops, two samples were collected at one shop and a single sample was collected at one shop.

Unfiltered samples

Summary data for VOCs in unfiltered separator water, including TICs, are presented in Table 15 and complete sample-by-sample results are provided in Appendix K.

Several TICs were identified that likely represent components of the Solvon K4™ dry cleaning solvent, including 1-butanol and dibutoxy-methanol.

| Analyte | Number of Samples Analyzed | Number of Samples >MRL | Range of MRLs | Range of Concentrations >MRL |
|--|----------------------------|------------------------|---------------|------------------------------|
| VOCs (µg/L) | | | | |
| Acetone | 7 | 7 (100%) | | 1300 - 3600 |
| Isopropyl alcohol | 7 | 7 (100%) | | 18,000 - 410,000 E |
| VOC TICs (µg/L) ≥10,000 µg/L in one or more samples | | | | |
| 1-Butanol | 7 | 4 (57%) | -- | 5800 - 14,000 |
| Butane, 1-(1-bromo-1-methylethoxy)- | 7 | 1 (14%) | -- | 49,000 - 49,000 |
| Furan, 2-propyl- | 7 | 2 (29%) | -- | 29,000 - 41,000 E |
| Methanol, dibutoxy- | 7 | 2 (29%) | -- | 140,000 - 140,000 |
| Morpholine | 7 | 3 (43%) | -- | 120 - 210,000 |
| Unknown | 7 | 2 (29%) | -- | 80,000 - 84,000 |
| E: Estimated concentration --: MRLs not applicable for TICs | | | | |

No samples designated as dangerous waste using the fish toxicity test (see Table 16). The pH of the unfiltered System K4™ separator water ranged from 6.3 to 7.68, the TOX concentrations ranged from <1.0 to 2.7 mg/L, and the flash points were >140 °F. Consequently, no samples designated for corrosivity, persistence, or ignitability. No samples of unfiltered separator water collected from System K4™ shops exceeded KCIW’s wastewater discharge levels for VOCs or non-polar FOG.

Filtered samples

Neither of the filtered samples from Shop #01 designated according to federal or Washington state waste regulations. These samples also did not exceed KCIW’s screening levels for VOCs or the limit for non-polar FOG (see Appendix K).

| Table 16. Waste designation of separator water (unfiltered) from System K4™ machines | | | | | | | |
|---|-----------------------------------|-------------------------|-----------------------------|----------------------------------|--------------------------------|----------------|----------------------------------|
| Sample Number | Endpoint | | | | Waste Designation Codes | | Waste Designation Summary |
| | Non-polar FOG Conc. (mg/L) | Flash point (°F) | Fish Toxicity (mg/L) | KCIW Wastewater Discharge | Washington-specific | Federal | |
| SW121611-01-K4 | NA | NA | NA | -- | -- | -- | -- |
| SW021012-01-K4 | NA | >210 | NA | -- | No | No | No |
| SW031212-01-K4 | 57 (Total) | >210 | >100 | No | No | No | No |
| SW042712-01-K4 | <6 | >210 | >100 | No | No | No | No |
| SW042012-14-K4 | <6 | >210 | >100 | No | No | No | No |
| SW052512-14-K4 | <6 | >210 | NA | No | No | No | No |
| SW080212-19-K4 | <3 | >210 | >100 | No | No | No | No |
| (Total): Sample analyzed for Total FOG NA: Sample not analyzed for specific test --: Indeterminate result | | | | | | | |

DISCUSSION

This study was comprised of a questionnaire and an extensive product- and waste-sampling campaign. The objectives were to gather information about: 1) the frequency of use of process chemicals and other operational details, 2) the chemical characteristics of the process chemicals, 3) the composition of the still bottoms and separator water wastes, and 4) linkages between work practices, process chemicals, and the chemical composition of the waste streams.

Dry Cleaning Operations

The characteristics of the shops sampled in this study were consistent with other businesses visited during routine field inspections and the results of the 2010 survey of King County dry cleaners.⁽²⁾ For example, the median age of the hydrocarbon dry cleaning machines sampled in this study (7 years) was similar to the median age of non-PERC machines reported in the survey (5 years). In addition, the median number of loads run per week in the hydrocarbon study shops (17 loads/week) was similar to the average number derived from the survey (15 loads/week). Note that comparison of System K4™ study shops to the survey data could not be performed because this technology appeared in King County after 2010.

Most of the study machines were purchased as new equipment and none had been converted from using PERC. Only two shops reported using spot cleaning products that contain PERC or TCE, although Picrin™ was observed on the spotting tables of three shops. Consequently, dry cleaners may not be aware that they are using products that contain chlorinated hydrocarbons.

Several shops appeared to be disposing of their wastes improperly. This situation likely reflects a lack of understanding of the hazardous waste management regulations that apply to these alternative solvents. Because the separator water generated by alternative solvent machines contains relatively low concentrations of chlorinated hydrocarbons, many shop owners assume that this waste stream is “non-toxic” and can be disposed of without characterization or treatment.

As mentioned previously, it was not possible to determine whether there were significant differences in operational characteristics between the hydrocarbon and System K4™ shops because only three System K4™ businesses were enrolled in the study.

Process Chemicals

Product inventory

There was considerable diversity in the spot cleaning chemicals used in hydrocarbon shops. Many continue to use products originally designed for PERC dry cleaning that may contain very high concentrations of chlorinated hydrocarbons. Because the waste streams in PERC operations typically designate as dangerous waste, contributions of residual chlorinated hydrocarbons from spot cleaners are generally inconsequential.

However, for operations that employ chlorine-free dry cleaning solvents, using these products increases the probability that their waste streams will fail regulatory benchmarks. While the separator water from several study shops that use chlorinated spot cleaners did not contain detectable concentrations of chlorinated hydrocarbons, the use of Picrin™ in Shop #02 was likely responsible for the exceedence of both wastewater discharge and dangerous waste thresholds.

Workers who are directly exposed to TCE via spot cleaning are at risk for a range of adverse health effects. Dry cleaners are mostly likely exposed to TCE by inhalation and skin contact. According to the Agency for Toxic Substances and Disease Registry (ATSDR), breathing small amounts of TCE may cause headaches, lung irritation, dizziness, poor coordination, and difficulty concentrating. Breathing large amounts may cause impaired heart function, unconsciousness, and death. Breathing TCE for long periods may cause nerve, kidney, and liver damage. Skin contact with TCE for short periods may cause skin rashes.⁽³⁰⁾ In addition, EPA's 2011 *Toxicological Review of Trichloroethylene* reaffirmed an earlier EPA conclusion that TCE is carcinogenic in humans by all routes of exposure.⁽³¹⁾

Several spot cleaning products have the potential to cause acute traumatic injury and illness. For example, the MSDS for A.L. Wilson's RustGo™ lists hydrogen fluoride as an ingredient at a concentration of 12%.⁽³²⁾ According to the MSDS, contact with this product may result in severe burns to the skin and permanent eye damage. The MSDS also states that inhalation of vapors may cause damage to lungs, respiratory system and pulmonary edema.

It is noteworthy that several businesses successfully spot-clean fabrics without using chlorinated products or other harmful chemicals. Several shops used consumer-grade detergents and other aqueous products to accomplish their spot cleaning.

Product MSDSs

A review of the MSDSs for several products used by hydrocarbon shops revealed that the quality of the health and safety information was extremely variable. As is permitted under Occupational Safety and Health Administration (OSHA) law, the ingredients of many products were labeled as "trade secrets". Consequently, product users are not aware of the hazardous ingredients in certain products.

OSHA law also dictates that product constituents are only required to be listed on MSDSs if they are present above relatively high threshold concentrations: 1% and 0.1% for noncarcinogenic substances and carcinogens, respectively. Consequently, workers may be exposed to hazardous substances at concentrations that fail to exceed these thresholds yet may still elicit adverse health effects.

These shortcomings in the quality of information presented on some MSDSs also present challenges when attempting to designate products according to dangerous waste regulations.

Consistent with the 2010 survey and field observations in King County, the majority of business owners enrolled in this study were first-generation Korean immigrants and their

employees were typically Hispanic. Because MSDSs are only available in English, they are frequently not accessible to those with limited English language skills.

Products in System K4™ operations

In contrast to the situation with hydrocarbon shops, all process chemicals used in System K4™ operations were manufactured by the solvent manufacturer, Kreussler GmbH. Spot cleaning was typically performed using the brushing agent, Prenett K4™, occasionally in combination with Solvon K4™. This unified source of process chemicals is clearly preferable, but likely reflects the fact that only three System K4™ operations were available to sample. This situation may also change if System K4™ gains market share, potentially resulting in reduced oversight by authorized vendors. Dry cleaners may also purchase different process chemicals when they deplete their supplies of System K4™ products.

Waste Characteristics

Summaries of the dangerous waste designation status and comparison to KCIW's wastewater discharge criteria are presented in Tables 17 and 18, respectively. The value "n" represents the total number of shops sampled per waste stream. Note that the number of shops for which specific test results are available may be less than the number of shops sampled because of occasional technical difficulties with the analyses or lack of resources to conduct the test on every sample.

