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Final Report

Dry cleaning with high-flashpoint hydrocarbon solvents

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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. Our 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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ACRONYMS AND ABBREVIATIONS

BTEX	Benzene, Toluene, Ethylbenzene, Xylenes
°C	Degrees Celsius
CARB	California Air Resources Board
CAS	Chemical Abstract Service
DFG	Deutsche Forschungsgemeinschaft (German)
DNAPL	Dense Nonaqueous Phase Liquid
DW	Dangerous Waste
EC number	European Community number
ECHA	European Chemicals Agency
Ecology	Washington State Department of Ecology
EHW	Extremely Hazardous Waste
EPA	United States Environmental Protection Agency
EU	European Union
°F	Degrees Fahrenheit
Gal.	Gallon
GC/MS	Gas Chromatography/Mass Spectrometry
HSPA	Hydrocarbon Solvents Producers Association
IRTA	Institute for Research and Technical Assistance
KCEL	King County Environmental Laboratory
KCIW	King County Industrial Waste
kPa	Kilopascal
LC_{50}	The median lethal test concentration that kills 50 percent of test organisms
LD_{50}	The median lethal test dose that kills 50 percent of test organisms
LHWMP	Local Hazardous Waste Management Program in King County
LNAPL	Light Nonaqueous Phase Liquid
MAK	Maximum Concentrations at the Workplace (English translation of German)
MDL	Method Detection Limit
mg/Kg	Milligrams per kilogram
mg/L	Milligrams per liter
mg/m^3	Milligrams per cubic meter
mmHg	Millimeters of mercury
µg/L	Micrograms per liter
mL	Milliliter
MRL	Method Reporting Limit
NIOSH	National Institute for Occupational Health & Safety
NOEL	No Observed Effect Level
NFPA	National Fire Protection Association
OECD	Organization for Economic Cooperation and Development
OSHA	Occupational Safety and Health Administration
PERC	Perchloroethylene / Tetrachloroethylene
PBiTE	Persistent, Bioaccumulative and inherently Toxic to the Environment
PSCAA	Puget Sound Clean Air Agency

REACH	Registration, Evaluation, Authorization, and Restriction of Chemicals
RDL	Reporting Detection Limit
SDS	Safety Data Sheet
TCE	Trichloroethylene
TIC	Tentatively Identified Compound
TURI	Toxic Use Reduction Institute
UVCB	Unknown or Variable composition, Complex reaction products or Biological material
VOA	Volatile Organic Analysis
VOC	Volatile Organic Compound

EXECUTIVE SUMMARY

Although perchloroethylene (PERC) has dominated the dry cleaning industry for several decades, alternative solvents have now entered the marketplace. The most common alternatives to PERC are high-flashpoint hydrocarbons, referred to as "hydrocarbon" by dry cleaners. In King County, Washington, these solvents are now used by more than twenty percent of dry cleaners, and their usage is increasing.

However, the potential for hydrocarbon solvents to adversely affect human health and the environment has not been well characterized. Although not specifically banned by any regulatory authorities, several jurisdictions do not encourage their use. For some programs and agencies, the preferred alternative to PERC dry cleaning is professional wet cleaning, which uses water rather than an organic solvent in the cleaning process.

Given this uncertainty and their increasing use in King County, we evaluated this product class through a literature review, interviews, fish bioassays, and chemical analyses. We analyzed the two high-flashpoint hydrocarbon solvents most frequently used locally: ExxonMobil's DF2000™ and Chevron-Phillips' EcoSolv™, as well as a new high-flashpoint hydrocarbon solvent, Calypsolv™ (Technichem, Inc.). Our analyses focused on detection of hazardous aromatic hydrocarbons, especially benzene. We also evaluated their aquatic toxicity in an acute fish toxicity test.

These products were confirmed to be complex mixtures of hydrocarbons, but no hazardous aromatic compounds were detected. None of them were acutely lethal to fish at the highest tested concentration (100 milligrams per liter (mg/L)), reflecting their very low water solubility. Therefore, we conclude that these solvents do not contain carcinogenic or mutagenic aromatic compounds and do not exhibit acute aquatic toxicity.

From our literature review and interviews, we conclude that toxicity evaluations of these high-flashpoint hydrocarbons are complicated by: 1) the inclusion of diverse products in the category of "hydrocarbon dry cleaning solvents," some of which may contain benzene and other hazardous substances, and 2) the inadequacy of Chemical Abstract Service (CAS) numbers to uniquely identify specific products within this chemical class.

However, we recognize the possibility for harm to human health and the environment from using these solvents. For example, there are data gaps regarding toxicity and bioaccumulation, in addition to outstanding questions about effects on ambient air quality. There is also potential for contamination of hydrocarbon dry cleaning machines by hazardous process chemicals, which may result in worker exposures. As petroleum-based products, these solvents rely on fossil fuel extraction. Waste streams may also be classified as Dangerous Waste (DW), and their increased flammability compared to PERC raises safety concerns. To prevent occupational exposures and environmental contamination, hydrocarbon machines must be maintained adequately, solvent spills prevented, and waste streams managed appropriately.

In summary, while professional wet cleaning is the preferred alternative to PERC, the hydrocarbon solvents described in this report are also viable alternatives, when used appropriately.

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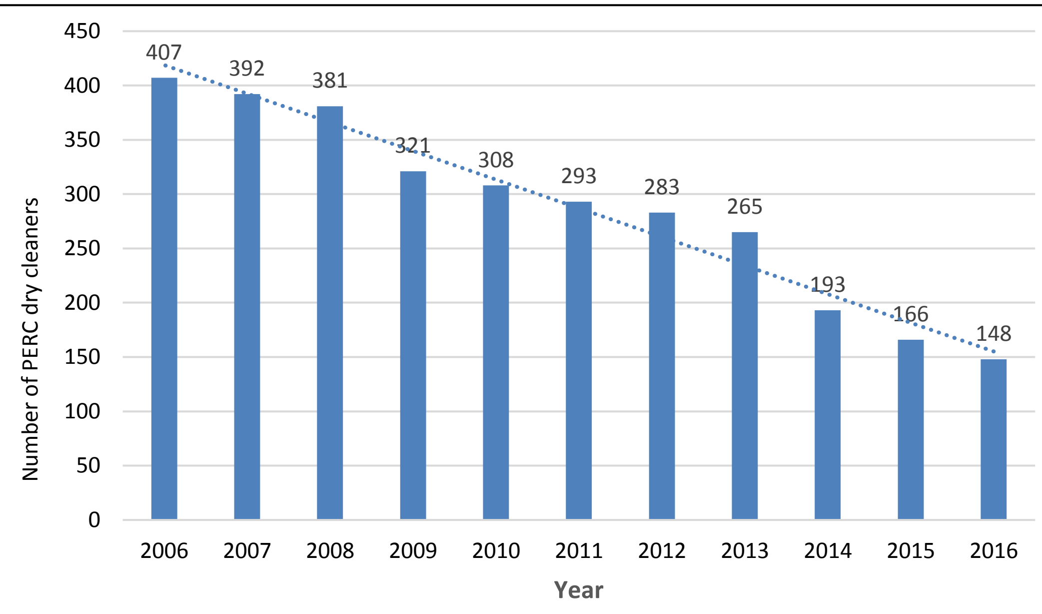
INTRODUCTION

Background

The use of PERC as a dry cleaning solvent has been decreasing nationally over the last several years. Figure 1 shows the reduction in the number of PERC dry cleaning businesses in King County, Washington, as indicated by the number of shops registered with the Puget Sound Clean Air Agency (PSCAA). Further review of PSCAA's registration database, site visits to PERC dry cleaning shops, and conversations with industry vendors revealed that there were only 80-85 PERC dry cleaners in King County as of July 2018 – a substantial decrease from the over 400 businesses registered in 2006.

Figure 1. Number of PERC dry cleaners in King County, Washington



There are several reasons for this downward trend, including 1) the purchase and consolidation of small businesses to create larger facilities that rely on drop-shops and offer pick-up and delivery services, 2) adoption of alternative dry cleaning solvents and 3) business closures, especially of financially struggling businesses that use older PERC machines.

Although PERC was used by almost all King County dry cleaners through the 1990s, we have noted the emergence of several solvent alternatives in the last two decades. This transition reflects the following factors:

- Insurance company and landlord opposition to installation of new PERC machines because of environmental liability concerns (i.e., costly cleanups).

- Regulatory activity in California to phase-out the use of PERC in dry cleaning, which has raised awareness among some dry cleaners and prompted the purchase of new equipment.
- Restrictions in the use of PERC by local jurisdictions in King County to protect their shallow aquifers from contamination (e.g., the City of Redmond).
- The United States Environmental Protection Agency's (EPA's) ban on the use of PERC dry cleaning machines co-located in residential buildings by 2020 (Final Amendments to Air Toxics Standards for Dry Cleaners, 40 CFR §63.322 (o)).
- Demonstrated efficacy of several alternative fabric cleaning technologies and solvents.
- Growing awareness among some dry cleaners of the health and environmental effects of PERC.
- Availability of funds from the Local Hazardous Waste Management Program in King County (LHWMP) to purchase high-flashpoint hydrocarbon and professional wet cleaning technology (11 grants were awarded between 2013 and 2015).
- Machine vendors marketing and installing alternative solvent dry cleaning machines, rather than replacing obsolete machines with new PERC equipment.

