IC2 Webinar: Safer Alternatives to Perchloroethylene in Garment Care

2018-04-03

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Today's Presenters

- Joy Onasch, Business & Industry Program Manager, TURI
- Ashley Pedersen, Policy Liaison, King County LHWMP
- Steve Whittaker, Ph.D.; Research Services Program Manager; King County LHWMP



Upcoming IC2 Webinars

IC2-BizNGO Webinar: The Chemical Hazard Data Commons Wednesday, April 18, 1:00 - 2:00 PM EDT/10:00 - 11:00 AM PDT https://attendee.gotowebinar.com/register/5690285324587364097





Alternatives to Perchloroethylene In Garment Care IC2 Webinar - April 3, 2018

Joy Onasch, P.E. Business & Industry Program Manager



What is Perc and Why is it a Problem?

Able to dissolve most organic materials, perchloroethylene (PCE or perc) is the most widely used dry cleaning solvent in Massachusetts and nationally.

A typical dry cleaning machine...





Though perc machines have improved emissions over time, there is still exposure to workers and the public through co-located residences and clothes taken home.



Short and long term health effects linked to use of perc include:



- Damage to liver & kidneys
- Neurotoxicity
- Reproductive toxicity
- Developmental toxicity
- Cancer



Misuse of perc can lead to soil and groundwater contamination.

75% of drycleaner sites in the US are contaminated.

Many are Superfund sites.



Alternatives Studied

- Wet cleaning
- **CO**₂
- High flash point hydrocarbons
- Acetals
- Propylene-glycol ethers
- Volatile methyl siloxanes
- n-Propyl bromide

2012

Assessment of Alternatives to Perchloroethylene for the Professional Garment Care Industry



Report No. 27



Methods and Policy

Key Criteria – 1st set

Technical/Performance Cycle time and load capacity Difficult materials Pretreatment and finishing requirements

Economic Equipment costs Chemical costs Energy costs



Key Assessment Criteria		Perc (reference)	Wet Cleaning ¹	Carbon Dioxide	High Flashpoint Hydrocarbons	Acetal	Propylene Glycol Ethers	Siloxane	n Propyl Bromide
Common Trade Names / Manufacturers of Equipment or Solvents			Wascomat, Miele, Continental, HwaSung, AquaSolo	Cool Clean Technologies, Solvair®	DF2000 [™] Fluid, EcoSolv [®] , ShellSol D60, Caled Hydroclene	Solvon K4	Solvair®, Rynex 3®, Impress®, Gen-X®	Green Earth® D5 solvent	Drysolv®, Fabrisolv™ XL
Solvent Chemical Identification [CAS#]		Perchloroethylene [127-18-4]	Solvent: Water Detergents: See full report ¹	Carbon Dioxide [124-38-9]	Naphtha (petroleum) hydrotreated heavy [64742-48-9]; C10-C13 Isoalkanes [68551-17-7]	1-(butoxy methoxy) butane (butylal) [2568-90-3]	dipropylene glycol tert-butyl ether, [132739- 31-2]; di- propylene glycol n-butyl ether, [29911-28-2]	Decamethylcyclo- penta siloxane (D5) [541-02-6]	N Propyl Bromide (nPB) [106-94-5]
	Cycle time (min)	45	20-40	35-45	60-75	60-65	>45	53-58	45
P .	Load capacity (lb)	50	20-75	60	35-90	40-90	43	55	50
Technical / Performance ²	Materials system may have difficulty with	Leather, suedes, beads, delicates	Leather, suede and fur	Triacetates, specially dyed acetates	Vinyl appliqués	Appliqués or decorations glued to fabric	None identified	None identified	Leather, suedes, beads, delicates
	Spotting requirements	Moderate	Low	High	Moderate	Low	Low	High	Low
	Equipment	\$40,000 - \$65,000	\$36,000 - \$61,000	\$100,000 - >\$150,000	\$38,000 - \$75,000	\$50,000 - \$100,000	\$56,000	\$30,500 - \$55,000	\$40,000 - \$60,000 or retrofit costs
Financ	Chemical cost per gallon	\$17	\$0.007/gal (water); \$25-\$31/gal (detergent)	\$0.18/lb (CO ₂); \$40/gal (detergent)	\$14-\$17	\$28-\$34	\$25-\$30	\$22-\$28	\$40-\$64
cial	Electricity usage ³ (kWh/100 lb)	26.6	9.3	30.9	35.5	Similar to hydrocarbon	Unavailable	54.2	Unavailable
	Typical cost per pound cleaned ⁴	\$0.63-\$1.94 avg.\$1.02	\$0.57-\$1.32 avg. \$1.10	\$1.40	\$0.73-\$1.02 avg. \$0.88	Unavailable	\$1.14	\$1.08-\$2.33 avg. \$1.71	Unavailable