Still bottoms

All still bottom samples designated as dangerous waste according to Washington state regulations. With a single exception, every sample submitted for fish bioassay was sufficiently toxic that it designated as dangerous waste. Five of the six still bottom samples from System K4™ machines were more toxic in the fish bioassay than those from hydrocarbon machines. A preliminary evaluation of the virgin dry cleaning solvents using the standard fish bioassay (i.e., Ecology 8-12 / Part A) revealed that the hydrocarbon solvent (DF2000™) failed to elicit fish mortality at 100 mg/L. However, Solvon K4™ caused 97% fish mortality at the same concentration (unpublished data). Consequently, the enhanced toxicity of the System K4™ still bottoms may at least partly reflect the toxicological properties of Solvon K4™.

The concentrations of several plasticizers (i.e., bis(2-ethylhexyl)phthalate, butylbenzylphthalate, and di-n-butylphthalate) and polycyclic aromatic hydrocarbons (i.e., benzo[a]pyrene, benzo[b]fluoranthene, benzo[j,k]fluoranthene, and chrysene) were substantially higher and statistically significantly different in System K4™ still bottoms compared to hydrocarbon still bottoms. The barium concentrations were also substantially higher and statistically significantly different in System K4™ shops. Because a large number of comparisons were conducted between hydrocarbon and System K4™ shops, $p < 0.01$ was considered to be statistically significant, rather than the more commonly used (and less conservative) $p < 0.05$. Examples of data plots are presented in Appendix L.

| Table 17. Dangerous waste designation summary | | | | |
|--|---------------------------------|------------------------------------|---------------------------------|-------------------------------|
| Category | Still Bottoms | | Separator Water* | |
| | Hydrocarbon shops (n=17) | System K4™ shops (n=8) | Hydrocarbon shops (n=14) | System K4™ shops (n=7) |
| Federal characteristic waste | | | | |
| Ignitability | 9/16 (56%): D001 | 2/8 (25%): D001 | 1/14 (7%): D001 | 0/6 (0%) |
| Toxicity | 0/14 (0%) | 0/7 (0%) | 1/14 (7%): D040 | 0/6 (0%) |
| Washington state toxicity criteria | | | | |
| Bioassay designation | 5/6 (83%): WT02 | 1/6 (17%): WT02 5/6 (83%): WT01 | 0/4 (0%) | 0/4 (0%) |
| Washington state persistence criteria | | | | |
| Halogenated organic compounds | 12/17 (71%): WP02 | 6/8 (75%): WP02 | 0/14 (0%) | 0/6 (0%) |
| *Data presented only for unfiltered/untreated separator water | | | | |
| Waste codes: D001: Flash point <140 °F (DW) D040: >0.5 mg/L trichloroethylene (TCE) (DW) WT02: Acute fish toxicity lethal concentration ≤100 mg/L (Washington state-only DW) WT01: Acute fish toxicity lethal concentration ≤10 mg/L (Washington state-only EHW) WP02: 0.01% to 1.0% halogenated organic compounds (Washington state-only DW) | | | | |

The plasticizers may originate from the plastic containers used to store the dry cleaning solvents, products used in the dry cleaning process (e.g., sizing agents), or the plastic-containing fabrics or components (buttons, etc.) that have been dry cleaned. Solvon K4™ may more effectively extract plasticizers from product containers and other materials than DF2000™. Alternatively, the containers used to store the System K4™ products may contain higher concentrations of plasticizers than those used for DF2000™. However, because extraction is affected by temperature and duration of contact, product storage conditions may also affect the plasticizer concentrations.

PAHs are byproducts of the incomplete combustion of fossil fuels and other organic material. Consequently, these compounds may be generated as the solvents, other process chemicals, and contaminants from cleaned clothing are heated in the dry cleaning machine. ATSDR considers there to be sufficient qualitative evidence to suggest that mixtures containing PAHs such as benzo[a]pyrene, chrysene, benz[a]anthracene, benzo[b]fluoranthene, and dibenz[a,h]anthracene may cause cancer in humans.⁽³³⁾ Dermal contact with PAHs has also been associated with skin disorders in humans. Because it was not possible to perform chemical analyses on the still bottoms directly, the magnitude of worker exposure to these substances could not be determined. However, it would be prudent for workers to wear adequate skin protection while cleaning machines, including chemical-resistant gloves and impervious coveralls.

Separator water

A separator water sample from a single shop designated as dangerous waste (see Table 17) and failed the KCIW Discharge Screening Levels (see Table 18). The hydrocarbon shop from which this sample was collected (Shop #02) was unique in that both business management and operations appeared to be in considerable disarray. The separator water from this shop had a ~5 mm immiscible solvent layer at the surface. This is in contrast to the separator water from the other shops, which occasionally contained no more than small (1 - 2 mm diameter) dispersed solvent droplets at the surface. Subsequent conversations with dry cleaning vendors and technicians revealed that excessive accumulation of solvent can occur if the separator unit is malfunctioning.

| Table 18. Summary of separator water results relative to KCIW criteria | | |
|---|---------------------------------|-------------------------------|
| Endpoint | Hydrocarbon shops (n=14) | System K4™ shops (n=7) |
| Non-polar FOG >100 mg/L | 0/9 (0%) | 0/5 (0%) |
| Trichloroethylene (TCE) >0.24 mg/L | 1/14 (7%) | 0/7 (0%) |
| Data presented only for unfiltered/untreated separator water | | |

The unique visual appearance of the separator water from Shop #02 may be a valuable indicator of machine status and the potential for the waste stream to fail regulatory benchmarks. The chemical composition of all other separator water samples was remarkably consistent and independent of solvent used.

Relatively high concentrations of isopropyl alcohol and acetone were detected in separator water from both hydrocarbon and System K4™ machines. A review of MSDSs revealed the presence of percentage levels of isopropyl alcohol in several products. In contrast, acetone was not listed on any MSDS and was not detected above MRLs in any product (data not presented). However, the MRLs for acetone in the product analyses were 1,000-2,000 mg/kg (ppm), whereas the highest concentration in hydrocarbon separator water was 18,000 µg/L (i.e., 18 ppm). Consequently, acetone in separator water may have originated from products, but the relative chemical complexity of concentrated products prevented quantification of acetone in the products.

No statistically significant differences in concentrations of target analytes were found in System K4™ vs. hydrocarbon separator water (p-value <0.01). However, this analysis was limited by the presence of a large number of “non-detected” values with widely varying MRLs.

However, several TICs were unique to the type of separator water tested. For example, the following TICs were only present at $\geq 10,000$ µg/L in System K4™ separator water: 1-butanol; 1-(1-bromo-1-methylethoxy)-butane; 2-propyl-furan; dibutoxy-methanol; and morpholine. However, several C₆-C₉ TICs were detected at $\geq 10,000$ µg/L only in the hydrocarbon separator water. These TICs are likely constituents of the respective dry cleaning solvents.

The finding that most unfiltered separator water passed regulatory benchmarks calls into question the utility of the Zerowaste™ machine. While this filtration device may reduce the concentrations of chlorinated hydrocarbons and other contaminants in shops with malfunctioning equipment, this treatment appears unnecessary for the majority of shops that use DF2000™ or Solvon K4™.

Comparison to previous studies

Previous King County study

In contrast to this current study, a previous investigation conducted in King County (unpublished) reported that PERC was detected in most still bottom samples collected from 15 hydrocarbon machines. The 2006 study reported that PERC concentrations ranged from 3.5 to 2300 µg/L (ppb) and the still bottoms from three shops exceeded the dangerous waste threshold of 700 µg/L (i.e., 0.7 ppm). The reasons for this difference in findings are unclear. One possible explanation is that the MRL for PERC in the earlier study was 1.0 µg/L, which is considerably lower than that achieved in this present study (MRLs ranged from 2.0 to 100 µg/L, with a median MRL of 50 µg/L). This disparity may reflect differences in sample handling, preparation, and analysis by different analytical laboratories. Additionally, the characteristics of the still bottoms from hydrocarbon operations may have changed in the last several years, reflecting changes in equipment and work practices. However, by design, the previous study did not collect

information concerning process chemicals or the conversion of PERC machines for use with hydrocarbon.

The previous study also detected PERC in the separator water of 10 hydrocarbon machines, with concentrations ranging from 1.0 to 32.1 µg/L (the MRL was 1.0 µg/L). In contrast, PERC was detected in a single sample in the present study, and the MRLs ranged from 10 to 1000 µg/L, with a median MRL of 100 µg/L.

As stated previously, changes in equipment and work practices could also potentially account for differences in separator water chemical composition. However, no samples from either study exceeded the KCIW wastewater screening level for PERC of 240 µg/L (i.e., 0.24 ppm).

California study

The small study of the health and environmental characteristics of the hydrocarbon process conducted in California involved sampling four dry cleaners that used tonsil filtration media and four that used the distillation process observed in the King County study shops.⁽¹⁴⁾

The California study evaluated still bottoms and separator water in an aquatic toxicity test that exposed fathead minnows for 96 hours. This investigation revealed that the still bottoms from cleaners that used the distillation process elicited fish toxicity at test concentrations <500 mg/L, which is consistent with the findings of this current study, where fish mortality was observed at 100 mg/L. However, samples derived from shops that used the tonsil process failed to elicit fish toxicity. Because detergents are not used in the tonsil cleaning process, the study authors postulated that detergents were responsible for the aquatic toxicity of still bottoms from machines that employed distillation.