However, it should also be noted that the total number of PERC shops also decreased because of business closures, resulting from:

- Financial stress stemming from the Great Recession in the United States (December 2007 – June 2009).
- Declining customer base because of: 1) changes in the types of fabrics now in common use, many of which do not require dry cleaning; 2) technological advances in residential washing machines and dryers, which allow the cleaning of wool and other delicate fabrics at home; and 3) the availability of in-house dry cleaning and "wash & fold services" at several major corporations.
- Business owner retirements, especially of immigrants from South Korea. We have observed that their children or other relatives are not adopting the family business. Newer immigrants to King County are also not opening dry cleaning businesses.

Status of dry cleaning in King County

To better understand the local industry, we conducted a survey of King County dry cleaners in 2010.[1,2] This survey revealed that while 69 percent of businesses were still using PERC, 21 percent used a high-flashpoint hydrocarbon solvent. Subsequent field visits and interviews with dry cleaners indicate that the use of hydrocarbon solvents is increasing. This pattern has also been noted in Massachusetts (i.e., decreasing PERC usage, reduction in the number of dry cleaners, and increased adoption of hydrocarbon solvents).[a] Dry cleaners consider hydrocarbon

[a] Personal communication with Suzi Peck, Associate Director for Planning, Evaluation, and Toxics, Business Compliance and Recycling Division, Bureau of Air and Waste, Massachusetts Department of Environmental Protection. September 10, 2018.

to be the preferred alternative to PERC because the technology and processes are very similar to those used with PERC. Consequently, very little training or business interruption is required to use the new machine and solvent.

We also learned that 84 percent of dry cleaning business owners self-identified as Korean. Among all dry cleaners, 84 percent were family-owned. Subsequent field visits to dry cleaning shops revealed that employees were typically Latinx.

Hydrocarbon solvents used in King County

High-flashpoint hydrocarbons are organic chemicals that ignite at relatively high temperatures (i.e., high-flashpoint) and contain only carbon and hydrogen (i.e., hydrocarbons). Although the flashpoints of these solvents are relatively high, they are more flammable than PERC and are generally classified by the National Fire Protection Association (NFPA) as Class IIIA solvents (i.e., flashpoints at or above 140 °F and below 200 °F).

These solvents are manufactured under several trade names; the products used most frequently in King County are EcoSolv (Chevron Philips Chemical Company, LLC) and DF2000 (ExxonMobil Corporation).[3,4] In addition, a new product has recently been introduced to the market: Calypsolv (Technichem, Inc.).

While the detailed chemical specifications are proprietary and vary by product, the solvents described above contain between 11 and 14 carbons as their primary structural backbone (i.e., C11 to C14).

Product information, including Safety Data Sheets (SDSs) for EcoSolv, DF2000, and Calypsolv, is presented in Appendix A. Summary information from these sources is shown in Table 1.

Table 1. Example high-flashpoint hydrocarbon dry cleaning solvents

Product name	EcoSolv	DF2000	Calypsolv
Manufacturer	Chevron Philips	ExxonMobil	Technichem
Flashpoint	142 °F	144 °F	142 °F
Carbon# range	C12-C14	C11-C13	Not specified[a]
Water solubility	“Negligible”	“Negligible”	“Negligible”
CAS number[b]	68551-19-9	64742-48-9	64741-65-7
EC number[c]	Not specified	920-901-0	Not specified

[a] Although not specified on the SDS, reported to be a similar chemical structure to DF2000 (personal communication with Mark Ng, Technichem, Inc., November 2017).
[b] Chemical Abstract Service number
[c] European Community number

For regulatory purposes, these solvents are characterized as "substances of unknown or variable composition, complex reaction products or biological materials" (UVCB) by the EPA and the European Chemicals Agency (ECHA).[5,6]

Current study

Even though high-flashpoint hydrocarbon dry cleaning solvents are being adopted widely across the United States and in King County (especially DF2000 and EcoSolv), their potential impacts on human health and the environment are not very well understood. Addressing this knowledge gap is particularly important as we consider the health and wellbeing of our dry cleaning community, the public, and the environment. Additionally, a better understanding of these potential hazards will inform the choice of technologies that we will promote through our financial incentive programs to help dry cleaners replace their PERC equipment. A key concept and concern in the field of alternatives assessment is "regrettable substitution," which is defined as replacing a toxic chemical with another chemical with equivalent or more severe health or environmental effects. Consequently, we are committed to ensuring that we are not encouraging the adoption of new solvents or technologies that are potentially more hazardous than PERC dry cleaning.

Across the United States, different jurisdictions have taken varying positions with regard to high-flashpoint hydrocarbons as acceptable dry cleaning alternatives. Some government agencies and other programs do not actively promote or subsidize hydrocarbon dry cleaning and only support professional wet cleaning, which relies on water, rather than an organic solvent. For example, the State of California (via the California Air Resources Board (CARB) and the air quality districts) permits the use of high-flashpoint hydrocarbon solvents but does not provide financial assistance to dry cleaners to adopt this technology.[7] However, other jurisdictions have provided funding to help PERC dry cleaners purchase hydrocarbon dry cleaning machines, reasoning that their highest priority is to remove aging PERC machines from operation.[8,9]

Conversations with colleagues in the environmental and regulatory communities revealed concerns about the mutagenic and carcinogenic potential of these hydrocarbon solvents, because they may contain benzene and other carcinogens typically associated with petroleum-based products.

To address the questions described above, this current study undertook the following lines of investigation:

- Chemical analysis of multiple manufacturers' lots of high-flashpoint hydrocarbon dry cleaning solvents to determine their aromatic hydrocarbon content; and
- Fish bioassays of the hydrocarbon solvents to determine their acute aquatic toxicity.

To complement and enhance the results of these analyses, we conducted additional research including:

- A literature review of this product class, including previous LHWMP studies, agency reports, the peer-reviewed literature, and manufacturers' specifications; and
- Interviews with manufacturer representatives, including chemists, toxicologists, and product specialists.

METHODS

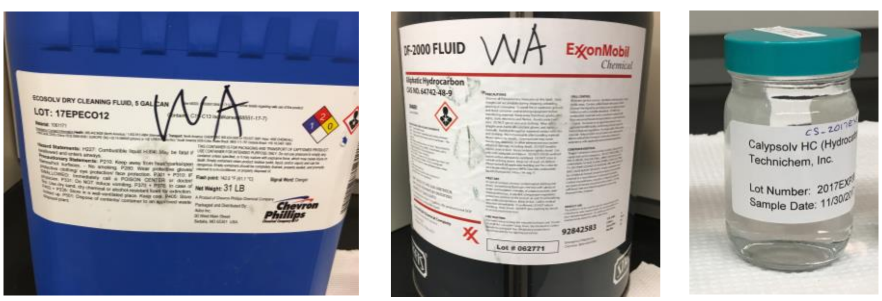
Overall strategy

The overall strategy of the experimental portion of this assessment was to: 1) analyze solvent samples to evaluate the presence of and lot-to-lot variability in aromatic hydrocarbon content, and 2) conduct fish bioassays to evaluate acute aquatic toxicity. Previous fish bioassays of DF2000 revealed that this solvent was not acutely lethal at 5,000 mg/L.(10) Given these prior results, and because DF2000, EcoSolv, and Calypsolv were presumed to be chemically very similar, only single samples of the latter two solvents were tested for acute aquatic toxicity. Additional samples would be tested if any fish toxicity was noted. The sample identities are summarized in Table 2.

Sample collection and storage

LHWMP and colleagues from the Washington State Department of Ecology (Ecology) purchased 5-gallon containers of EcoSolv and DF2000 from a local vendor (S.K.Y. & Company, Auburn, Washington), ensuring that the products were derived from different manufacturing lots. Technichem, Inc. (Hayward, California) also provided 250 milliliter (mL) samples of Calypsolv and EcoSolv. Example product containers are shown in Figure 2.

Figure 2. Solvent product containers



Solvents in 5-gallon product containers were transferred to pre-cleaned 40-mL capacity Volatile Organic Analysis (VOA) vials and 250-mL capacity I-CHEM jars (I-CHEM #220-0250) using a 100-mL capacity disposable serological pipette. The 250-mL product containers provided by Technichem, Inc. were delivered directly to the King County Environmental Laboratory (KCEL). All sample containers were delivered to KCEL at room temperature.

Table 2. High-flashpoint hydrocarbon dry cleaning solvent samples evaluated in this study						
Product	**Lot number**	**Supplier**	**Container size**	**Sample number**	**Chemical analysis**	**Fish bioassay**
DF2000	062771	S.K.Y.	5 gal.	DF-062771	X	
	073171	S.K.Y.	5 gal.	DF-073171	X	
	020671	S.K.Y.	5 gal.	DF-020671	X	
	052371	S.K.Y.	5 gal.	DF-052371	X	
EcoSolv	17HPECO05-1	Technichem	250 mL	ES-17HPECO05-1	X	X
	17EPECO12	S.K.Y.	5 gal.	ES-17EPECO12	X	
	16HPECO06	S.K.Y.	5 gal.	ES-16HPECO06	X	
	15KPECO05	S.K.Y.	5 gal.	ES-15KPECO05	X	
Calypsolv	2017EXP38-1	Technichem	250 mL	CS-2017EXP38-1	X	X

Chemical analyses

Samples were analyzed by KCEL staff using EPA Method 624 - a purge and trap gas chromatograph/mass spectrometer (GC/MS) method for volatile organic chemical (VOC) analysis of wastewater.[(11)] The focus of the analysis was benzene, toluene, ethylbenzene, and xylenes (BTEX), where m-xylene, p-xylene, and o-xylene concentrations were reported individually.