Are Alternatives Effective and Affordable?

All options are technically feasible Some may have impact on throughput Some have limitations on the fabrics they can handle

Most options are affordable CO₂-based options not economically feasible (for majority of smaller MA shops)



Key Criteria – 2nd set

Environmental

Persistence Bioaccumulation Aquatic Toxicity

Health and Safety Exposure limits

CNS effects Carcinogenicity Repro/developmental toxicity Flammability



Key Assessment Criteria		Perc (reference)	Wet Cleaning ¹	Carbon Dioxide	High Flashpoint Hydrocarbons	Acetal	Propylene Glycol Ethers	Siloxane	n Propyl Bromide
Environmental	Persistence ⁵ (water, soil, sediment, air)	M (water), H (soil, sed, air)	L (water, soil, air), M (sed)	NA	L (water, soil, air), M (sed)	L (water, soil, air), M (sed)	L (water, soil, air), M (sed)	L (water), M (soil), H (sed, air)	L (water, soil), M (sed), H (air)
	Bioaccumulation ⁶	Low	Low	NA	Moderate	Low	Low	Moderate	Low
	Aquatic Toxicity ⁷	Moderate	Low to Moderate ⁸	Low	High	Moderate ⁹	Low	High	High
Human Health	Recommended Exposure limits ¹⁰	25 ppm	NE	5000 ppm	100 ppm ¹¹	NE	NE	10 ppm ¹²	10 ppm
	Central Nervous System Effects	Yes	No ¹³	No ¹⁴	Yes	No data available	Yes	Som e evid ence	Yes
	Carcinogenicity	IARC Probable human carcinogen	Not classified by IARC	Not classified by IARC	Not classified by IARC	Not classified by IARC	Not classified by IARC	Som e evid ence	Clear evidence in animal studies by NTP
	Reproductive / Developmental Toxicity	Yes	Negligible ¹⁵	No data available	No data available	No data available	No ¹⁶	Studies indicate concern	Yes
Safety	Flash Point/ Flammability	NA / Not Flammable	NA / Not Flam mable	NA / Not Flammable	140-145ºF / Combustible liquid	144ºF / Combustible liquid	160-212ºF / Combustible liquid	171ºF / Combustible liquid	NA ¹⁷



Are the Alternatives Safer than Perc?

All are less persistent; HC and Siloxanes are more bioaccumulative and toxic in aquatic environment

Most are safer to humans ... EXCEPT ...

- nPB is carcinogenic, reproductive toxic and neurotoxic NOT a safer alternative
- **Data gaps** present concern for alternatives that are new to the market (e.g., Solvon K4 acetals)



Key Criteria – 3rd set: Applicable Regulations

Hazardous Air Pollutants

Designated VOCs

Massachusetts regulations

- Listed toxics under TURA
- Environmental Results Program

Hazardous waste disposal issues

Wastewater discharge restrictions



Key Assessment Criteria		Perc (reference)	Wet Cleaning ¹	Carbon Dioxide	High Flashpoint Hydrocarbons	Acetal	Propylene Glycol Ethers	Siloxane	n Propyl Bromide
	Clean Air Act Hazardous Air Pollutant (HAP)	Yes, HAP	No	No	No	No	No	No	No
Applicable Regulations	Clean Air Act NAAQS VOC ¹⁸	No, Exempt ¹⁹	No ²⁰	No	VOC	voc	VOC	No, Exempt ¹⁹	VOC
	Massachusetts regulated (TURA, ERP)	TURA Higher Hazard Substance, ERP	No	No	No	No	No	No	TURA
	Hazardous waste disposal required	Yes - Listed hazardous waste	No	No	Yes Waste Oil = Hazardous Waste in MA	No	No	No	No; monitor for residual perc if using retrofitted machine
	Wastewater discharge restrictions	No	Discharge to sewer or holding tank ²¹	No	No	No	No	No	No



Are the Alternatives More Regulated than Perc?