Also consistent with this current study, none of the California separator water samples elicited fish toxicity at test concentrations of 500 mg/L.

Considering only the waste samples collected from shops that used distillation, the California study detected PERC in three of the four separator water samples, with concentrations ranging from 17 to 16,000 µg/L (ppb). PERC was also detected in three of the four still bottom samples, with concentrations ranging from 2 to 130 mg/Kg (ppm). The other VOCs detected in sludge and separator water were consistent with those identified in this current study.

Again, disparities in the analytical results between the California study and this present study likely reflect differences in sample handling, preparation, and analysis, in addition to differences in equipment and work practices. It is noteworthy that the California study authors postulated that a source of PERC in the waste streams could be spot cleaning chemicals, whereas PERC was detected only in two of the products sampled in King County.

Linkages Between Process Characteristics and Waste Composition

Plots of process characteristics vs. chemical components of the waste streams were reviewed for hydrocarbon shops, with consideration of the resulting correlation coefficients and associated p-values. The EOX concentration was negatively correlated with the machine size (Spearman's $\rho = -0.71$, $p = 0.007$). No other statistically significant correlations were found between the characteristics of the shops or the dry cleaning machines (as recorded on the questionnaire) and the chemical composition of the waste streams ($p < 0.05$ was considered statistically significant for this analysis). However, field observations suggested that the single shop with overt deficiencies in business management and machine maintenance generated the most chemically-complex separator water that also exceeded regulatory thresholds. Insufficient System K4TM shops were sampled to conduct a statistical analysis for this technology.

Strengths and Limitations of the Study

Limitations

The principal limitation of this study was the small sample size of sixteen dry cleaners. In particular, only three System K4TM shops were available to sample. While sufficient samples were collected to characterize the waste streams from the study machines, this investigation was not large enough to draw definitive conclusions about the causal relationships between work practices, product usage, and waste characteristics. In addition, the participating shops generally had previous working relationships with LHWMP and may not be representative of all dry cleaners in King County. It is noteworthy that the single shop with separator water that failed regulatory benchmarks (Shop #02) dropped out of the study and is lost to follow-up.

Although the questionnaire was answered by the most knowledgeable individuals in the shops, several questions were difficult to convey or were difficult for the dry cleaners to answer. These difficulties reflect the demographics of the industry; many business owners and employees have limited English language skills. The question concerning the fraction of "repeat customers" presented considerable difficulty to the dry cleaners, both in terms of comprehension and providing an estimate. Subsequent to the data analysis, it was also recognized that questions concerning the frequency of machine servicing and the identity of the individual performing the service (i.e., shop owner, independent service contractor, or manufacturer representative) would have provided valuable information. Given sufficient resources, solutions to these impediments include more extensive pre-testing of the questions, translation of the questionnaire into Korean and Spanish, and the use of interpreters during field visits.

Resource constraints also limited the extent to which the same products found at different shops could be sampled and analyzed. Although samples were always collected from original product bottles, it could not be known with certainty whether they actually contained the product described on the label. Sampling the same product at multiple

business locations would have helped alleviate concerns about the identity of the sampled material. Unused products could have also been purchased for chemical analysis.

Identifying products that were used for “pre-spotting” compared to “post-spotting” also presented difficulties, as did achieving reliable estimates of the fraction of fabrics that required pre-spotting.

Because the products are typically concentrated solutions of petroleum hydrocarbons and other complex mixtures, the MRLs for VOCs and SVOCs achieved in the product analyses were typically in the 100s - 1000s mg/Kg (ppm). Although the analyses were adequate to detect the principal ingredients, they could not identify relatively low concentrations of constituents that may ultimately contaminate the waste streams. For example, the MRLs achieved in the analysis of separator water were occasionally three orders of magnitude lower than those achieved in products.

Because the separator water typically accumulated for several days in a bucket external to the dry cleaning machine, the possibility of adulteration prior to sampling cannot be excluded. Although still bottoms were sampled by a study investigator when the machine was opened for routine cleaning, the heterogeneity of this waste stream presented significant challenges. Although attempts were made to ensure that liquid and semi-solid/viscous material was collected in the appropriate proportion, the composition of the sample may not have been entirely representative.

Once collected, the still bottoms tended to stratify within the sample container. This stratification posed challenges to the analytical laboratory because it was essential that the sample be mixed thoroughly prior to preparation and analysis. The chemical complexity of the still bottoms also obligated the laboratory to analyze TCLP extracts, rather than virgin samples. Three samples formed a precipitate during TCLP extraction, preventing complete characterization of the waste streams. In addition, several TCLP extracts were sufficiently complex that the laboratory was occasionally forced to dilute the samples, resulting in elevated MRLs.

Chromatographic peaks for TICs were evaluated against an analytical “library”, and the laboratory reported compounds for which there was more than a 50 percent probability of a match. However, the TIC data should be interpreted with caution because the identity of these compounds cannot be determined definitively without reference to a known standard. For example, the TICs identified in System K4™ separator water as “Unknown”, dibutoxy-methanol, and 1-(1-bromo-1-methylethoxy)-butane could be chemically identical, reflecting variability in the library matching procedure.

Because the MRLs achieved for VOAs and SVOAs were higher than those reported in previous investigations, it was not possible to identify waste stream contaminants at concentrations <10 µg/L (ppb). However, the MRLs achieved in this study were adequate for waste characterization.

The evaluation of separator water relative to industrial wastewater criteria was based solely on limits administered by KCIW. However, other King County sewer districts have different regulations, which may be more or less restrictive. Consequently, it is not

possible to generalize about separator water management from the results of this study. Liquid waste generators should seek technical guidance from their local sewer district before selecting a method of disposal.

Strengths

This was the first comprehensive evaluation of the products used by alternative solvent dry cleaners in King County and the waste streams generated by these processes. To our knowledge, this study represents the first investigation of separator water and still bottoms generated by System K4™ dry cleaning.

Specific strengths of this study include:

1. The contributions of local analytical chemists and waste characterization experts to the study design ensured that the resulting data fulfilled regulatory requirements;
2. The excellent working relationships developed between LHWMP and the local dry cleaning community resulted in successful recruitment of every business owner that was asked to participate;
3. Analyzing both the products and the waste streams facilitated identification of the source of chlorinated hydrocarbon contamination in a hydrocarbon shop;
4. The use of a Zerowaste™ device at two shops permitted evaluation of the efficacy of separator water treatment prior to disposal; and
5. Data of sufficient quality was generated to support specific recommendations for product selection and waste disposal.

CONCLUSIONS AND RECOMMENDATIONS

The overall conclusions to this study of hydrocarbon and System K4TM dry cleaning operations are:

1. Several shops appeared to be disposing of their wastes improperly;
2. Still bottoms designate as dangerous waste in Washington state (DW) and occasionally as EHW. Some still bottoms were federally regulated hazardous waste for ignitability;
3. Separator water typically does not typically designate as dangerous waste and does not exceed wastewater discharge levels;
4. Deficiencies in dry cleaning equipment, like malfunctioning separators, may cause separator water to fail regulatory benchmarks due to contamination by spot cleaning chemicals;
5. Visual inspection of separator water may be a valuable indicator of the potential for failure of regulatory benchmarks; and
6. Treatment of separator water prior to disposal is unnecessary in properly functioning alternative solvent dry cleaning machines.

Specific recommendations resulting from this study's findings include:

1. Efforts should be directed towards removing hazardous spot cleaning chemicals from hydrocarbon dry cleaners. This may be achieved via regulation, education and training, and providing financial incentives and subsidies.
2. Unused or contaminated dry cleaning solvent and contaminated materials from spill cleanup should be disposed of as hazardous waste. This is particularly important for Solvon K4TM because this solvent designates according to Washington state toxicity criteria.
3. Unused spot cleaners should also be disposed of as hazardous waste, unless the product's MSDS provides sufficient information that a judgment can be rendered from the list of ingredients.
4. Dry cleaners are required to chemically characterize their wastes, including still bottoms and separator water. Discharge of separator water to the sewer is not appropriate unless a clearance is provided by the appropriate authority. The results of this study indicate that chemical analyses of separator water may be limited to determining the concentrations of PERC, TCE, and non-polar FOG, in addition to flash point.
5. Dry cleaners should be discouraged from evaporating separator water into indoor workspaces or adding this waste to cooling towers.

6. KCIW and other sewer districts should consider developing policies that allow alternative solvent dry cleaners to discharge their separator water to the sewer if the waste passes regulatory benchmarks.

Other recommendations include:

1. The Washington state OSHA program should consider extending its jurisdiction to include all owner-operated businesses. The lack of regulatory oversight and consultation assistance experienced by the dry cleaning industry is likely at least partially responsible for the deficiencies in health & safety practices observed in many shops.
2. The quality of the MSDSs for dry cleaning process chemicals requires significant improvement. Although the Globally Harmonized System of classification and labeling of chemicals is anticipated to improve communications on chemical hazards and safe handling practices, the information must be provided to end-users in a culturally-appropriate format.
3. The toxicological properties of the alternative solvents should be critically evaluated by independent investigators. Without this information, it is not possible to make definitive recommendations concerning adoption of these technologies.
4. Independent exposure assessments should be conducted to evaluate the potential for dermal contact with PAHs in still bottoms and inhalation of formaldehyde from Solvon K4™. This information would inform the selection of gloves, coveralls, and respiratory protection.
5. Local agencies and programs should engage the dry cleaning community and work collaboratively to develop consistent messaging regarding regulatory requirements and best management practices. Education and outreach strategies should be developed by engaging and partnering with this underserved working population.