A 5-mL aliquot of sample was diluted in 50 mL of reverse osmosis water and shaken for 2 minutes. The aqueous portion of the sample/water mix was removed and loaded into a 40-mL capacity VOA vial. Helium gas was bubbled through the aqueous portion at ambient temperature. After purging was completed, the trap was heated and back-flushed with helium to desorb the purgeables onto a gas chromatographic column (J&W DB-VRX column, 30 m long, 0.250 mm ID with a 1.4 um coating thickness).

The gas chromatograph was temperature-programmed to separate the purgeables, which were then detected with a mass spectrometer (Agilent 5975C/7890A GC/MS with a Teledyne Tekmar Atomx autosampler).

D4-Dichlorobenzene; Fluorobenzene; and D5-Chlorobenzene were used as internal standards. D8-Toluene; D4-1,2-Dichloroethane; and 4-Bromoflorobenzene were used as surrogates.

Analysis for Tentatively Identified Compounds (TICs) was performed on peaks that were >3% of the D4-Dichlorobenzene internal standard.

Fish bioassays

Acute aquatic toxicity tests were conducted by KCEL staff according to Ecology's *Biological Testing Methods for the Designation of Dangerous Waste*.[(12)] This test involved exposing juvenile rainbow trout to solvent samples for 96 hours at two concentrations (10 mg/L and 100 mg/L) in a "non-renewal" static acute fish toxicity bioassay (i.e., Ecology's Part A: Method 80-12).

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RESULTS

Chemical analyses

BTEX was not present above the detection limits in any sample. The Method Detection Limit (MDL) was 10 micrograms/liter (μg/L) and the Reporting Detection Limit (RDL) was 20 μg/L.

A representative chromatogram from the GC/MS analysis of EcoSolv (sample# ES-17HPECO05-1) is presented in Figure 3. The labels indicate the expected locations of the peaks for BTEX. The EcoSolv sample displayed chromatographically as a mound that contained multiple peaks between 19.326 minutes and 21.365 minutes. Nineteen TICs were identified within these retention times. TICs present at the highest concentrations were:

- 2,2,5-trimethyl-decane (315 μg/L)
- 2,2-dimethyl-heptane (249 μg/L)
- 3-methyl-decane (185 μg/L)
- 2,2,5-trimethyl-decane (126 μg/L)
- 2,7,10-trimethyl dodecane (119 μg/L)

A review of the TICs associated with the other product samples revealed similar chemical profiles.

Acetone was present in multiple samples and was likely a laboratory contaminant.

PERC was detected in a single sample of EcoSolv (sample# ES-16HPECO06) at 48 μg/L. This result was confirmed upon analysis of another sample from the same 5-gallon container. However, PERC was not detected in samples from two additional 5-gallon containers from the same lot of EcoSolv (i.e., 16HPECO06), where the MDL and RDL were 10 μg/L and 20 μg/L, respectively.

Fish bioassays

Neither EcoSolv nor Calypsolv were acutely lethal at the highest test concentration (100 mg/L). An immiscible layer of solvent was present on the surface of the test vessels. Detailed results are provided in Appendix B.

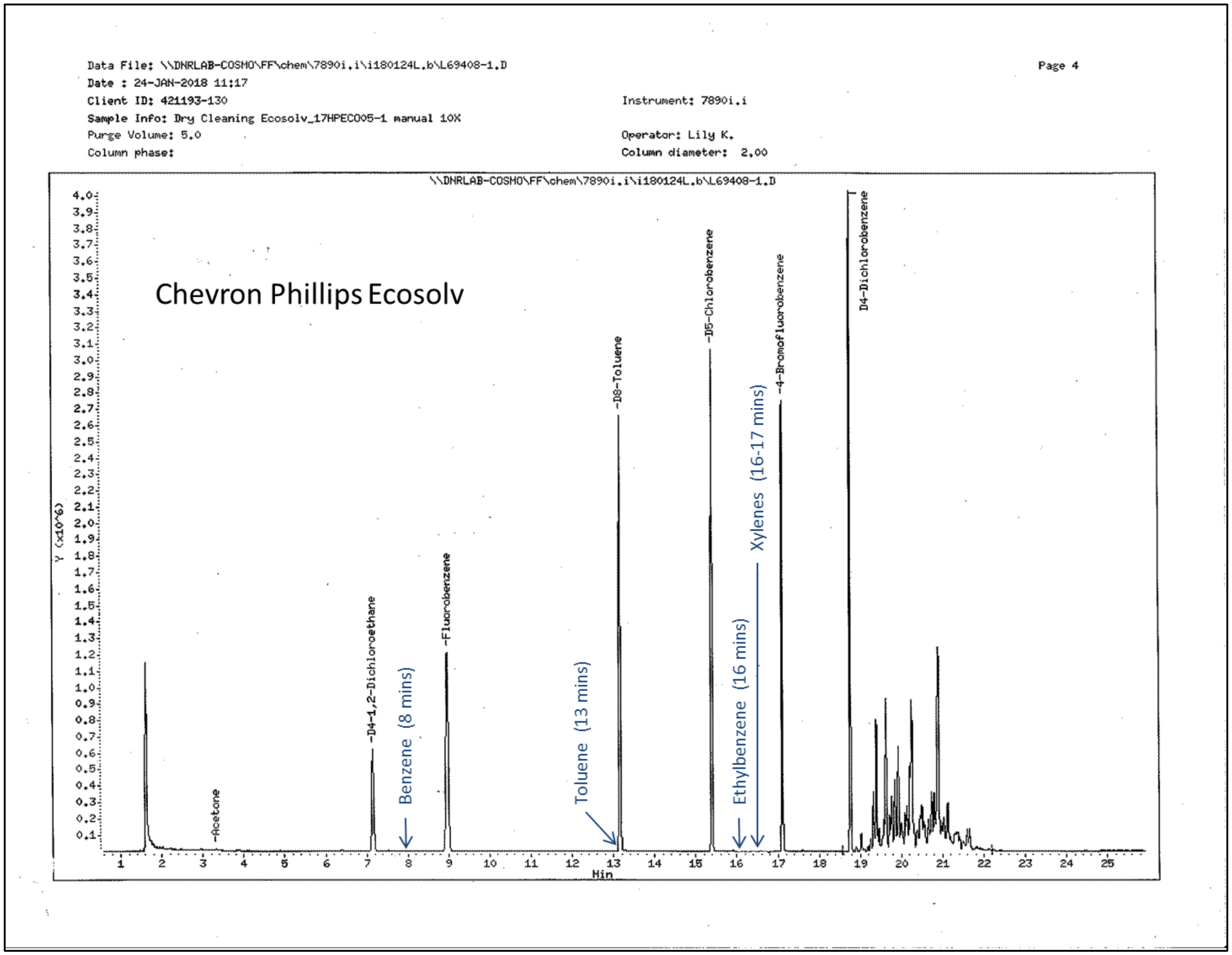


Figure 3. Chromatogram from GC/MS analysis of EcoSolv

DISCUSSION

Experimental findings

These high-flashpoint hydrocarbon dry cleaning solvents were confirmed to be multicomponent hydrocarbons. Toxic aromatics (i.e., BTEX) were not detected. These findings mirror the results of previous analyses of DF2000 conducted in a collaboration between the National Institute for Occupational Health & Safety (NIOSH)[13,14] and LHWMP.[10]

The origin of the trace levels of PERC in one 5-gallon container of EcoSolv is unclear. Conversations with the local vendor (S.K.Y. and Company) revealed that their supplier distributed the solvent from 55-gallon drums into the 5-gallon plastic containers provided for this study. We surmised that the supplier's solvent distribution equipment may have been used previously to dispense PERC. It is also noteworthy that the 5-gallon containers of EcoSolv were not sealed upon delivery and the screw-caps were readily opened. By contrast, the containers of DF2000 were sealed with a plastic ring-pull. We recently learned that EcoSolv is now shipped in sealed metal containers.[a]

The fish bioassay results for Calypsolv and EcoSolv were identical to the findings from our previous studies with DF2000. Neither of these solvents were acutely lethal at the maximum test concentration of 100 mg/L and LD_{50}s could not be determined. They all formed an immiscible solvent layer on the surface of the test vessel, reflecting their negligible water solubility (see Table 1). An extensive evaluation of DF2000's acute aquatic toxicity we conducted previously revealed that this solvent was not lethal to fish at a maximum test concentration of 5,000 mg/L.[10]

Overall, we conclude that these three solvents do not exhibit acute aquatic toxicity because they are essentially insoluble in water, resulting in very low exposures to the fish. Below we provide additional discussion of the aquatic toxicity of this product class.

