Local Hazardous Waste Management Program in King County, Washington

LHWMP_0247
October 2015

Final Report

Aquatic Toxicity of PERC Still Bottom Wastes: A Pilot Study

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This report was prepared by the Local Hazardous Waste Management Program in King County (LHWMP), Washington, a coalition of local governments. Our customers are residents, businesses and institutions with small quantities of hazardous wastes. LHWMP'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.

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Publication Number LHWMP_0247

Whittaker, Stephen G. *Aquatic Toxicity of PERC Still Bottom Wastes: A Pilot Study.* Seattle, WA: Local Hazardous Waste Management Program in King County, 2015.

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ACRONYMS AND ABBREVIATIONS

DW	Dangerous Waste
Ecology	Washington State Department of Ecology
EHW	Extremely Hazardous Waste
LHWMP	Local Hazardous Waste Management Program in King County
mg/L	Milligrams per liter
PERC	Perchloroethylene
ppm	Parts per million
QAPP	Quality Assurance Project Plan
TCE	Trichloroethylene
WAC	Washington Administrative Code

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EXECUTIVE SUMMARY

Although perchloroethylene (PERC) is used as a solvent by most dry cleaners in King County, the still bottom wastes from PERC machines have not been fully evaluated according to Washington state-only waste designation criteria.

The goal of this pilot study was to: 1) evaluate the aquatic toxicity of PERC still bottoms and 2) assign waste codes according to state-only toxicity criteria.

Still bottom samples were collected from four dry cleaners that used PERC dry cleaning machines. One sample elicited 7 percent fish survival at 10 mg/L and 0 percent survival at 100 mg/L. Consequently, this sample was Extremely Hazardous Waste (EHW, waste code WT01).

For the remaining three samples, fish survival was 100 percent at 10 mg/L and 0 percent at 100 mg/L. Therefore, these samples were Dangerous Waste (DW/WT02).

The results of this pilot study suggest that the toxicity of still bottoms varies from shop-to-shop. This variability may reflect varying concentrations of PERC and other toxic constituents, such as detergents, spot cleaners, other additives, and material extracted from the cleaned fabrics.

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INTRODUCTION

In 2010, the Local Hazardous Waste Management Program in King County (LHWMP) conducted a survey of the dry cleaning industry, which revealed that 69 percent of the approximately 200 dry cleaners in King County were using PERC as their primary cleaning solvent.[1,2]

LHWMP subsequently designated the wastes generated by dry cleaners that use alternative solvents to PERC: hydrocarbon (Exxon Mobil DF2000™) and acetal (Kreussler Solvon K4™).[3] At a meeting with the Washington State Department of Ecology (Ecology) personnel to discuss these results (December 2013), it became apparent that Ecology was not aware of any fish toxicity data for the still bottoms from PERC dry cleaning operations. Consequently, this waste stream had never been fully designated.

This pilot study was designed in partnership with Ecology to help evaluate the toxicity of still bottom wastes generated by PERC dry cleaners.

Dry cleaning procedures and generation of still bottoms

A detailed description of the dry cleaning process and the hazards associated with using PERC in dry cleaning is presented in LHWMP's report, *A Profile of the Dry Cleaning Industry in King County, Washington*.[1]

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 typically aqueous products that are used to remove water soluble stains from clothing. Dry-side agents are generally based on non-aqueous solvents and alcohols, and may include chlorinated solvents like trichloroethylene (TCE). These products are used to remove stains comprised of oils, fats, waxes, grease, cosmetics, paints, and plastics.[4] Fabrics may also be "post-spotted" with many of the same products if the dry cleaning process fails to remove stains.