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APPENDIX A
QUESTIONNAIRE

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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. _____

3. _____

APPENDIX B

PRODUCT SAMPLING FORM

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PRODUCT SAMPLE

Business name / City: _____

Date sampled: _____

Sampled by: _____

Product sampled: _____

Lot #: _____

Sample #: _____

Comments: _____

Business name / City: _____

Date sampled: _____

Sampled by: _____

Product sampled: _____

Lot #: _____

Sample #: _____

Comments: _____

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APPENDIX C

STANDARD OPERATING PROCEDURE FOR PRODUCT SAMPLING

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Standard Operating Procedure: Drycleaner product sample collection

Revised: 22 October 2012

Preparation:

Print out latest versions of “Shops for sampling.xlsx” and “Sample_tracking.xlsx”.

Print out maps to locations or program GPS/Smartphone

Equipment:

Tyvek lab coat

Safety glasses

Nitrile gloves

Clipboard

Pen

Sharpie

Sample labels

Ziploc bags

Paper towels/pads

Sample vials- Screw-capped amber glass vials from Friedman and Bruya

Pipettes- disposable glass 25ml

Scissors

Product Sample Form

Cooler

Ice packs

5-gallon bucket containing trash bags

Camera

Wheeled cart (if room in vehicle)

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. Complete chain of custody form and retain a copy.

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

APPENDIX D

**STANDARD OPERATING PROCEDURE FOR STILL
BOTTOM SAMPLING**

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Standard Operating Procedure: Still Bottoms sample collection
Revised: 07 November 2012

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- 8 oz I_CHEM jars
Scissors
Questionnaire
Cooler
Ice packs
Stainless steel ladle
Stainless steel pitcher

Procedure:

7. Obtain sampling kit from Friedman and Bruya
8. Put on all PPE
9. Label sample jars
10. Collect 1-3 oz sample of still bottoms with the stainless steel ladle and pour into pitcher
 Still Bottoms are not homogenous- stir the sample or pour back and forth between two vessels to ensure that all jars have similar consistency.
11. Firmly screw on the sample jar caps and place in a Ziploc bag
12. Place the samples in the cooler with the ice
13. Handle with care- avoid shaking/turning upside down, etc.
14. Wipe the dipper with a paper towel and place in the container with other waste.
15. Transport samples to Friedman & Bruya and KCEL as soon as possible.
16. Complete chain of custody form and retain a copy.

Labeling:

3. 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
4. Label the Ziploc bag with initials and the date

APPENDIX E

STANDARD OPERATING PROCEDURE FOR SEPARATOR WATER SAMPLING

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Standard Operating Procedure: Separator Water sample collection
Revised: 20 September 2012

Equipment:

- Lab coat
- Safety glasses
- Nitrile gloves
- Clipboard
- Sample info sheets
- Pen
- Sharpie
- Sample labels
- Ziploc bags
- Paper towels/absorbent pads
- Sample containers:
 - 3 - 40 ml VOA vials for VOC analysis
 - 2 - 500 ml amber bottle for halogen analysis, pH, and flash point
 - 1 - 500 ml amber bottle with H₂SO₄ preservation for FOG analysis
 - 1 - 250ml HDPE bottle with HNO₃ preservation for metals analysis
 - 1 - 250 ml I-Chem jar for fish toxicity testing
- Glass funnel
- Pipettes- disposable glass 25ml
- Scissors
- Questionnaire
- Cooler
- Ice packs
- Stainless steel pitcher (1 L)

Procedure:

1. Obtain sample containers from Friedman and Bruya.
2. Put on PPE.
3. Label sample containers (see below).
4. Fill VOA vials with glass pipette by ejecting the liquid from the pipette gently down the side of the vial to reduce introduction of air into the sample. Fill the sample vial to the top.
5. Collect large volume (250-500 ml) samples with the stainless steel pitcher and glass funnel.
6. Firmly screw on the container caps and place samples in a Ziploc bag.
7. Place the samples in the cooler with the ice.
8. Transport samples to Friedman & Bruya and KCEL as soon as possible.
9. Complete chain of custody form and retain a copy.

Labeling:

Label sample containers as follows: XXMMDDYY_##_WSS

Where:

- i. XX= Sampler's initials
- ii. ##= Drycleaner shop number
- iii. W= separator water
- iv. SS= Sample number

APPENDIX F
WASTE SAMPLING FORM

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WASTE SAMPLE

Business name / City: _____

Date sampled: _____

Sampled by: _____

Waste sampled: _____

Sample #: _____

Comments: _____

Business name / City: _____

Date sampled: _____

Sampled by: _____

Waste sampled: _____

Sample #: _____

Comments: _____

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APPENDIX G

PRODUCTS IDENTIFIED IN SHOPS

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| Table G-1. Products used in hydrocarbon shops | | | | | | | | | | | | | |
|--|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Products | Shop 02 | Shop 03 | Shop 04 | Shop 05 | Shop 06 | Shop 07 | Shop 08 | Shop 09 | Shop 10 | Shop 11 | Shop 16 | Shop 17 | Shop 18 |
| Detergents | | | | | | | | | | | | | |
| Adco C-300 detergent | | X | | | | | | | | | | | |
| Adco Dyanite Xtra detergent | | | | | | | | | X | | | | |
| Answer UHD ex detergent | | | | | | | | | | X | | | |
| Bigen HC detergent | | | | | | | | X | | | | | |
| CPS Hydroinject detergent* | | | | | | | X | | | | | | |
| New Green Solutions detergent | | | | X | | | | | | | | | |
| Sanitone Performance detergent 8916 | X | | | | | | | | | | | | |
| Street's Pinnacle detergent | | | X | | X | X | | | | | X | X | X |
| Sizing agents | | | | | | | | | | | | | |
| Adco Texture Life sizing | | X | | | | | | | | | | | |
| Sanitone Injection sizing 8851 | X | | | | | | | | | | | | |
| Spot cleaners | | | | | | | | | | | | | |
| Adco Blood & Protein Remover (BPR) | | | | | X | | | | | | | | |
| Adco Easy Out | | | | | X | | | | | | | | |
| Adco Hydro Spot | | | | | X | | | | X | | | | |
| Adco Knock Out (Ink Remover) | X | | | | | | | | | | | | |
| Adco-Laidlaw Pull-Out Premium-V | | X | | | | | | | | | | | |
| Adco SpeedDee 7 | | | | | X | | | | | | | | |
| Caled RX Hydroclene POG | | | | | | | | X | | | | | |
| Forrest Paint Amyl Acetate | X | X | | | | | | | | | | | |
| Kreussler Prenett CS | | | | | | | | | | X | | | |
| Laidlaw Hydrocarbon Leveling Agent | | | | | | | | | X | | | | |
| Laidlaw Hydrocarbon Wetspo | | | | X | | | | | | | | | |
| Ramsey Scram Blood | | | | X | | | | | | | | | |
| Stamford POG | X | | | | | | | | | | | | |
| Street's MultiSpot | | X | | | | | | | | | | | |
| Street's NuTec Pyratex | | | | | | X | | | | | | | |
| Street's Picrin | X | X | X | | | | | | | | | | |

| Table G-1. Products used in hydrocarbon shops | | | | | | | | | | | | | |
|--|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Products | Shop 02 | Shop 03 | Shop 04 | Shop 05 | Shop 06 | Shop 07 | Shop 08 | Shop 09 | Shop 10 | Shop 11 | Shop 16 | Shop 17 | Shop 18 |
| Street's Pyratex | | X | X | | | | | | | | | | |
| Street's Spotless | | | X | | | | X | | | | | | |
| Street's StreePro | | | X | | | | | | | | X | | |
| Street's StreeTex | | | | | | | | X | | | | | |
| Wilson Bongo Speed Spotter | | | | | X | | | | | | | | |
| Wilson InkGo** | | | | | | | X | | | | | | |
| Wilson QwikGo Speed Spotter | | | | | | | X | | | | | | |
| Wilson RustGo*** | | | X | | | | | | X | | | | |
| Wilson TarGo EF | | | | | | X | | | | | | | |
| <p>*Not sampled because container not accessible. **Not sampled because insufficient product available. ***Not sampled because reportedly comprised of ~12% hydrogen fluoride, with no organic chemical ingredients.</p> | | | | | | | | | | | | | |

| Table G-2. Products used in System K4™ shops | | | |
|---|--------------------|--------------------|--------------------|
| Products | Shop 01 | Shop 14 | Shop 19 |
| Detergents | | | |
| Kreussler Clip K4 | X | X | X |
| Spot cleaners | | | |
| Kreussler Desprit Professional 2 / Green | | X | |
| Kreussler Desprit Professional 4 / White | | X | |
| Kreussler Desprit Professional 6 / Purple | | X | |
| Kreussler Prenett K4 | X | X | X |
| Kreussler Solvon K4 | | X | X |
| Other | | | |
| Kreussler Peramon Acid Binding and Disinfecting Agent | | X | |