Most options are combustible or flammable, requiring additional control for safety

Several options are VOCs

Most options involve industrial waste disposal, though not hazardous waste disposal

Wet Cleaning poses issues for facilities on septic

nPB newly regulated under TURA and is a higher hazard substance!



Wet Cleaning and CO2 are considered the most environmentally friendly options. Wet Cleaning technology is the more affordable of the two.

Washer and dryer use biodegradable detergents and conditioners Finishing equipment re-shapes and dries the slightly damp clothes







MA Conversions to Wet Cleaning

From 2008 through 2018 TURI has given 19 grants to dry cleaners to eliminate the use of perc and switch to dedicated professional wet cleaning

- Cleaners save money on solvent, waste, water, and electricity
- Cleaners are fully satisfied with the process and product; there is less regulatory oversight and risk of contamination
- The work environment is greatly improved
- Customers are very pleased with quality



KMK Cleaners in Walpole Creates Healthier Workplace

40% reduction in electricity costs

Greater than 50% drop in water use

Saving about \$1,500 per month in operating costs

"As a family run business, we've been interested in getting away from perc for quite a while, and professional wet cleaning was the right answer. It makes the shop a healthier place for my Dad and me, our employees, and for future generations." – Kristy Mead, Manager, KMK Cleaners



AB Cleaners in Westwood Creates Safer Work Environment with Improved Quality

Reduced electric use by almost 30%

Reduced water use by over 50%

Saving over \$400 per month in operating costs

"We knew that perc was not good for us. I was concerned for the health of my pregnant wife and baby and also for my employees. With wet cleaning, there has been a huge improvement in the way the air smells and the clothes come out cleaner without any shrinkage or the feel of chemicals." – Joon Han, owner of AB Cleaners



Business & Industry Program Manager: Joy Onasch

Phone: 978-934-4343 Email: joy@turi.org Web: www.turi.org/drycleaning



Helping dry cleaners switch from PERC to professional wet cleaning

Ashley Pedersen, Policy Liaison Local Hazardous Waste Management Program in King County, WA



IC2 Presentation April 3, 2018

Federal Changes = Local Opportunities

Local Risks **Federal Changes Local Opportunities** New chemical review process Insufficiently protective Local review, prioritization, regulations and action on key chemicals EPA's final decisions will of concern preempt local and state **Regrettable substitution** (chemical "whack-a-mole") regulations EPA creates the 'sticks' and LHWMP creates the 'carrots' for positive change phthalates LHWMP is uniquely positioned to work with businesses and residents

Graphic: nrdc.org



Chemicals being reviewed by EPA

Chemical	Health impacts	Examples of uses
1,4-dioxane	Cancer	Dyes, varnishes, waxes
1-bromopropane	Cancer, developmental and reproductive effects	Foam cushions, dry cleaning
Asbestos	Cancer	Insulation, brake pads
Carbon tetrachloride	Cancer	Industrial uses
Cyclic Aliphatic Bromide Cluster	Developmental effects	Flame retardant, insulation
Methylene chloride	Cancer, developmental effects	Paint stripper
N-methylpyrrolidone	Developmental and reproductive effects	Paint stripper
Pigment Violet 29	Harms aquatic organisms	Dye for paints and plastics
Perchloroethylene (PERC)	Cancer	Dry cleaning, spot removers
Trichloroethylene	Cancer, developmental and reproductive effects	Dry cleaning and degreasers



EPA Scope of Risk Evaluation

2020:

PERC dry cleaning machines prohibited from co-location in residential buildings.