Fabrics are then sorted by color and fabric type, placed in the drum of the dry cleaning machine, and the drum door is closed. Dry cleaning solvent and detergent are then introduced to the drum and the fabrics are agitated in this mixture. Once the washing cycle is complete, the machine enters a drying cycle that involves blowing hot air into the fabrics. In modern dry cleaning machines, the heated solvent vapors pass through a refrigerated condenser, which cools the air and condenses the solvent vapor for recovery. Recovered solvent is then pumped into a vacuum still, which is integral to the dry cleaning machine. Steam coils in the still transfer heat to the solvent, causing it to boil. This distillation process prevents impurities from building up in the solvent. The semi-solid material generated from the distillation process is referred to as "still bottoms." A process diagram is presented in Figure 1.

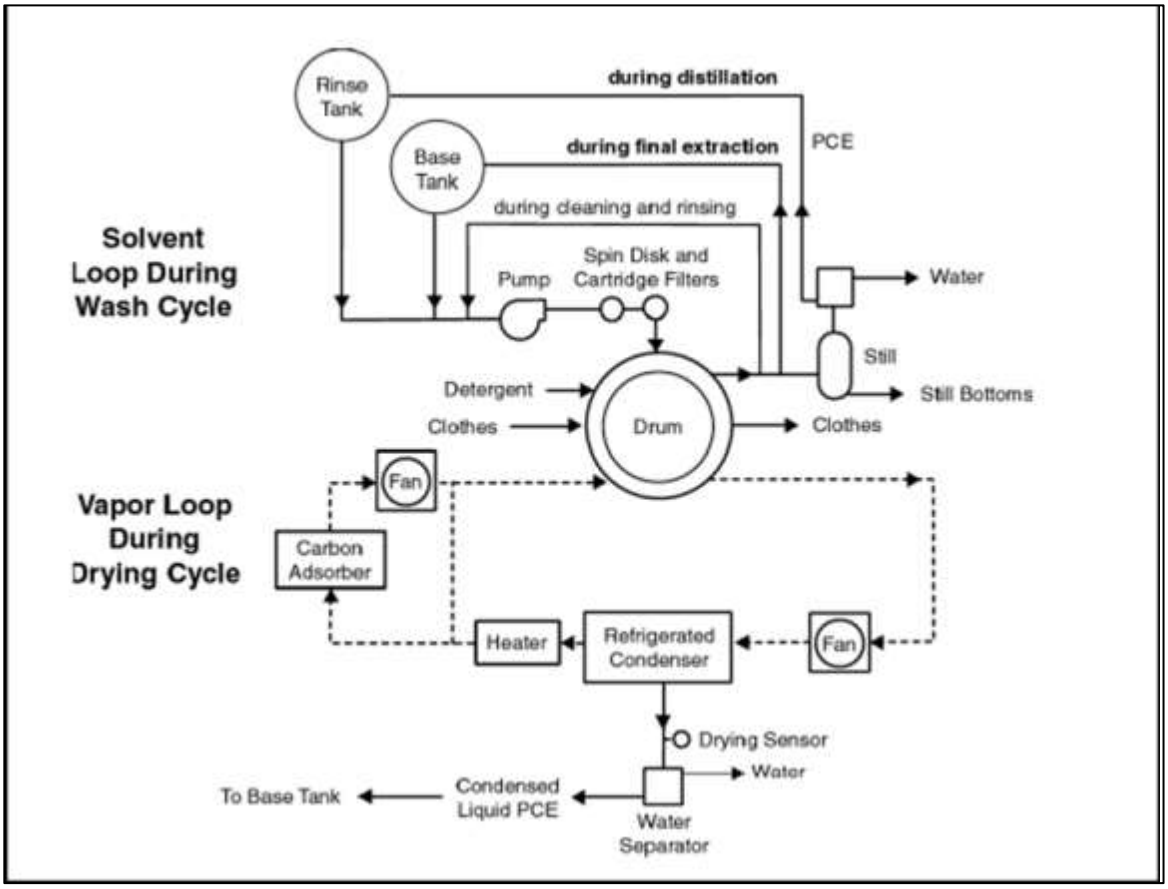

Figure 1. Simplified dry cleaning process diagram

The still bottoms contain residual solvents from spot cleaners and the washing solvent (such as PERC and TCE) in addition to non-volatile components, such as detergent, waxes, oils, and greases. After the machine has cooled (usually overnight), the operator transfers the still bottoms to 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. Each still bottom cleaning generates at least 5 to 10 pounds of still bottom material.