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APPENDIX H

**STILL BOTTOM DATA FOR HYDROCARBON DRY
CLEANERS**

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| Analysis | SW021312-02-HC | SW021712-03-HC | SW050812-03-HC | JT021912-04-HC |
|-------------------------------|----------------|----------------|---------------------|----------------|
| TCLP Metals (mg/L) | | | | |
| Barium | 0.29 | NA | <0.2 | 0.34 |
| Cadmium | <0.02 | NA | <0.02 | <0.02 |
| Chromium | 0.09 | NA | 0.066 | 0.024 |
| Lead | <0.2 | NA | <0.2 | 0.74 |
| TCLP SVOCs (µg/L) | | | | |
| Phenol | <10 | NA | <830 | <50 |
| Naphthalene | 41 | NA | 210 | 93 |
| 2-Methylnaphthalene | 1.2 | NA | <170 | <5 |
| 1-Methylnaphthalene | <1 | NA | <170 | <5 |
| Dimethylphthalate | <10 | NA | <830 | <50 |
| Acenaphthylene | 16 | NA | <42 | <5 |
| Acenaphthene | <1 | NA | <42 | <5 |
| Diethylphthalate | 310 | NA | <830 | 2200 |
| 4-Nitroaniline | 62 | NA | <830 | <50 |
| Phenanthrene | <1 | NA | <42 | <5 |
| Di-n-butylphthalate | <10 | NA | 2100 | 94 |
| Fluoranthene | 3.4 | NA | <42 | <5 |
| Pyrene | <1 | NA | <42 | <5 |
| Butylbenzylphthalate | <10 | NA | <830 | <50 |
| bis-2-Ethylhexyladipate | <50 | NA | <4200 | <250 |
| Benzo[a]anthracene | 0.28 | NA | 7.7 | <0.5 |
| Chrysene | <0.1 | NA | <4.2 | <0.5 |
| bis(2-Ethylhexyl)phthalate | 67 | NA | 18,000 | 240 |
| Benzo[b]fluoranthene | <0.1 | NA | 33 | <0.5 |
| Benzo[j,k]fluoranthene | <0.1 | NA | 38 | <0.5 |
| Benzo[a]pyrene | 0.27 | NA | 22 | <0.5 |
| Indeno[1,2,3-cd]pyrene | <0.1 | NA | <4.2 | <0.5 |
| Dibenz[a,h]anthracene | <0.1 | NA | <4.2 | <0.5 |
| Benzo[g,h,i]perylene | <0.1 | NA | <4.2 | <0.5 |
| TCLP VOCs (µg/L) | | | | |
| Chloromethane | 130 | <500 | <100 | <100 |
| Acetone | <500 | <2500 | <500 | <500 |
| Trichloroethene | 26 | <100 | <20 | <20 |
| Other | | | | |
| pH | 4.96 | 5.77 | 6.8 | 6.09 |
| Flash point (°F) | 159 | 140 | <u>125</u> | 230 |
| Ext. Organic Halogens (ppm) | <u>150</u> | <u>220</u> | <u>150</u> | <u>210</u> |
| Fish toxicity (mg/L) | NA | NA | <u>100</u> | NA |
| Waste designation | | | | |
| Washington-specific (Ecology) | WP02 | WP02 | WP02/WT02 | WP02 |
| Federal (RCRA) | No | No | D001 | No |
| Summary | WA only | WA only | WA & Fed | WA only |

| Analysis | SW022712-05-HC | SW022712-06-HC | SW050712-06-HC |
|-------------------------------|---------------------|---------------------|----------------|
| TCLP Metals (mg/L) | | | |
| Barium | <0.2 | NA | <0.2 |
| Cadmium | <0.02 | NA | <0.02 |
| Chromium | 0.027 | NA | 0.05 |
| Lead | <0.2 | NA | <0.2 |
| TCLP SVOCs (µg/L) | | | |
| Phenol | <10 | NA | <100 |
| Naphthalene | <1 | NA | <5 |
| 2-Methylnaphthalene | <1 | NA | <5 |
| 1-Methylnaphthalene | <1 | NA | <5 |
| Dimethylphthalate | <10 | NA | <100 |
| Acenaphthylene | 8.1 | NA | <5 |
| Acenaphthene | <1 | NA | <5 |
| Diethylphthalate | 86 | NA | 1300 |
| 4-Nitroaniline | <10 | NA | <100 |
| Phenanthrene | <1 | NA | <5 |
| Di-n-butylphthalate | 24 | NA | 150 |
| Fluoranthene | <1 | NA | <5 |
| Pyrene | <1 | NA | <5 |
| Butylbenzylphthalate | <10 | NA | <100 |
| bis-2-Ethylhexyladipate | <50 | NA | <500 |
| Benzo[a]anthracene | 0.15 | NA | 1.5 |
| Chrysene | <0.1 | NA | 1.1 |
| bis(2-Ethylhexyl)phthalate | 81 | NA | 2000 |
| Benzo[b]fluoranthene | <0.1 | NA | 1.6 |
| Benzo[j,k]fluoranthene | <0.1 | NA | <0.5 |
| Benzo[a]pyrene | <0.1 | NA | 1.1 |
| Indeno[1,2,3-cd]pyrene | <0.1 | NA | 1.3 |
| Dibenz[a,h]anthracene | <0.1 | NA | 1.1 |
| Benzo[g,h,i]perylene | <0.1 | NA | 0.9 |
| TCLP VOCs (µg/L) | | | |
| Chloromethane | <100 | NA | 250 |
| Acetone | <500 | NA | <500 |
| Trichloroethene | <20 | NA | <20 |
| Other | | | |
| pH | 5.32 | 6.34 | 6.4 |
| Flash point (°F) | <u>110</u> | <u>132</u> | 157 |
| Ext. Organic Halogens (ppm) | <u>210</u> | <u>680</u> | <u>130</u> |
| Fish toxicity | NA | NA | NA |
| Waste designation | | | |
| Washington-specific (Ecology) | WP02 | WP02 | WP02 |
| Federal (RCRA) | D001 | D001 | No |
| Summary | WA & Fed | WA & Fed | WA only |

| Analysis | SW030412-07-HC | SW030512-08-HC | SW021112-09-HC | SW042612-09-HC | SW021612-10-HC | SW052412-10-HC |
|-------------------------------|---------------------|----------------|----------------|----------------|---------------------|----------------|
| TCLP Metals (mg/L) | | | | | | |
| Barium | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 |
| Cadmium | <0.02 | <0.02 | <0.02 | 0.023 | <0.02 | <0.02 |
| Chromium | 0.065 | 0.21 | 0.26 | 0.072 | 0.024 | 0.031 |
| Lead | <0.2 | <0.2 | 0.27 | <0.2 | <0.2 | <0.2 |
| TCLP SVOCs (µg/L) | | | | | | |
| Phenol | <100 | <100 | <50 | <100 | <10 | <100 |
| Naphthalene | <1 | <1 | <10 | <1 | <1 | <10 |
| 2-Methylnaphthalene | <1 | 1.5 (B) | <10 | <1 | <1 | <10 |
| 1-Methylnaphthalene | <1 | 1 | <10 | <1 | <1 | <10 |
| Dimethylphthalate | <100 | <100 | <50 | <100 | <10 | <100 |
| Acenaphthylene | <1 | <1 | <10 | <10 | 9.5 | <10 |
| Acenaphthene | <1 | <1 | <10 | <10 | <1 | <10 |
| Diethylphthalate | 570 | 290 | 150 | 350 | 190 | 120 |
| 4-Nitroaniline | <100 | <100 | <50 | <100 | <10 | <100 |
| Phenanthrene | <1 | <1 | <10 | <10 | <1 | <10 |
| Di-n-butylphthalate | <100 | <100 | 540 | <100 | 31 | <100 |
| Fluoranthene | <1 | <1 | <10 | <10 | 1.3 | <10 |
| Pyrene | <1 | <1 | <10 | <10 | <1 | <10 |
| Butylbenzylphthalate | <100 | <100 | <50 | <100 | <10 | <100 |
| bis-2-Ethylhexyladipate | <500 | <500 | <250 | <500 | <50 | <500 |
| Benzo[a]anthracene | 0.33 | <0.1 | 9 | 0.27 | <0.1 | <1 |
| Chrysene | 0.19 | <0.1 | 1.2 | 0.24 | 0.21 | <1 |
| bis(2-Ethylhexyl)phthalate | 680 | <100 | 3800 | 450 | 110 | 160 |
| Benzo[b]fluoranthene | <0.1 | <0.1 | <1 | 1.3 | <0.1 | <1 |
| Benzo[j,k]fluoranthene | <0.1 | <0.1 | <1 | 0.41 | <0.1 | <1 |
| Benzo[a]pyrene | <0.1 | 0.24 | 2.6 | 0.54 | 0.18 | <1 |
| Indeno[1,2,3-cd]pyrene | <0.1 | <0.1 | <1 | <0.1 | <0.1 | <1 |
| Dibenz[a,h]anthracene | <0.1 | <0.1 | <1 | <0.1 | <0.1 | <1 |
| Benzo[g,h,i]perylene | <0.1 | <0.1 | <1 | <0.1 | <0.1 | <1 |
| TCLP VOCs (µg/L) | | | | | | |
| Chloromethane | <100 | <100 | <100 | <100 | <100 | <100 |
| Acetone | <500 | <500 | <500 | <500 | <500 | <500 |
| Trichloroethene | <20 | <20 | <20 | <20 | <20 | <20 |
| Other | | | | | | |
| pH | 6.28 | 6.75 | 5.86 | 5.9 | 5.96 | 6.4 |
| Flash point (°F) | <u>133</u> | 149 | 155 | NA | <u>120</u> | 145 |
| Ext. Organic Halogens (ppm) | <u>620</u> | <u>270</u> | <u>250</u> | 80 | <u>320</u> | 33 |
| Fish toxicity (mg/L) | NA | <u>100</u> | NA | NA | NA | <u>100</u> |
| Waste designation | | | | | | |
| Washington-specific (Ecology) | WP02 | WP02/WT02 | WP02 | No | WP02 | WT02 |
| Federal (RCRA) | D001 | No | No | -- | D001 | No |
| Summary | WA & Fed | WA only | WA only | -- | WA & Fed | WA only |