Health & environmental perspectives on hydrocarbon solvents

Defining hydrocarbon dry cleaning solvents

The three high-flashpoint hydrocarbon dry cleaning solvents under consideration in this study (EcoSolv, DF2000, and Calypsolv) appear to share similar chemical structures, comprised of almost 100% isoparaffinic hydrocarbons (isoalkanes) with carbon chain lengths between C11 and C14. None of these products contain toxic aromatic hydrocarbons (i.e., BTEX) above detection limits. However, some authors have also categorized other solvents with varying chemical compositions as "hydrocarbon" dry cleaning products. For example, in its 2012 review of alternatives to PERC in dry cleaning, the Toxic Use Reduction Institute (TURI) included several

[a] Personal communication with S.K.Y & Company. June 2018.

products with varying chemistries in the category "high flash hydrocarbons."[15] Although TURI mostly focused on DF2000 and EcoSolv, they also included:

- ShellSol D60™ - manufactured via refining crude oil followed by hydrotreating to remove aromatics. This class of products is not considered to be isoparaffinic,[16]
- Caled Hydroclene™ - a C10 to C13 solvent that also contains 2-10% aliphatic propylene glycol ether base mixture,[17] and
- Niran Technology PureDry™ - reportedly a C9 to C12 solvent supplemented with several perfluorinated compounds, with a much higher flashpoint than other products included in this category (i.e., 350 °F).[15]

CARB's 2006 review, in support of its rulemaking, also included Stoddard solvent (CAS number 8052-41-13) in the "hydrocarbon solvent cleaning" category.[18] However, the chemical, physical and toxicological properties of Stoddard solvent are very different from the hydrocarbon dry cleaning solvents under consideration in this study. This petroleum distillate mixture of C7 to C12 hydrocarbons has several possible formulations, with varying levels of paraffins, cycloparaffins, and aromatic hydrocarbons. Some forms of Stoddard solvent also contain C6 and C8 hydrocarbons, including aromatics such as benzene. Flashpoints for Stoddard solvent range from 100 °F to 140 °F.[19]

In conclusion, general summaries of the chemical composition of hydrocarbon dry cleaning solvents are confounded by the inclusion of several products in this category with widely differing chemical compositions.

Issues with classification & nomenclature

According to the EPA, the composition and physical properties of substances with the CAS number assigned to DF2000 (64742-48-9) can vary considerably, depending on the raw material and the production processes.[20] EPA's conclusions are supported in a review by Mckee et al.,[21] which states that hydrocarbons assigned CAS number 64742-48-9 may have carbon backbones in the C6 to C13 range. Therefore, CAS number 64742-48-9 is not specific for the DF2000 product.

This issue extends beyond DF2000. Our conversations with product manufacturers revealed that, in some circumstances, the CAS numbers for this chemical class refer to the feedstocks from the refinery and the specific final processing step, rather than the finished products. Thus, a single CAS number can refer to several different hydrocarbon solvents with varying chemical, physical, and toxicological properties.

Recognizing this difficulty, the Hydrocarbon Solvents Producers Association (HSPA) worked with the ECHA to develop a more specific nomenclature -- the European Community number (EC number) -- for products sold in the European Union (EU) to comply with the requirements of the Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) regulation. Per REACH requirements, the adoption of the new, more specific names and identifiers necessitated the removal of CAS numbers. ReachCentrum provides a crosswalk between the EC numbers and the CAS numbers they replaced.[22] While this system aims to improve the specificity of product classification, it should be emphasized that EC numbers are only available for products sold and registered in the EU.

We conclude that the predominant chemical nomenclature system used by environmental and public health practitioners, the CAS number, is not sufficiently specific for this class of hydrocarbon solvents, resulting in misidentification of products and consequent uncertainty about their chemical and physical properties (including toxicity).

Understanding the manufacturing process

Because the efficacy with which hazardous aromatic hydrocarbons are removed from the petroleum feedstock during manufacturing is an important consideration in evaluating carcinogenic potential, we considered it essential to understand how these solvents are manufactured.

Although specific manufacturing details for these products are proprietary and vary by product, a generalized schema is illustrated in Figure 4, as described by petroleum industry chemists. This schema is similar to published hydrocarbon manufacturing processes[23] and a description provided by Mckee et al.[21] The feedstock for high-flashpoint hydrocarbon dry cleaning solvents may be of two types, depending on the manufacturer and product. The first type uses a petroleum distillate feedstock, which is treated to remove BTEX and other relatively light constituents. The second type is of synthetic origin, typically resulting from the alkylation or oligomerization of C3 to C5 light gases and/or lower olefins, followed by hydrogenation or extraction to form alkanes. Although originally derived from a petroleum feed, the feedstocks used to manufacture these synthetic products are reportedly free of BTEX. Regardless of the origin of the feedstock, fractionation steps are used to yield products with the desired carbon chain lengths with properties (such as flashpoint) suitable to the end-use application.

We conclude that the manufacturing processes for these hydrocarbon dry cleaning solvents are unlikely to result in contamination with BTEX, based on 1) the Customer Specifications for these products, which specifically address the aromatic hydrocarbon content (see Appendix A) and 2) conversations with several product manufacturers, who suggested that these processes are specifically designed to remove BTEX.

Internet-based hazard screening tools can provide misleading results

Many practitioners in the field of alternatives assessment use internet-based tools to evaluate the intrinsic hazards of environmental chemicals and other substances. One such tool is the Healthy Building Network's Pharos scoring system,[24] which assigns color codes that reflect the highest hazard for a health- or environmental- endpoint, as determined from an authoritative hazard list. The Pharos scoring system is informed by the GreenScreen® for Safer Chemicals, a benchmarking system to rank the safety of chemicals on a four-point hazard scale.[25] Hazard data may be retrieved by either entering a chemical's name or CAS number.

Entering the CAS numbers for DF2000 and Calypsolv into Pharos revealed that they were classified as carcinogens and mutagens, based on authoritative lists from the EU (see Figures 5 and 6, respectively).

However, considering the Customer Specifications for EcoSolv, DF2000, and Calypsolv (see Appendix A); the manufacturing process; and our experimental findings, we surmise that these solvents are free of hazardous aromatic hydrocarbons. The supporting documentation for the EU classification of carcinogenicity for DF2000 (CAS number 64742-48-9) cited in Pharos states that the classification as a carcinogen need not apply if it can be shown that the substance contains less than 0.1 % w/w benzene.[26] Therefore, the limitations associated with the assigned CAS numbers present considerable difficulties when using hazard screening tools to evaluate the health and environmental impacts of this product class.

Toxicity evaluation

Toxicity information described in the SDSs for DF2000, EcoSolv, and Calypsolv (see Appendix A) is summarized in Table 3. Limited independent data exist for the toxicological effects of these specific hydrocarbon solvents; most data are derived from industry assessments. An additional limitation is that some data are derived from structurally-similar compounds (i.e., via "read-across" methods) rather than the specific product of interest.

Toxicity information for a range of hydrocarbon solvents was recently described by Mckee et al.[(21)] In this review by industry-affiliated authors, these dry cleaning solvents were categorized as "C9-C14 Aliphatic Hydrocarbon Solvents (<2% aromatics)." Mckee et al. concluded that this solvent class "…does not produce acutely toxic effects except at very high levels and/or under unusual circumstances..." Mckee et al. reported limited or no evidence for adverse outcomes relevant to human health in repeated dose studies and tests of genetic toxicity, developmental and reproductive toxicity, carcinogenicity, and neurotoxicity.

An earlier review by the Cosmetic Ingredient Review Expert Panel also noted no evidence of mutagenicity or genotoxicity. They reported that kidney toxicity had been documented in rodent studies, although this pathway is not relevant for humans. The panel also referenced limited studies to suggest possible irritation and sensitization from occupational exposure.[(27-29)]

The Organization for Economic Cooperation and Development (OECD) also reviewed this class of hydrocarbon solvents in 2012[(30)] and provided the following summary classification:

> *Chemicals in the category C9-C14 aliphatic (<2% aromatics) hydrocarbon solvents possess properties indicating a hazard for human health (chemical pneumonitis if taken in to the lungs as liquids, severe irritant dermatitis due to defatting with prolonged or repeated exposure, liver enlargement and kidney changes in male rats in repeated dose toxicity studies [oral and inhalation; these changes may be secondary findings], increase in the frequency of kidney and adrenal gland tumors in male rats and liver tumors in female mice, potential for central nervous system effects). Adequate screening-level data are available to characterize the human health hazards of substances in the C9-C14 aliphatic (≤2%* aromatics) *hydrocarbon solvent category for the purposes of the OECD Cooperative Chemicals Assessment Programme.*