Note that a second waste stream, called "separator water", is also generated by the dry cleaning machine. Although separator water may also contain residual dry cleaning solvent and other process chemicals, this aqueous waste stream is not being considered in this current investigation.

Dangerous waste designation

The term "dangerous waste" encompasses federally-regulated "hazardous wastes" and those identified as dangerous waste only by Washington state's regulations.[5] Washington state 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 be regarded as dangerous waste. The definition of hazardous

waste, based on the Resource Conversation and Recovery Act (RCRA), is presented in Title 40 of the Code of Federal Regulations (CFR), Part 261 and is incorporated into Washington State Code (WAC) Title 173 Chapter 303 (WAC 173-303). In Washington state, generators must follow these federal rules and additional state-only rules.[5] Washington state's dangerous waste regulations are more stringent than the federal hazardous waste rules, and include "state-only" toxicity and persistence criteria.

Generators must determine whether their wastes are dangerous wastes as described in WAC 173-303-070. If the waste is dangerous waste, it is assigned an appropriate "waste code" and identified as either DW or EHW.

As discussed with Ecology personnel, this pilot study focuses solely on state-only toxicity; the toxicity of still bottom material was tested in juvenile rainbow trout according Ecology's *Biological Testing Methods for the Designation of Dangerous Waste*.[6]

Current study

To address the questions about the toxicity of PERC still bottom wastes, the goals of this pilot study were to: 1) evaluate the aquatic toxicity of PERC still bottoms and 2) designate the wastes according to state-only toxicity criteria.

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METHODS

Sampling procedures conformed to the *Quality Assurance Project Plan (QAPP): Characterizing the Still Bottoms from Perchloroethylene (PERC) Dry Cleaning Machines*. This document was prepared in cooperation with Ecology personnel and is included as Exhibit A.

Shop recruitment

Introductions to three dry cleaning business owners were made by a representative of the Korean Dry Cleaners Association. A survey conducted by LHWMP revealed that the majority of dry cleaning businesses in King County are owned by individuals of Korean ancestry.[1,2] One English-speaking business was recruited by a local vendor to the dry cleaning industry.

In order to arrange the field sampling visits to Korean businesses, a Korean interpreter contacted the business owners via telephone and explained the purpose of the study. The interpreter arranged for the sampling visit to take place when the dry cleaner typically cleaned their still. Telephone calls to the English-speaking dry cleaner were made by LHWMP staff.

Sampling visits

LHWMP staff collected samples of still bottom wastes from these four local dry cleaners in May and June, 2015.

The interpreter accompanied LHWMP staff to the Korean-owned businesses on the day of sampling to assist with administration of questions and ensure reliable communication during the sampling.

Questionnaire administration

A questionnaire was then administered verbally and covered establishment history, machine specifications and history, waste disposal practices, and product usage. The questions were derived from a survey that had been administered previously to dry cleaners.[1] The questionnaire was modified from the version presented in the QAPP and is presented as Exhibit B.

Still bottom sampling

Sampling procedures are described in the QAPP (Exhibit A). The still bottoms are typically comprised of a relatively light liquid fraction and a heavier semi-solid fraction. Because the objective of the sampling was to retrieve a representative sample, the two fractions were combined in the sample container in the same approximate proportions as existed in the still. Samples of the two fractions were also collected individually (in separate sample containers) for future analysis.

Fish bioassays

Fish toxicity tests were conducted on samples of still bottoms according to Ecology's *Biological Testing Methods for the Designation of Dangerous Waste*[6] by the King County Environmental Laboratory (Seattle, WA). This test involved exposing juvenile rainbow trout to still bottom wastes for 96 hours at two concentrations (10 mg/L and 100 mg/L) in a "non-renewal" static acute fish toxicity bioassay (i.e., Part A: Method 80-12). The laboratory technician was instructed to ensure that the sample was well-mixed prior to preparation.