| Analysis | SW022312-11-HC | SW062512-16-HC | SW062912-17-HC | SW070612-18-HC |
|-------------------------------|---------------------|---------------------|---------------------|----------------|
| TCLP Metals (mg/L) | | | | |
| Barium | <0.2 | <0.2 | NA | <0.2 |
| Cadmium | 0.025 | 0.089 | NA | <0.02 |
| Chromium | 0.065 | 0.13 | NA | 0.045 |
| Lead | <0.2 | <0.2 | NA | <0.2 |
| TCLP SVOCs (µg/L) | | | | |
| Phenol | <10 | 28 | NA | <100 |
| Naphthalene | 2.3 | <5 | NA | <10 |
| 2-Methylnaphthalene | <1 | <5 | NA | <10 |
| 1-Methylnaphthalene | <1 | <5 | NA | <10 |
| Dimethylphthalate | <10 | 12 | NA | <100 |
| Acenaphthylene | 14 | 10 | NA | <10 |
| Acenaphthene | <1 | <5 | NA | <10 |
| Diethylphthalate | 160 | 140 | NA | 210 |
| 4-Nitroaniline | 140 | <10 | NA | <100 |
| Phenanthrene | <1 | <5 | NA | <10 |
| Di-n-butylphthalate | <10 | 52 | NA | 300 |
| Fluoranthene | <1 | <5 | NA | <10 |
| Pyrene | <1 | <5 | NA | <10 |
| Butylbenzylphthalate | <10 | 11 | NA | 110 |
| bis-2-Ethylhexyladipate | <50 | <50 | NA | <500 |
| Benzo[a]anthracene | <0.1 | 0.99 | NA | <5 |
| Chrysene | 0.1 | <0.5 | NA | 2 |
| bis(2-Ethylhexyl)phthalate | <10 | 510 B | NA | 2900 |
| Benzo[b]fluoranthene | <0.1 | <0.5 | NA | 3.0 |
| Benzo[j,k]fluoranthene | <0.1 | <0.5 | NA | 1.1 |
| Benzo[a]pyrene | 0.28 | <0.5 | NA | 3.3 |
| Indeno[1,2,3-cd]pyrene | <0.1 | <0.5 | NA | <1 |
| Dibenz[a,h]anthracene | <0.1 | <0.5 | NA | <1 |
| Benzo[g,h,i]perylene | <0.1 | <0.5 | NA | <1 |
| TCLP VOCs (µg/L) | | | | |
| Chloromethane | <100 | 60 | <100 | <100 |
| Acetone | <500 | 77 | <500 | <500 |
| Trichloroethene | <20 | <2 | <20 | <20 |
| Other | | | | |
| pH | 6.22 | 6.7 | 6.9 | 6.6 |
| Flash point (°F) | <u>120</u> | <u>75</u> | <u>107</u> | <u>107</u> |
| Ext. Organic Halogens (ppm) | <u>820</u> | 22 | 41 | 36 |
| Fish toxicity (mg/L) | NA | <u>100</u> | <u>100</u> | >100 |
| Waste designation | | | | |
| Washington-specific (Ecology) | WP02 | WT02 | WT02 | No |
| Federal (RCRA) | D001 | D001 | D001 | D001 |
| Summary | WA & Fed | WA & Fed | WA & Fed | Fed |

APPENDIX I

STILL BOTTOM DATA FOR SYSTEM K4™ DRY CLEANERS

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| Analysis | SW121611 -01-K4 | SW021012 -01-K4 | SW030212 -01-K4 | SW031612 -01-K4 | SW042712 -01-K4 |
|-------------------------------|--------------------|--------------------|---------------------|--------------------|--------------------|
| TCLP Metals (mg/L) | | | | | |
| Barium | 0.69 | <0.2 | 0.29 | NA | 0.3 |
| Cadmium | <0.02 | <0.02 | 0.032 | NA | <0.02 |
| Chromium | 0.25 | 0.15 | 0.19 | NA | 0.61 |
| Lead | 0.41 | <0.2 | <0.2 | NA | <0.2 |
| TCLP SVOCs (µg/L) | | | | | |
| Phenol | <600 | <600 | <100 | NA | <1000 |
| Naphthalene | <30 | <30 | <10 | NA | <100 |
| 2-Methylnaphthalene | <30 | <30 | <10 | NA | <100 |
| 1-Methylnaphthalene | <30 | <30 | <10 | NA | <100 |
| Dimethylphthalate | <600 | <600 | <100 | NA | <1000 |
| Acenaphthylene | 61 | 33 | <10 | NA | <100 |
| Acenaphthene | 290 | 110 | <10 | NA | 100 |
| Diethylphthalate | 650 | 660 | 450 | NA | <1000 |
| 4-Nitroaniline | <600 | <600 | <100 | NA | 2300 |
| Phenanthrene | <30 | <30 | <10 | NA | <100 |
| Di-n-butylphthalate | 3900 | 3400 | 1300 | NA | 1900 |
| Fluoranthene | <30 | <30 | <10 | NA | <100 |
| Pyrene | <30 | <30 | <10 | NA | <100 |
| Butylbenzylphthalate | <600 | <600 | <200 | NA | 1000 |
| bis-2-Ethylhexyladipate | <3000 | <3000 | <1000 | NA | <5000 |
| Benzo[a]anthracene | 9.5 | 15 | 4.5 | NA | 19 |
| Chrysene | 9.4 | 4.3 | <1 | NA | 13 |
| bis(2-Ethylhexyl)phthalate | 24,000 | 22,000 | 12,000 | NA | 25,000 |
| Benzo[b]fluoranthene | 28 | 15 | <1 | NA | 56 |
| Benzo[j,k]fluoranthene | 14 | 5.2 | <1 | NA | 56 |
| Benzo[a]pyrene | 14 | 17 | <1 | NA | 24 |
| Indeno[1,2,3-cd]pyrene | <3 | <3 | <1 | NA | <10 |
| Dibenz[a,h]anthracene | <3 | 4.3 | <1 | NA | <10 |
| Benzo[g,h,i]perylene | <3 | <3 | <1 | NA | <10 |
| TCLP VOCs (µg/L) | | | | | |
| Chloromethane | <250 | <500 | <250 | NA | <250 |
| Acetone | <1300 | <2500 | <1300 | NA | <1300 |
| Trichloroethene | <50 | <100 | <50 | NA | <50 |
| Other | | | | | |
| pH | 6.17 | 5.78 | 5.46 | 6.68 | 6.0 |
| Flash point (°F) | 172 | 176 | <u>110</u> | 169 | 150 |
| Ext. Organic Halogens (ppm) | <u>280</u> | <u>490</u> | <u>170</u> | <u>200</u> | <u>130</u> |
| Fish toxicity (mg/L) | NA | NA | <u>100</u> | <u>10</u> | <u>10</u> |
| Waste designation | | | | | |
| Washington-specific (Ecology) | WP02 | WP02 | WP02/WT02 | WP02/WT0 1 | WP02/WT0 1 |
| Federal (RCRA) | No | No | D001 | No | No |
| Summary | WA only | WA only | WA & Fed | WA only | WA only |