Figure 4. Manufacture of high-flashpoint hydrocarbon dry cleaning solvents

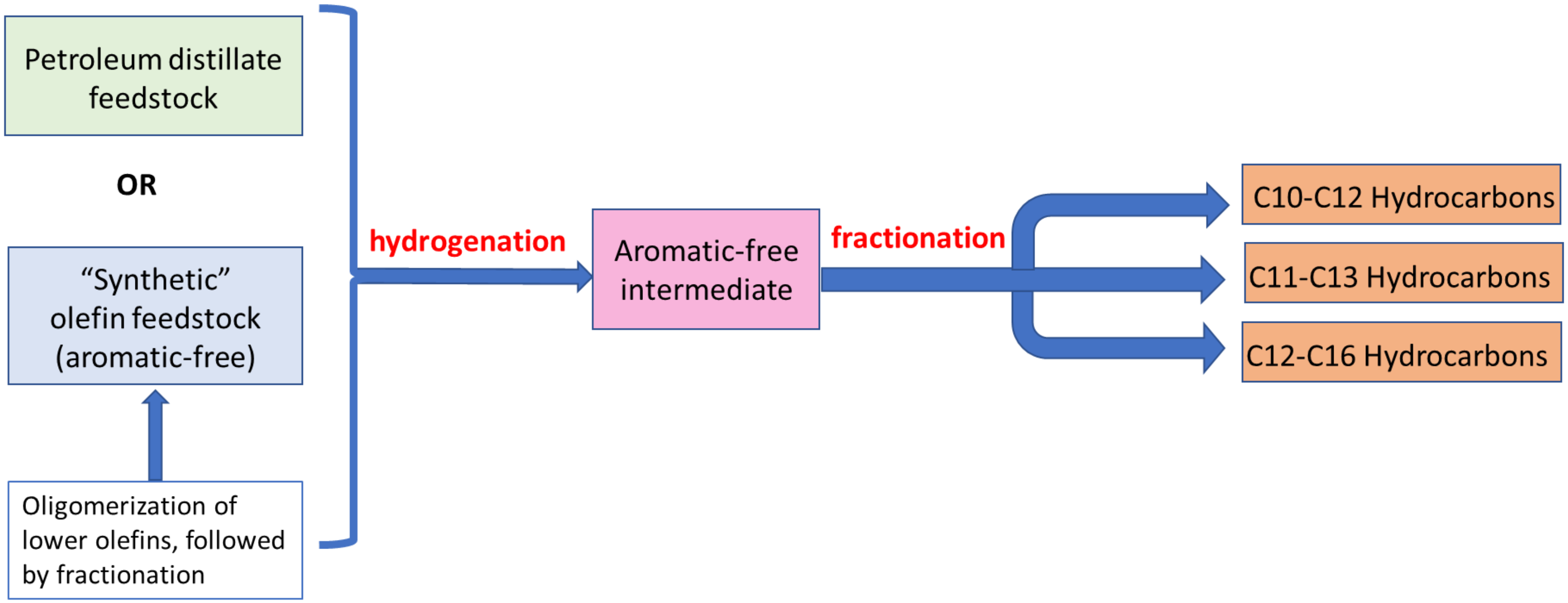


Figure 5. Pharos results for DF2000

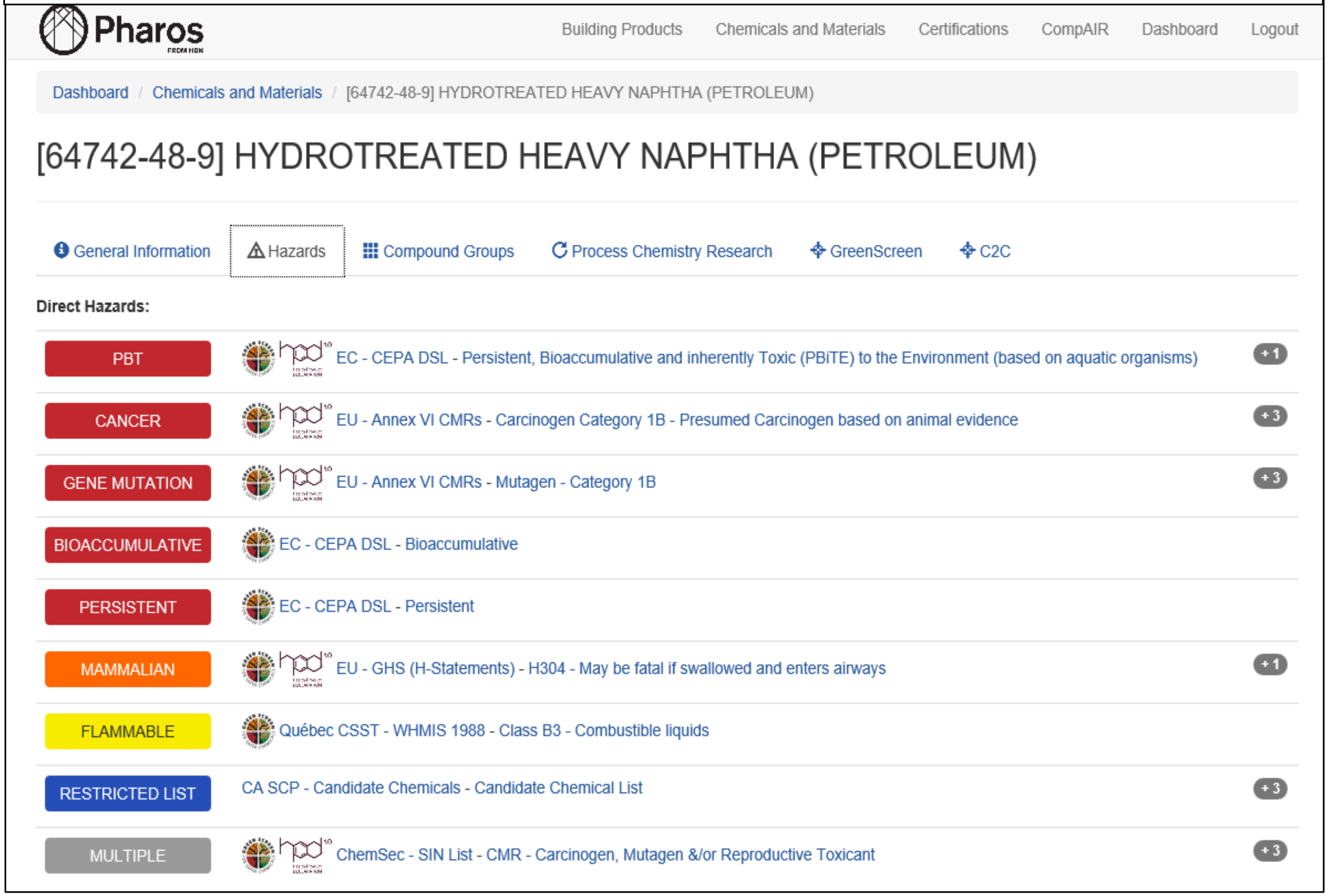
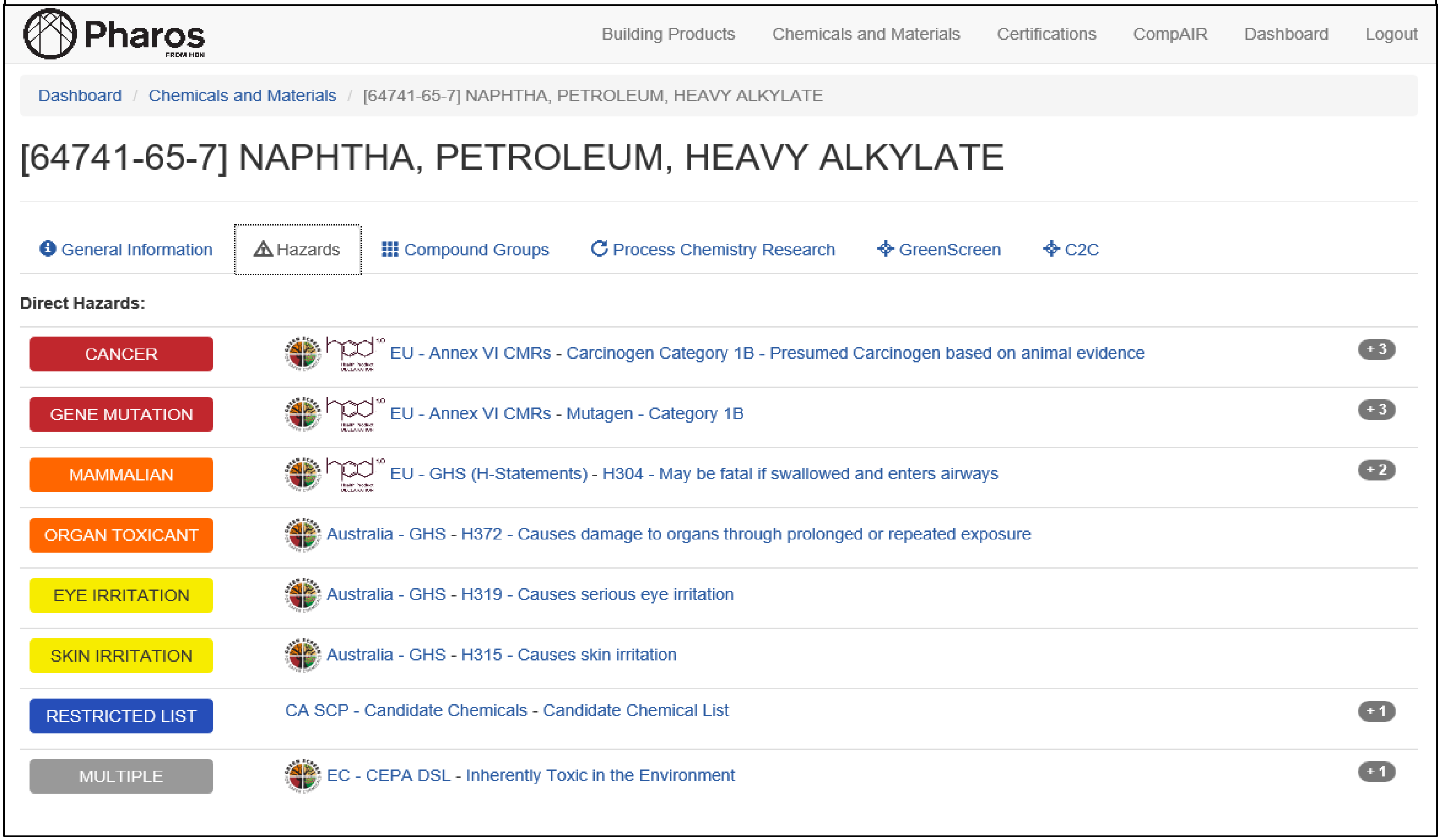


Figure 6. Pharos results for Calypsolv



In conclusion, the most important reported human health outcomes result from aspiration into the lungs and dermal contact. There is also potential for CNS depression resulting from acute inhalation exposures. However, in contrast to the findings obtained by entering product CAS numbers into Pharos (see Figures 5 and 6), we conclude – based on our literature review, the OECD classification, and the SDS information – that there is no evidence that DF2000, EcoSolv, or Calypsolv are linked to reproductive toxicity, mutagenicity, or carcinogenicity.