Waste codes

The results of the fish bioassay were evaluated according to the criteria presented in Table 1. Note that this is a simplified representation; State-only designation can only be determined following statistical analysis where fish survival is <100 percent in the control group and/or >0 percent in the test group, as described in *Biological Testing Methods for the Designation of Dangerous Waste*.[6]

Table 1. Evaluation criteria for the fish bioassay

Survival at 10 mg/L	Survival at 100 mg/L	Waste code
100%	100%	None
100%	0%	DW (WT02)
0%	0%	EHW (WT01)

RESULTS

Shop characteristics

The results of the questionnaire administered at the shops are summarized in Table 2. Questions were answered by male shop owners, three of whom were Korean and the fourth was Caucasian. The most relevant findings were:

- Still bottoms were typically removed from the machine twice a month. One shop (Shop 03) cleaned their still 3-4 times per month.
- Still bottoms were removed on a Saturday, after the machine had been switched off and allowed to cool overnight.
- All cleaners used a variety of spot cleaning products. Shops 01 and 02 only applied spot cleaners before fabrics were dry cleaned ("pre-spotting"). Shop 04 only spot-cleaned fabrics after they were cleaned ("post-spotting"). Shop 03 spot-cleaned both pre- and post- dry cleaning.

Fish bioassay

The fish bioassay results are presented in Table 3. The original laboratory reports are presented in Exhibits C through E.

Note that the sample labelled as "01A", which was collected from Shop 01, was retrieved from a 5-gallon waste drum located on the shop floor. Although the shop owner stated that this drum contained only still bottom waste, further inspection revealed that it contained a mixture of separator water and still bottoms. Sample 01B was collected during a return field visit, and was taken directly from the still while the shop owner removed the still bottoms. The samples collected from Shops 02, 03, and 04 were also taken directly from the still during clean-out.

With the exception of the sample collected from Shop 02, the samples were DW (WT02), based on 100 percent fish survival at 10 mg/L and 0 percent survival at 100 mg/L.

The sample collected from Shop 02 elicited 7 percent fish survival at 10 mg/L and 0 percent survival at 100 mg/L. To determine whether fish mortality at 10 mg/L was significantly different from the control, a statistical analysis was conducted according to *Biological Testing Methods for the Designation of Dangerous Waste*.[6] The variance ratio F-test was used to determine whether the variances were equal in the control vs. the test group (i.e., 10 mg/L). Because the variance in the control group was 0 (based on zero fish mortality), the variances were unequal. Therefore, the modified one-tailed t-test was applied. The calculated t-statistic (6.503) exceeded the critical t-value (-1.886) [$t(2)=6.503$, $p>0.10$] and the null hypothesis was accepted: LC50 < 10 mg/L; the waste is EHW (WT01). The statistical evaluation is presented in Exhibit C.