| Analysis | SW42012-14-K4 | SW052512-14-K4 | SW080212-19-K4 |
|-------------------------------|----------------|----------------|---------------------|
| TCLP Metals (mg/L) | | | |
| Barium | 0.35 | 0.28 | 0.31 |
| Cadmium | <0.02 | <0.02 | <0.020 |
| Chromium | 0.28 | 0.15 | 0.068 |
| Lead | <0.2 | <0.2 | 1.4 |
| TCLP SVOCs (µg/L) | | | |
| Phenol | <760 | <1000 | <1000 |
| Naphthalene | <150 | <100 | <100 |
| 2-Methylnaphthalene | <150 | <100 | <100 |
| 1-Methylnaphthalene | <150 | <100 | <100 |
| Dimethylphthalate | <760 | <1000 | <1000 |
| Acenaphthylene | <150 | <100 | <100 |
| Acenaphthene | <750 | 180 | 190 |
| Diethylphthalate | 890 | 1900 | <1000 |
| 4-Nitroaniline | <760 | <1000 | <1000 |
| Phenanthrene | <150 | <100 | 170 |
| Di-n-butylphthalate | 3300 | 7400 | 1700 |
| Fluoranthene | <150 | <100 | 290 |
| Pyrene | <150 | <100 | 150 |
| Butylbenzylphthalate | 2900 | 3000 | 1000 |
| bis-2-Ethylhexyladipate | <3800 | 46,000 | 30,000 |
| Benzo[a]anthracene | <75 | <10 | <10 |
| Chrysene | <15 | 14 | 49 |
| bis(2-Ethylhexyl)phthalate | 74,000 (B) | 91,000 | 31,000 |
| Benzo[b]fluoranthene | 61 | 180 | 110 |
| Benzo[j,k]fluoranthene | <15 | 30 | 120 |
| Benzo[a]pyrene | 20 | 43 | <10 |
| Indeno[1,2,3-cd]pyrene | <15 | <10 | <10 |
| Dibenz[a,h]anthracene | <15 | <10 | <10 |
| Benzo[g,h,i]perylene | <15 | <10 | <10 |
| TCLP VOCs (µg/L) | | | |
| Chloromethane | <250 | <250 | <250 |
| Acetone | <1300 | <1300 | <1300 |
| Trichloroethene | <50 | <50 | <50 |
| Other | | | |
| pH | 5.82 | 6.4 | 6.9 |
| Flash point (°F) | 175 | 150 | <u>134</u> |
| Ext. Organic Halogens (ppm) | 76 | 28 | <u>1830</u> |
| Fish toxicity (mg/L) | <u>10</u> | <u>10</u> | <u>10</u> |
| Waste designation | | | |
| Washington-specific (Ecology) | WT01 | WT01 | WPO2/WT01 |
| Federal (RCRA) | No | No | D001 |
| Summary | WA only | WA only | WA & Fed |

APPENDIX J

SEPARATOR WATER DATA FOR HYDROCARBON DRY CLEANERS

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| Analysis | SW021312-02-HC* | SW021712-03-HC | SW050812-03-HC** |
|---|-----------------|----------------|------------------|
| VOCs (µg/L) | | | |
| Tetrachloroethene | <100 | <200 | <100 |
| Acetone | 7000 | 2800 | <1000 |
| 2-Butanone | <1000 | <2000 | <1000 |
| 1,2,4-Trimethylbenzene | 200 | <200 | <100 |
| Trichloroethene | <u>13,000</u> | <200 | <100 |
| Methyl isobutyl ketone | 10,000 | <2000 | <1000 |
| 1,2-Dichlorobenzene | 140 | <200 | <100 |
| Toluene | 240 | <200 | <100 |
| Naphthalene | 150 | <200 | <100 |
| Isopropyl alcohol | 1,200,000 E | 42,000 | <10,000 |
| Ethanol | 480,000 | <100,000 | <100,000 |
| 2-Propanol, 2-methyl- | <5000 | <5000 | <5000 |
| VOC TICs (µg/L) ≥10,000 µg/L in one or more samples | | | |
| 1-Hexanol, 2-ethyl- | ND | ND | ND |
| Nonane, 3-methyl-5-propyl | ND | ND | ND |
| Octane, 2,4,6-trimethyl- | ND | ND | 12,000 |
| Hexane, 2,2,5-trimethyl- | ND | ND | 12,000 |
| Unknown | 14,000 | ND | ND |
| Other parameters | | | |
| pH | 5.97 | 7.44 | 7.55 |
| Oil & Grease – non-polar (mg/L) | NA | NA | <6 |
| Flash point (°F) | <u>138</u> | >210 | >210 |
| Total Organic Halogens (mg/L) | 12 | <5.0 | <5.0 |
| Fish toxicity (mg/L) | NA | NA | NA |
| KCIW discharge screening | Fail (TCE) | -- | Pass |
| Waste designation | | | |
| Washington-specific (Ecology) | No | No | No |
| Federal (RCRA) | D001 & D040 | No | No |
| Waste designation summary | Fed | No | No |
| *Sample SW021312-02-HC contained 23,000 µg/L of the VOC TIC, Acetic acid, pentyl ester. No other sample contained this TIC. | | | |
| **Sample SW050812-03-HC contained 11,000 µg/L of the VOC TIC, Nonane, 2,3-dimethyl. No other sample contained this TIC. | | | |

| Analysis | SW022712-06-HC (filtered) | SW051012-06-HC (filtered) | SW051412-06-HC (unfiltered) |
|--|---------------------------|---------------------------|-----------------------------|
| VOCs (µg/L) | | | |
| Tetrachloroethene | <10 | <10 | <20 |
| Acetone | <100 | 590 | 1900 |
| 2-Butanone | <100 | <100 | <200 |
| 1,2,4-Trimethylbenzene | <10 | <10 | 74 |
| Trichloroethene | <10 | <10 | 33 |
| Methyl isobutyl ketone | <100 | <100 | <200 |
| 1,2-Dichlorobenzene | <10 | <10 | <20 |
| Toluene | <10 | <10 | <20 |
| Naphthalene | <10 | <10 | <20 |
| Isopropyl alcohol | NA | <1000 | 2100 |
| Ethanol | NA | <10,000 | <20,000 |
| 2-Propanol, 2-methyl- | NA | <500 | <1000 |
| VOC TICs (µg/L) ≥10,000 µg/L in one or more samples | | | |
| 1-Hexanol, 2-ethyl- | ND | ND | ND |
| Nonane, 3-methyl-5-propyl | ND | ND | ND |
| Octane, 2,4,6-trimethyl- | ND | ND | ND |
| Hexane, 2,2,5-trimethyl- | 1100 | ND | ND |
| Unknown | ND | ND | ND |
| Other parameters | | | |
| pH | 6.92 | 6.48 | 6.67 |
| Oil & Grease – non-polar (mg/L) | 210 (Total) | <6 | 7.8 |
| Flash point (°F) | >210 | >210 | >210 |
| Total Organic Halogens (mg/L) | <5.0 | <5.0 | <5.0 |
| Fish toxicity (mg/L) | NA | NA | NA |
| KCIW discharge screening | -- | Pass | Pass |
| Waste designation | | | |
| Washington-specific (Ecology) | No | No | No |
| Federal (RCRA) | No | No | No |
| Waste designation summary | No | No | No |

| Analysis | SW030412-07-HC | SW030512-08-HC | SW021112-09-HC | SW042612-09-HC |
|--|----------------|----------------|----------------|----------------|
| VOCs (µg/L) | | | | |
| Tetrachloroethene | 15 | <10 | <100 | <100 |
| Acetone | 140 | 18,000 E | 5100 | 1600 |
| 2-Butanone | <100 | 230 | <1000 | <1000 |
| 1,2,4-Trimethylbenzene | <10 | <10 | <100 | <100 |
| Trichloroethene | <10 | <10 | <100 | <100 |
| Methyl isobutyl ketone | <100 | 240 | <1000 | <1000 |
| 1,2-Dichlorobenzene | <10 | <10 | <100 | <100 |
| Toluene | <10 | <10 | <100 | <100 |
| Naphthalene | <10 | <10 | <100 | <100 |
| Isopropyl alcohol | <1000 | 6100 | 1,700,000 E | 56,000 E |
| Ethanol | <10,000 | <10,000 | <100,000 | <100,000 |
| 2-Propanol, 2-methyl- | <500 | 1000 | <5000 | <5000 |
| VOC TICs (µg/L) ≥10,000 µg/L in one or more samples | | | | |
| 1-Hexanol, 2-ethyl- | 460 | ND | ND | 37,000 |
| Nonane, 3-methyl-5-propyl | ND | ND | ND | ND |
| Octane, 2,4,6-trimethyl- | ND | ND | ND | ND |
| Hexane, 2,2,5-trimethyl- | ND | ND | ND | ND |
| Unknown | ND | ND | 22,000 | ND |
| Other parameters | | | | |
| pH | 5.71 | 6.12 | 6.93 | 7.61 |
| Oil & Grease – non-polar (mg/L) | 49 (Total) | <6 (Total) | NA | <6 |
| Flash point (°F) | >210 | >210 | >210 | >210 |
| Total Organic Halogens (mg/L) | <5.0 | 6.1 | <5.0 | <5.0 |
| Fish toxicity (mg/L) | NA | >100 | NA | NA |
| KCIW discharge screening | Pass | Pass | -- | Pass |
| Waste designation | | | | |
| Washington-specific (Ecology) | No | No | No | No |
| Federal (RCRA) | No | No | No | No |
| Waste designation summary | No | No | No | No |