Potential for human exposure

According to the OECD, workers are primarily exposed to these solvents through the inhalation of vapor due to the volatility of the constituents, although dermal exposures are also possible.[30] Dry cleaners are potentially exposed to high-flashpoint dry cleaning solvents when they operate their dry cleaning machines, remove cleaned fabrics from the machine, press the cleaned fabrics, and handle the waste streams generated by the cleaning process.

Inhalation and dermal exposure of dry cleaners to DF2000 was evaluated in a collaborative study between NIOSH and LHWMP in 2013.[13,14] Personal- and area air- samples for DF2000 were collected in two shops. The highest personal airborne exposures occurred when workers loaded and unloaded the dry cleaning machines and pressed dry cleaned fabrics. The highest detected air concentration in any shop was 21 milligrams/cubic meter (mg/m^3), which is very low relative to the occupational exposure limit of 300 mg/m^3.[a]

Dermal exposures were evaluated by applying PERMEA-TEC™ pads[b] (i.e., glove and protective breakthrough indicators) on the dry cleaner's skin. We noted very little opportunity for the dry cleaners to come into direct contact with DF2000. The greatest opportunity for dermal exposure occurred when the solid waste (still bottoms) was removed from the still for disposal. PERMEA-TEC™ pads were applied to the operator's skin before he donned disposable nitrile gloves to clean the still. DF2000 was detected at very low levels in two of the six pad samples and not detected in the other four pads.

We recognize that these exposure evaluations were limited to only two shops and that the hydrocarbon machines were relatively new and not yet prone to leakage. Nonetheless, these findings suggest low inhalation and dermal exposure potential for workers in shops using hydrocarbon dry cleaning solvents, at least with relatively new machines.

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[a] NIOSH selected the German Deutsche Forschungsgemeinschaft (DFG) maximum concentrations at the workplace (MAK) of 300 mg/m^3, expressed as an 8-hour time weighted average.
[b] SKC Limited, Blandford Forum, Dorset, U.K.

Table 3. Summary of toxicity information from Safety Data Sheets (SDS) of high-flashpoint hydrocarbon solvents			
Endpoint	**EcoSolv**	**DF2000**	**Calypsolv**
Inhalation			
Acute toxicity	*LC50[1]: >5.3 mg/L (rat)*	*Minimally toxic: LC50 > 5000 mg/m³ (rat)*	LC50: *>5.3 mg/L (rat)*
Irritation	No data provided	No data	No data provided
Ingestion			
Acute toxicity	*Minimally toxic: LC50 > 5000 mg/Kg (rat)*	*Minimally toxic: LC50 > 5000 mg/Kg (rat)*	*Minimally toxic: LC50 > 5000 mg/Kg (rat)*
Skin			
Acute toxicity	No data provided on SDS	*Minimally toxic: LD50[2] > 5000 mg/Kg (rabbit)*	No data provided
Skin corrosion/irritation	*No skin irritation effects*	*May dry skin, causing discomfort or dermatitis*	*No skin irritation effects*
Eye			
Eye damage/irritation	*No eye irritation effects*	*May cause mild, short term discomfort to eyes*	*No eye irritation effects*
Sensitization			
Respiratory sensitization	*Does not cause sensitization in laboratory animals*	No data	*Does not cause sensitization in laboratory animals*
Skin sensitization	*Does not cause sensitization in laboratory animals*	*Not expected to be skin sensitizer*	*Does not cause sensitization in laboratory animals*
Aspiration	May be fatal if swallowed and enters airways	May be fatal if enters airway after swallowing**	May be fatal if swallowed and enters airways
Mutagenicity	Bacterial cells, mammalian cells, and in vivo tests do not show mutagenic effects	*Not expected to be germ cell mutagen*	Bacterial cells, mammalian cells, and in vivo tests do not show mutagenic effects
Carcinogenicity	Limited evidence of carcinogenicity in animal studies	*Not expected to cause cancer*	Limited evidence of carcinogenicity in animal studies
Reproductive toxicity	*No adverse effects expected*	*Not expected to be a reproductive toxicant*	*No adverse effects expected*
Lactation	No data provided on SDS	No data available	No data provided on SDS

Table 3. Summary of toxicity information from Safety Data Sheets (SDS) of high-flashpoint hydrocarbon solvents

Endpoint	EcoSolv	DF2000	Calypsolv
Specific Target Organ Toxicity Single Exposure Repeated Exposure	No data provided on SDS *Inhalation NOEL[3]: >654 ppm (monkey)* *Oral NOEL: >1000 mg/Kg/d (rat)*	No data available *Not expected to cause organ damage from prolonged or repeated exposures*	No data provided on SDS *Inhalation NOEL: >654 ppm (monkey)* *Oral NOEL: >1000 mg/Kg/d (rat)*

**Italics indicate that data was derived from structurally similar compounds ("read-across") rather than specified product*

**Based on physicochemical properties of the material

[1] LC50 = The median lethal test concentration that kills 50% of the test organisms

[2] LD50 = The median lethal test dose that kills 50% of the test organism

[3]NOEL = No observed effect level

Potential for environmental impacts

As with human toxicity, evaluating the potential for these solvents to impact the environment is also confounded by the complexity of this chemical class and problems with nomenclature and classification. Our literature review failed to uncover many specific studies on the environmental effects of high-flashpoint hydrocarbon dry cleaning solvents, other than for the endpoints described below.

However, it should be noted that an overarching concern expressed by some is that promoting this petroleum-based technology increases our dependence on fossil fuels, which is associated with multiple human health and environmental impacts.[31]

Aquatic toxicity and bioaccumulation

The Pharos results for CAS number 64742-48-9 (i.e., DF2000) suggest that this chemical is "Persistent, Bioaccumulative and inherently Toxic (PBiTE) to the Environment (based on aquatic organisms)." This classification originates from the Canadian Environmental Protection Act - Environmental Registry - Domestic Substances List (summarized in Figure 6). TURI reported that high flash hydrocarbons exhibit moderate bioaccumulation potential and high aquatic toxicity.[15]

However, in their 2012 review, OECD concluded that aliphatic hydrocarbon solvents containing less than 2% aromatics with a carbon length of C11 and above are not expected to exhibit acute aquatic toxicity due to water solubility limitations and slow uptake kinetics.[30] OECD also stated that determining the bioaccumulation potential for this chemical class is challenging and that this represents a key data gap that should be addressed.

In our previous evaluation of DF2000 in a fish bioassay, no acute lethality was seen at the maximum test concentration of 5,000 mg/L.[10] Measured DF2000 concentrations in the test vessels containing fish were below the RDL (236 µg/L).

The experimental findings from this study and our previous fish bioassays suggest that these solvents do not exhibit acute aquatic toxicity in rainbow trout. Therefore, we conclude that the classification of these products as PBiTE (based on aquatic organisms) is likely not appropriate because of their limited water solubility.[10]

Sediment toxicity

A report prepared for the Massachusetts Department of Environmental Protection states that: *"…the toxicity of hydrocarbons in sediments to benthic organisms is caused by the hydrocarbons that partition from the organic fraction of sediment particles into porewater and from porewater into the tissues of sediment-dwelling organisms.*[32] *Both bioaccumulation and toxicity of hydrocarbons increase as the octanol-water partition coefficient of the hydrocarbon increases."*

This report then suggests that C9 to C12 hydrocarbons are sufficiently soluble in water that they may contribute to sediment toxicity. However, higher molecular weight aliphatic hydrocarbons (i.e.., C13 to C18 and above) have such low water solubilities and high octanol-water partition coefficients that little partitions into the water phase where it can be bioconcentrated by aquatic organisms.

As discussed in the section above, *Aquatic toxicity and bioaccumulation*, the hydrocarbon dry cleaning solvents evaluated in this report have very limited water solubility. Therefore, it is unlikely that these products would contribute significantly to sediment toxicity.

Air quality and smog formation

High-flashpoint hydrocarbons have been described as VOCs by several authors, including TURI and CARB.(15,18) The principal concern with regard to air quality is the formation of ground level ozone (i.e., "smog") from a mixture of VOCs, nitrogen oxides, oxygen, and sunlight.(18)

EPA's Safer Choice program provides a definition of a VOC-exempt solvent based on 40 CFR 59.203 – Standards for Consumer Products:(33)

- Has a vapor pressure of less than 0.1 millimeters of mercury (mmHg) at 20 °C; or, if the vapor pressure is unknown:
    - Consists of more than 12 carbon atoms; or
    - Has a melting point higher than 20 °C and does not sublime.