Table 2. Shop characteristics

Question	Shop 01	Shop 02	Shop 03	Shop 04
Demographics of site guide	Male/Korean	Male/Korean	Male/Korean	Male/Caucasian
Site guide title	Shop owner	Shop owner	Shop owner	Shop owner
No. years a dry cleaner at this location	30	22	>15	60
Machine manufacturer	Bowe Permac	Bowe Permac	Realstar	Bowe Permac
Machine model	P25	P536	M340	P25
Machine capacity (lbs.)	55	35	40	55
No. loads run per week	25	18	15	20
Age of machine (years)	25	23	8	16
Bought the machine new?	No	No	Yes	Yes
No. years current owner has had the machine	5	14	8	16
Who cleans out the still bottoms?	Shop owner	Shop owner	Shop owner or employee	Shop owner
No. times per month still bottoms are cleaned out	2	3.5	2	2
PPE used when cleaning out still bottoms	None	Gloves, dust mask	None	Gloves
When are the still bottoms removed?	Saturday afternoon	Saturday morning	Saturday morning	Saturday morning
Still bottoms disposal	Transferred to 5 gal. container and self-transported to HHW facility	Transferred to 5 gal. container and then 30 gal. drum. Disposed of by vendor	Transferred to 30 gal. drum. Disposed of by vendor	Transferred to 30 gal. drum. Disposed of by vendor
Separator water disposal	Transferred to 5 gal. container with still bottoms and self-transported to HHW facility	Transferred to 30 gal. drum with still bottoms	Filtered in a ZeroWaste machine and then evaporated indoors	Placed in cooling tower
EnviroStars business/number of stars?	Yes - 3	Yes - 4	Yes - 4	Yes - 3
Spot cleaners used regularly	• Pyratex (pre)[a] • WetSpo (pre) • RustGo (pre) • StreePro (pre) • Legacy of Clean Prewash Spray (pre)	• Pyratex NuTec (pre) • StreePro (pre) • StreeTan (pre) • RustGo (pre)	• StreeTan (pre and post[b]) • QwikGo (pre and post)	• StreeTAN (post) • TarGo (post) • RustGo (post) • POG (post) • ScramBlood (post) • 2-1 Formula (post)
Barriers to purchasing a non-PERC machine	Financial	Financial	Financial, and lack of knowledge about solvents	Financial
Preferred solvent, if purchased new machine	Unsure – maybe hydrocarbon	Doesn't know	Technology with no still/cooking	Maybe hydrocarbon
Assistance requested	Financial help	Financial help to replace machine	Provide information about PSCAA fee	Financial help
Sample numbers	01A: SW050915_01_W01[c] 01B: SW062715_01_SB(m)	02: SW053015_02_B01	03: SW061315_03_SB(m)	04: SW062615_04_SB(m)

[a] Spot cleaner used for pre-cleaning
[b] Spot cleaner used for post-cleaning
[c] Sample was a mixture of still bottoms and separator water combined in a 5-gallon waste container. All other samples were still bottoms only – sampled directly from the still.

Table 3. Fish toxicity testing results for PERC still bottoms					
Sample Concentration (mg/L)	**Percent Fish Survival**				
	Shop 01A[a]	**Shop 01B**	**Shop 02**	**Shop 03**	**Shop 04**
10	100	100	7	100	100
100	0	0	0	0	0
[a] Mixture of still bottoms and separator water in waste container					

Quality control

This study's procedures and data were compliant with the specifications described in the QAPP (Exhibit A). No errors or omissions were identified and no corrective actions were required.

The single change from the QAPP was a modification of the questionnaire, in order to gather more broadly applicable information.

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CONCLUSIONS

The results of this pilot study indicate that the toxicity of the still bottoms varies from shop-to-shop. This variability may reflect varying concentrations of PERC and other toxic constituents, such as detergents, spot cleaners, other additives, and material extracted from the cleaned fabrics.

It is important to note that the data gathered during this study are not representative of PERC dry cleaners as an industry. By design, this study was limited to four shops in order to gather pilot data for further consideration by LHWMP and Ecology.

Collection of still bottom samples from additional PERC shops would allow for a critical evaluation of the frequency by which these businesses generate DW vs. EHW. Testing for additional federal and state-only endpoints would provide a more comprehensive designation of these wastes. Finally, collecting additional samples in concert with questionnaire data may allow for a critical evaluation of the factors that influence the toxicity, chemical composition, and physico-chemical characteristics of PERC still bottoms.

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ACKNOWLEDGMENTS

Samuel Iwenofu, Aurana Lewis, and Jeffrey Gutschmidt (Department of Ecology) provided valuable advice and guidance during the preparation of the QAPP.

Gary Yoshida and Fran Sweeney (King County Environmental Laboratory) conducted the fish bioassays and assisted with data interpretation.

Alice Chapman, PE (Engineer, LHWMP) provided a detailed technical review of this document.

Ryan Kellogg (Performance Manager, LHWMP) provided a valuable policy perspective on this document.

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