| Analysis | SW021612-10-HC | SW052412-10-HC | SW022312-11-HC |
|--|----------------|----------------|----------------|
| VOCs (µg/L) | | | |
| Tetrachloroethene | <10 | <10 | <10 |
| Acetone | 1800 | 1900 | 2200 |
| 2-Butanone | <100 | 100 E | 200 |
| 1,2,4-Trimethylbenzene | <10 | <10 | <10 |
| Trichloroethene | <10 | <10 | <10 |
| Methyl isobutyl ketone | <100 | <100 | <100 |
| 1,2-Dichlorobenzene | <10 | <10 | <10 |
| Toluene | <10 | <10 | <10 |
| Naphthalene | <10 | <10 | <10 |
| Isopropyl alcohol | <1000 | 900 E | NA |
| Ethanol | <10,000 | <10,000 | NA |
| 2-Propanol, 2-methyl- | <500 | <500 | 980 |
| VOC TICs (µg/L) ≥10,000 µg/L in one or more samples | | | |
| 1-Hexanol, 2-ethyl- | ND | ND | 5000 |
| Nonane, 3-methyl-5-propyl | ND | 1300 | ND |
| Octane, 2,4,6-trimethyl- | ND | 330 | ND |
| Hexane, 2,2,5-trimethyl- | ND | ND | ND |
| Unknown | ND | ND | ND |
| Other parameters | | | |
| pH | 6.71 | 6.66 | 6.65 |
| Oil & Grease – non-polar (mg/L) | NA | <6 | NA |
| Flash point (°F) | >210 | >210 | >210 |
| Total Organic Halogens (mg/L) | <5.0 | <1.0 | <5.0 |
| Fish toxicity (mg/L) | NA | NA | NA |
| KCIW discharge screening | -- | Pass | -- |
| Waste designation | | | |
| Washington-specific (Ecology) | No | No | No |
| Federal (RCRA) | No | No | No |
| Waste designation summary | No | No | No |

| Analysis | SW062512-16-HC | SW070612-17-HC* | SW071112-18-HC |
|---|----------------|-----------------|----------------|
| VOCs (µg/L) | | | |
| Tetrachloroethene | <10 | <100 | <100 |
| Acetone | 2700 E | 1300 | 2300 |
| 2-Butanone | <100 | <1000 | <1000 |
| 1,2,4-Trimethylbenzene | <10 | <100 | <100 |
| Trichloroethene | <10 | <100 | <100 |
| Methyl isobutyl ketone | <100 | <1000 | <1000 |
| 1,2-Dichlorobenzene | <10 | <100 | <100 |
| Toluene | <10 | <100 | <100 |
| Naphthalene | <10 | <100 | <100 |
| Isopropyl alcohol | 520 | <1000 | <1000 |
| Ethanol | <10,000 | <100,000 | <100,000 |
| 2-Propanol, 2-methyl- | 690 | <5000 | <5000 |
| VOC TICs (µg/L) ≥10,000 µg/L in one or more samples | | | |
| 1-Hexanol, 2-ethyl- | 540 | ND | ND |
| Nonane, 3-methyl-5-propyl | ND | 20,000 | ND |
| Octane, 2,4,6-trimethyl- | ND | ND | ND |
| Hexane, 2,2,5-trimethyl- | ND | ND | ND |
| Unknown | ND | ND | ND |
| Other parameters | | | |
| pH | 7.43 | 6.57 | 6.18 |
| Oil & Grease – non-polar (mg/L) | <6 | 81 | <6 |
| Flash point (°F) | >210 | >210 | >210 |
| Total Organic Halogens (mg/L) | <1.0 | 15 | <1.0 |
| Fish toxicity (mg/L) | >100 | >100 | >100 |
| KCIW discharge screening | Pass | Pass | Pass |
| Waste designation | | | |
| Washington-specific (Ecology) | No | No | No |
| Federal (RCRA) | No | No | No |
| Waste designation summary | No | No | No |
| *Sample SW070612-17-HC contained 16,000 µg/L of the VOC TIC, Heptadecane. No other sample contained this TIC. | | | |

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APPENDIX K

**SEPARATOR WATER DATA FOR SYSTEM K4™ DRY
CLEANERS**

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| Analysis | SW121611-01-K4 (unfiltered) | SW021012-01-K4 (unfiltered) | SW031212-01-K4 (unfiltered) | SW031212-01-K4 (filtered) | SW042712-01-K4 (filtered) | SW042712-01-K4 (unfiltered) |
|--|-----------------------------|-----------------------------|-----------------------------|---------------------------|---------------------------|-----------------------------|
| VOCs (µg/L) | | | | | | |
| Tetrachloroethene | <100 | <100 | <10 | <10 | <10 | <100 |
| Acetone | 1700 | 1300 | 1400 | 680 | 1500 | 2600 |
| 2-Butanone | <1000 | <1000 | <100 | <100 | 140 | <1000 |
| 1,2,4-Trimethylbenzene | <100 | <100 | <10 | <10 | <10 | <100 |
| Trichloroethene | <100 | <100 | <10 | <10 | <10 | <100 |
| Methyl isobutyl ketone | <1000 | <1000 | <100 | <100 | <100 | <1000 |
| 1,2-Dichlorobenzene | <100 | <100 | <10 | <10 | <10 | <100 |
| Toluene | <100 | <100 | <10 | <10 | <10 | <100 |
| Naphthalene | <100 | <100 | <10 | <10 | <10 | <100 |
| Isopropyl alcohol | 140,000 E | 18,000 | 130,000 E | 31,000 E | 190,000 E | 200,000 E |
| Ethanol | NA | <100,000 | <10,000 | <10,000 | <10,000 | <100,000 |
| 2-Propanol, 2-methyl- | NA | <5000 | NA | NA | <500 | <5000 |
| VOC TICs (µg/L) ≥10,000 µg/L in one or more samples | | | | | | |
| Methanol, dibutoxy- | 140,000 E | ND | ND | 1400 | ND | ND |
| Morpholine | ND | 210,000 | ND | ND | ND | 200,000 |
| Butane, 1-(1-bromo-1-methylethoxy)- | ND | ND | ND | ND | 37,000 | ND |
| Furan, 2-propyl- | 41,000 J | ND | ND | ND | ND | ND |
| 1-Butanol | ND | 14,000 | 6100 | 7000 | 6100 | 11,000 |
| 1-Hexanol, 2-ethyl- | ND | ND | ND | ND | 520 | ND |
| Unknown | ND | ND | 80,000 | 62,000 | ND | ND |
| Other parameters | | | | | | |
| pH | NA | 6.99 | 7.00 | 6.64 | 6.57 | 7.23 |
| Oil & Grease – non-polar (mg/L) | NA | NA | 57 (Total) | 49 (Total) | <6 | <6 |
| Flash point (°F) | NA | >210 | >210 | >210 | >210 | >210 |
| Total Organic Halogens (mg/L) | NA | <5.0 | <5.0 | <5.0 | <5.0 | <5.0 |
| Fish toxicity (mg/L) | NA | NA | >100 | >100 | >100 | >100 |
| KCIW discharge screening | -- | -- | Pass | Pass | Pass | Pass |
| Waste designation | | | | | | |
| Washington-specific (Ecology) | No | No | No | No | No | No |
| Federal (RCRA) | No | No | No | No | No | No |
| Waste designation summary | No | No | No | No | No | No |

| Analysis | SW042012-14-K4 | SW052512-14-K4 | SW080212-19-K4 |
|--|----------------|----------------|----------------|
| VOCs (µg/L) | | | |
| Tetrachloroethene | <10 | <20 | <100 |
| Acetone | 1400 | 1900 | 3600 |
| 2-Butanone | <100 | <200 | <1000 |
| 1,2,4-Trimethylbenzene | <10 | <20 | <100 |
| Trichloroethene | <10 | <20 | <100 |
| Methyl isobutyl ketone | <100 | <200 | <1000 |
| 1,2-Dichlorobenzene | <10 | <20 | <100 |
| Toluene | <10 | <20 | <100 |
| Naphthalene | <10 | <20 | <100 |
| Isopropyl alcohol | 150,000 E | 290,000 E | 410,000 E |
| Ethanol | <10,000 | <20,000 | <100,000 |
| 2-Propanol, 2-methyl- | <500 | <1000 | <5000 |
| VOC TICs (µg/L) ≥10,000 µg/L in one or more samples | | | |
| Methanol, dibutoxy- | ND | ND | 140,000 |
| Morpholine | 120 | ND | ND |
| Butane, 1-(1-bromo-1-methylethoxy)- | 49,000 | ND | ND |
| Furan, 2-propyl- | ND | ND | 29,000 |
| 1-Butanol | 5800 | ND | ND |
| 1-Hexanol, 2-ethyl- | ND | ND | ND |
| Unknown | ND | 84,000 | ND |
| Other parameters | | | |
| pH | 7.68 | 7.33 | 6.30 |
| Oil & Grease – non-polar (mg/L) | <6 | <6 | <3 |
| Flash point (°F) | >210 | >210 | >210 |
| Total Organic Halogens (mg/L) | <5.0 | <1.0 | 2.7 |
| Fish toxicity (mg/L) | >100 | NA | >100 |
| KCIW discharge screening | Pass | Pass | Pass |
| Waste designation | | | |
| Washington-specific (Ecology) | No | No | No |
| Federal (RCRA) | No | No | No |
| Waste designation summary | No | No | No |
| | | | |

APPENDIX L

DATA PLOTS AND STATISTICAL ANALYSES FOR SELECT ANALYTES IN STILL BOTTOMS

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