While the high-flashpoint hydrocarbon solvents evaluated in this report include carbon chain lengths of greater than 12, they do not meet the exemption criteria because their vapor pressures exceed EPA's 0.1 mmHg threshold (see Appendix A):

- DF2000: 0.3 mmHg (at 20 °C).
- EcoSolv: 1.5 mmHg (at 38 °C).
- Calypsov: 0.11 kPa = 0.83 mmHg (at 20 °C).

A smog chamber study by Presto et al. suggested that secondary organic aerosols may be formed from the photo-oxidation of low volatility precursors, like high molecular weight alkanes.(34) A 2018 study by McDonald et al. suggested that volatile chemical product emissions, such as those that may result from the use of high-flashpoint hydrocarbon dry cleaning solvents, may make a significant contribution to overall fossil fuel-derived VOC emissions in industrialized cities.(35)

We conclude that this product class may have adverse effects on air quality, which is a major concern in ozone non-attainment areas. As of June 30, 2018, no counties in Washington state were regarded as ozone nonattainment areas.(36) However, two areas are regarded by Ecology as "problem areas" for ozone: the western foothills of the Cascade Mountains and the Tri-Cities area (Kennewick, Pasco, Richland).(37)

Groundwater contamination

These high-flashpoint hydrocarbon solvents are less dense than water and thus are considered "Light Nonaqueous Phase Liquids" (LNAPLs). CARB concluded that groundwater contamination by hydrocarbon dry cleaning solvents is less problematic than for PERC, which is classified as a Dense Nonaqueous Phase Liquid" (DNAPL).(18) While LNAPLs can still spread laterally underground, they float near the top of the water table. Consequently, LNAPL contamination is much more easily remediated, compared to contamination by DNAPLs, which can sink deep into underground aquifers. Natural biodegradation of aqueous phase LNAPLs can also facilitate remediation.(38,39)

Nevertheless, any non-aqueous phase liquid, regardless of its density relative to water, can represent a long-term source of groundwater contamination.

Soil contamination

Hydrocarbon solvents used in dry cleaning, like other petroleum hydrocarbons, can contaminate soil through sorption (attachment) of LNAPL components to soil particles. While natural biodegradation processes can remove or reduce levels of these solvents in the environment, residual particles may serve as long-term sources of soil and water pollution.(38)

Vapor intrusion

Vapor intrusion refers to the infiltration of VOC vapors from underground sources into buildings, which can result in inhalation exposures.

Hydrocarbon dry cleaning solvents typically biodegrade at a moderate rate under aerobic (oxygen-rich) conditions, and no toxic byproducts are created. Because of this moderately rapid degradation process, only relatively low concentrations of hydrocarbon solvent vapors are typically present beneath the ground surface. Consequently, vapor intrusion is typically less of a concern. However, there are several specific scenarios in which vapor intrusion may still be a concern for non-chlorinated hydrocarbons, such as if methane is generated under anaerobic conditions.(39)

Dry cleaning process considerations

It is important to recognize that the use of a hydrocarbon dry cleaning solvent is only one component of the overall potential for exposure to hazardous chemicals during the dry cleaning process.

Before being placed in the dry cleaning machine, stained fabrics may be pre-cleaned or "pre-spotted" with spot treatment products.(40) We have observed multiple opportunities for harmful exposures to workers while using spot cleaners. In a chemical inventory of hydrocarbon dry cleaners, we noted the use of spotting agents containing PERC, trichloroethylene (TCE), methylene chloride, hydrofluoric acid, and other hazardous substances.(3,4) These products are typically used without personal protective equipment.

Following spot treatment, the fabrics are placed in the dry cleaning machine where they are typically agitated with solvent and a detergent. Consequently, residual spot cleaning chemicals may be introduced to the machine, resulting in contamination with chlorinated hydrocarbons and other substances.

Additives may also be introduced to the machine during cleaning. The most common additive is "sizing," which is typically comprised of plastic-based hydrocarbon resins in a petroleum solvent carrier, and is used to restore shape, body, and texture to fabrics.(40) We have observed the inadvertent contamination of a hydrocarbon dry cleaning machine with a sizing agent designed for use with PERC operations (this shop was supplied with Adco Renew Liquid Sizing®, which contains up to 50 percent PERC).

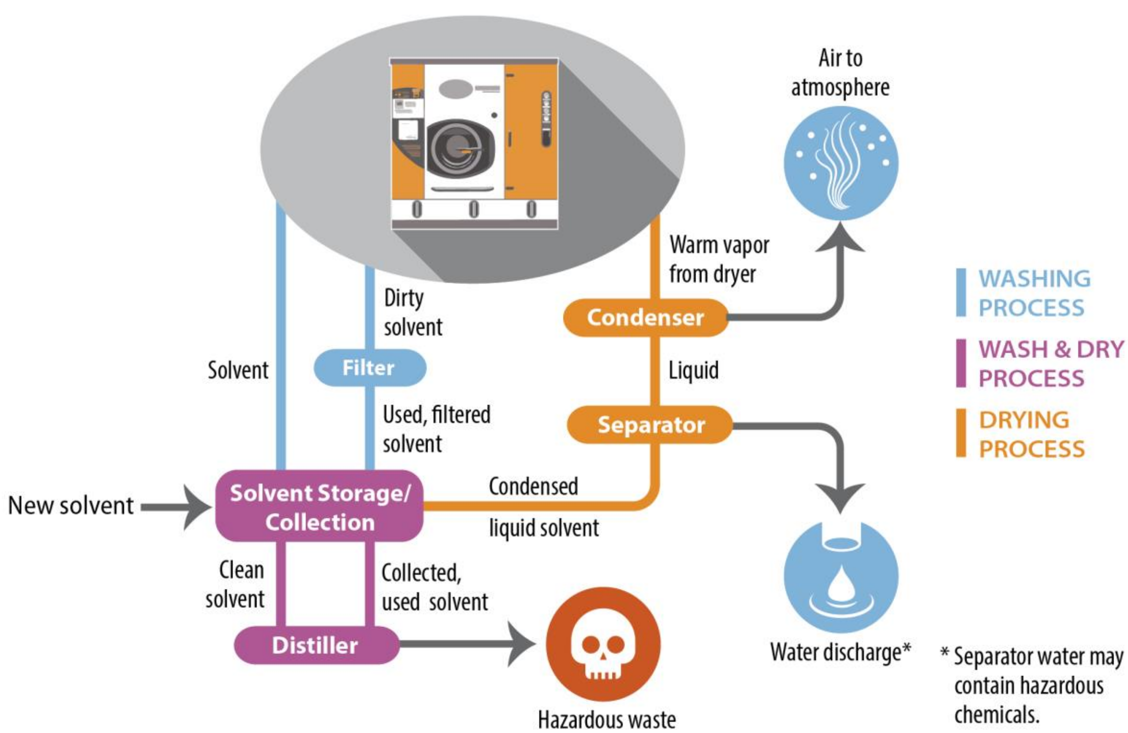
In conclusion, workers may be exposed to several harmful substances while dry cleaning with high-flashpoint hydrocarbon solvents. Although relatively safe spot cleaning products and other process chemicals are now available, many hydrocarbon dry cleaners continue to use products originally designed for use with PERC machines that contain PERC, TCE, and other hazardous substances. These products may then harm the workers and contaminate their machines and waste streams (see below).

Waste stream considerations

Overview of waste generation in dry cleaning

A typical dry cleaning process is shown in Figure 7. In most modern dry cleaning machines, heated solvent vapors generated during the drying cycle pass through a refrigerated condenser. The condenser cools the air and condenses the solvent vapor, which is recovered.(41) 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. The solvent vapors flow to a condenser, and condensed solvent and water flow to a water separator.(42) This distillation process prevents impurities from building up in the solvent and generates a concentrated waste material called "still bottoms." This semi-solid waste contains residual solvent and non-volatile components, such as, detergent, sizing, waxes, oils, and greases.(41,43,44) After the machine has cooled (usually overnight), the still bottoms are transferred 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.(3,4)

Figure 7. Dry cleaning process



The water separator receives the mixture of solvent and water from several sources, including condensates from the still and the refrigerated condenser. These mixtures separate into immiscible solvent and water layers. The water phase is either periodically drained from the machine's storage tank or allowed to continuously fill an external container (typically a 5-gallon plastic bucket).[3,4] This "separator water" usually contains <1 parts per million (ppm) of solvent, unless the phases do not fully separate or the water contains detergents or other impurities.[41]

Other waste streams include used filters, contaminated "mop water," and absorbent materials used to clean up accidental spills.

Characterization of waste streams in hydrocarbon dry cleaning

In Washington state, the term "dangerous waste" includes two types of wastes: 1) "hazardous waste," which is regulated by the federal government, and 2) "dangerous waste," which is defined only by Washington state's regulations (i.e., "state-only" wastes). Washington further divides all federal and state-only dangerous wastes into two categories: Dangerous Waste (DW) and Extremely Hazardous Waste (EHW).

Waste codes are then assigned to the hazardous waste, if applicable, including those specified in federal regulations (i.e., F, K, P, U, or D codes) and those specific to Washington state:

- WP01—Persistent dangerous wastes, halogenated organic compounds (EHW).
- WP02—Persistent dangerous wastes, halogenated organic compounds (DW).
- WP03—Persistent dangerous wastes, polycyclic aromatic hydrocarbons (EHW).
- WPCB—Wastes that designate as state-specific PCB sources (DW).
- WT01—Toxic dangerous waste, extremely hazardous (EHW).
- WT02—Toxic dangerous waste (DW).
- WSC2—Solid or semi-solid corrosive waste (DW).

For more information, the reader is referred to *Chapter 173-303 WAC: Dangerous Waste Regulations*.[45]

We conducted an extensive field campaign in 2011 and 2012 to characterize the waste streams generated by 13 hydrocarbon dry cleaners.[3,4]

Reviewing our data against Washington state's dangerous waste regulations, we learned that the still bottoms generated by hydrocarbon operations were typically DW with waste code WT02, based on their acute toxicity to juvenile rainbow trout in Ecology's Method 80-12 fish bioassay.[3,4] A subsequent LHWMP study found that the high acute aquatic toxicity of these still bottoms (relative to the high-flashpoint hydrocarbon solvent) likely reflected, at least in part, the presence of residual surfactants (present in detergents), which are extremely toxic to juvenile rainbow trout.[46]

We also learned that the separator water from most hydrocarbon shops typically met the King County Industrial Waste (KCIW) program's wastewater discharge limits.[3,4] Consequently, this separator water may be discharged to the sewer once the shop has received a permit from KCIW. However, we found that the separator water from one hydrocarbon shop contained 13,000 μg/L TCE and failed KCIW's criteria. Although the source of TCE was never determined, we suspected contamination from either residual spot cleaning product (R.R. Street's Picrin® is 100 percent TCE) or the inadvertent addition of a TCE-containing process chemical directly to the dry cleaning machine.[3,4]

In conclusion, the still bottoms from hydrocarbon machines are typically DW and the separator water is typically eligible for discharge to the sewer in the absence of chlorinated spot cleaners and other chlorinated process chemicals.

Filtration technologies

Although most hydrocarbon dry cleaning machines rely on distillation to clean and regenerate their solvent, some machines use filtration. As described in a 2005 report from the Institute for Research and Technical Assistance (IRTA),[47] suppliers of "tonsil" filtration media claim that it has the following advantages:

- Absorbs moisture in the hydrocarbon solvent and makes it much easier to control bacterial growth.
- Makes distillation unnecessary, allowing the machine's footprint to be much smaller than that of a typical dry cleaning machine.
- Eliminates the need for detergent.
- Readily scavenges dyes that would cause bleeding and transfer of the dye to other garments.

IRTA also reported that the still bottoms from dry cleaning facilities that did not use tonsil filter were toxic to fish. In contrast, the samples from those that used tonsil were not toxic. IRTA suggested that one possible explanation for this result is that the facilities that used tonsil filter media did not use detergents, whereas the facilities that did not use tonsil did use detergent.[47]

More recently, UNISEC introduced a "non-distilling, no-steam, no-water" hydrocarbon dry cleaning system.[48] This manufacturer claims that this technology reduces gas, electric, water, and maintenance costs.

Consequently, solvent regeneration processes based on filtration, rather than distillation, may offer additional advantages, insofar that they may offer savings in energy and water usage. The waste filtration material is typically disposed of as solid waste, rather than hazardous waste. However, it is not clear whether these waste streams have been adequately characterized according to Washington state's dangerous waste regulations.

Flammability

As stated previously, these high-flashpoint hydrocarbon dry cleaning solvents are regarded as Class IIIA solvents, with flashpoints between 142 °F and 145 °F. Although they are less flammable than other hydrocarbon solvents previously used for dry cleaning (e.g., Stoddard solvent), they are more flammable than PERC, which is regarded as nonflammable.

This increased flammability may have important implications for dry cleaners when they replace their PERC machines. Some jurisdictions may require the installation of fire suppression systems and fire-retardant building materials, adding to the cost of conversion. However, in a local multiagency workgroup collaboration, local fire departments recognized that hydrocarbon dry cleaning machines are typically equipped with integrated fire suppression systems. Consequently, the Washington state fire code was updated in 2015 to permit installation of adequately equipped hydrocarbon machines without requiring automatic sprinkler systems (Section 2108.2).[(49)]

Dry cleaners' perspectives

Our program has enjoyed a 25-year working relationship with our local dry cleaning community, having provided technical assistance, recruitment into our "EnviroStars" environmental recognition program, and funding to help dry cleaners replace their PERC machines. We have also convened focus groups, conducted surveys and one-on-one interviews, and hosted meetings of the now defunct Korean Dry Cleaners Association.

Consequently, we have had many opportunities to discuss their preferred alternatives to PERC dry cleaning and learn about the motivators and barriers associated with adopting new technologies. We have learned that many dry cleaners are not aware of the human health effects associated with PERC. However, they are aware of its potential environmental impacts because of costly cleanups in the region and subsequent pressure exerted by landlords and insurance companies to replace their PERC machines. Some dry cleaners are also fearful of impending federal regulations to ban PERC under the Clean Air Act and the Toxic Substances Control Act.

Although many in the environmental and public health communities consider professional wet cleaning to be the most environmentally-friendly alternative to PERC, there remains resistance among dry cleaners to adopting this technology as their exclusive cleaning process. Stated reasons include concern that customers want them to use organic solvents to clean their clothes effectively, decades of familiarity with an organic solvent cleaning system, the belief that "nothing cleans like PERC," and lack of first-hand experience with professional wet cleaning.

Underlying many of these concerns is the fact that dry cleaners are critically dependent on their cleaning machines for their livelihood. Given that most shops are only marginally profitable, any interruption to their business or added expense is extremely problematic. The capital expense associated with adopting professional wet cleaning is prohibitive for many dry cleaners. In addition, many cannot afford the business interruption and training associated with learning new cleaning technology. There is also a perception that it is very difficult to clean fabrics like wool, suede, and leather using professional wet cleaning because of problems with shrinkage. Many dry cleaners are also concerned about the additional labor costs and time associated with tensioning fabrics that are professionally wet cleaned. Thus, most dry cleaners would prefer to replace their PERC equipment with hydrocarbon machines.

A compromise approach currently being used in California is to provide funding for PERC dry cleaners to purchase professional wet cleaning equipment, while allowing them to also purchase a small capacity filtering hydrocarbon machine with their own funds.[a] This allows the dry cleaner to incorporate professional wet cleaning into their business while also allowing them to effectively clean the relatively small fraction of problematic fabrics with a more familiar process.

[a] Personal communication with Eugene Rabin, Air Pollution Specialist, California Air Resources Board. May 2018.

CONCLUSIONS

To our knowledge, this study is the first to assess the aromatic hydrocarbon content and determine the acute aquatic toxicity of the hydrocarbon dry cleaning solvents most frequently used in King County. Our chemical analyses and fish bioassays confirmed that DF2000, EcoSolv, and Calypsolv are complex hydrocarbons that do not contain detectable concentrations of harmful aromatics, such as benzene. These results match the information provided on the Customer Specifications for these products. We also found that these products are not acutely toxic to fish, likely reflecting their negligible water solubility.

However, we recognize the following limitations of the experimental portion of this study:

- We only evaluated the two most frequently-used hydrocarbon solvents available in our local market (i.e., DF2000 and EcoSolv) and a single sample of a new product (i.e., Calypsolv). Consequently, we cannot generalize about other products marketed as hydrocarbon dry cleaning solvents.
- Logistical problems and resource constraints prevented us from evaluating additional product lots. The finding of low levels of PERC in a single container of EcoSolv highlights the importance of analyzing multiple samples of product.
- Our chemical analyses focused primarily on BTEX and other VOCs. Consequently, other hazardous constituents may have been present in these products that would not be detected using our analytical methods.
- The fish bioassay used in this study was Ecology's standard method for evaluating acute aquatic toxicity and does not address chronic effects. Given the limited water solubility of these products, a more comprehensive evaluation of aquatic toxicity would include longer-term tests with a more sensitive test species, such as *Daphnia*.

Based on our literature review and interviews, we also conclude that toxicity evaluations of these high-flashpoint hydrocarbons are complicated by: 1) the inclusion of diverse products in the hydrocarbon dry cleaning solvent category, and 2) the inadequacy of CAS numbers to uniquely identify products in this chemical class. These issues prevent accurate characterization of these solvents with existing hazard evaluation systems.

Despite our findings that these products do not contain detectable levels of BTEX and are not acutely toxic to fish, we recognize the possibility for harm to human health and the environment from using these solvents. For example, there are outstanding questions about their effects on ambient air quality and the potential for contamination of hydrocarbon dry cleaning machines with harmful legacy process chemicals. There is also a lack of independent (i.e., non-industry) toxicology data. As petroleum-based products, these solvents rely on fossil fuel extraction. Waste streams may also be classified as Dangerous Waste and their increased flammability compared to PERC raises safety concerns. To mitigate worker exposures and environmental contamination, it is critically important that hydrocarbon machines are maintained adequately, solvent spills are prevented, and the waste streams managed appropriately.

We conclude that although the preferred alternative to PERC is professional wet cleaning, the hydrocarbon solvents described in this report appear to be viable alternatives to PERC for dry cleaners. We do not consider EcoSolv, DF2000, or Calypsolv to be “regrettable substitutes” for PERC, given that they do not appear to contain BTEX and are not acutely toxic to fish. However, because several diverse products are frequently included in the hydrocarbon category, our results cannot be generalized beyond the specific high flashpoint hydrocarbon solvents examined in this study.

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- Donald Ward (New York State Department of Environmental Quality)
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We also wish to express thanks to the industry representatives who shared their expertise with regard to the chemistry, toxicology, and manufacture of hydrocarbon dry cleaning solvents.

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