2021:

EPA is expected to ban or restrict PERC usage in dry cleaning facilities.

https://www.epa.gov/sites/production/ files/2017-06/documents/perc_scope_06-22-17.pdf



United States Environmental Protection Agency EPA Document# EPA-740-R1-7007 June 2017 Office of Chemical Safety and Pollution Prevention

Scope of the Risk Evaluation for Perchloroethylene (Ethene, 1,1,2,2-Tetrachloro)

CASRN: 127-18-4





The problem with PERC



probable
human
carcinogen
contaminates
groundwater,
surface water,
and soil

By the Numbers: PERC in King County

~90 PERC dry cleaners

15 years recommended life span of PERC machines

18 years

median age of PERC machines in King County

189 sites

contaminated by PERC



Professional Wet Cleaning

✓ effective

- ✓ safer for workers
- ✓ safer for the environment
- ✓ uses less energy
- ✓ saves money

Washer Machine



Metering System





Policy strategies for shifting away from PERC

Strategy	Description	Jurisdiction
Demonstrations	Educational or pilot programs that target local businesses	California New York Massachusetts South Coast Air Quality Mgmt. Distr. (SCAQMD)
Financial Assistance	Grants intended to help dry cleaning shops switch to alternative solvents	California New York Massachusetts SCAQMD City of Philadelphia
Ban	Phase-out or complete ban of PERC at different levels of jurisdiction	California SCAQMD Philadelphia Minneapolis
Signage	"Right to know" legislation requiring signage of chemical usage in dry cleaning businesses.	New York Massachusetts



Grant Program

Goal: A PERC-free King County

- ✓ 2017 Research
- ✓ 2018 Pilot
- Review and revise
- ✓ 2019 Launch

Thinking about buying new dry cleaning equipment?



Savinga in

utilitycosts

WE ARE OFFERING

to help you replace your perchloroethylene (PERC) dry cleaning machine with professional wet cleaning equipment.

"We made the switch to wet cleaning and are very happy with the results. There has been a huge improvement in the way the air smells and the clothes come out cleaner without any shrinkage or the feel of chemicals." - Joon Han, Owner, AB Cleaners, Westwood, Massachusetts

的体系主义

Safer for

worker health

Wet Cleaning Benefits

Grant Recipients Must

- Be located in King County and use a PERC. dry cleaning machine
- Clean out and dispose of your PERC machine safety
- Buy and install a professional wat cleaning system, including new detergents and spot cleaners
- Dispose of your old detergents, spot cleaners, and other chemicals you used with your PERC machine (we can help you dispose of these for free)
- Allow us to verify that you have disposed of your old machine and chemicals properly and
- that your new chemicals are relatively safe

For more information contact Patrick Hoermann: 노 206-263-1658 🛛 🖂 Patrick. Hoermann@kingcounty.gov

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anviranment

Bigibility for EnviroStara

recognition.

Alternative Formats Available 206-263-1650 TTY Relay: 711

1802 SMSTE Dry Cleaner Plot Project they WLR Hay Waters

of people in King County

prefer environmentally-

friendly businesses

Thank You!

Ashley Pedersen

Local Hazardous Waste Management Policy Liaison

ashley.pedersen@kingcounty.gov | 206.477.3761 www.hazwastehelp.org



What do we know about "hydrocarbon" dry cleaning solvents?

Steve Whittaker, Ph.D. Research Services Program Manager Local Hazardous Waste Management Program in King County, WA





Local Hazardous Waste Management Program in King County

IC2 Presentation April 3, 2018

Outline



- LHWMP's survey & field work
- What are "hydrocarbons"?
- Hazard evaluation
- Classification systems
- Manufacture
- Specifications
- Chemical analysis
- The Good and The Bad



LHWMP's survey & field work (2010-2012)



- 69% dry cleaners in King County using PERC
- 21% using "hydrocarbon":
 - The alternative of choice
 - Usage increasing
 - Separator water may be discharged to sewer (with permit)
 - Still bottoms are Dangerous Waste (DW) in WA (but not EHW)



What are "hydrocarbon" dry cleaning solvents?





- C10-C13 isoparaffinic naphthas / isoalkanes
- Class IIIA liquids (flash point 140-150 °F)
- Products:
 - Exxon Mobil DF-2000 most common in WA & MA
 - Chevron Philips EcoSolv
 - Technichem Calypsol
 - Others but not available in King County


Hazard evaluation of "hydrocarbon" solvents

DF-2000: CAS# 64742-48-9





How toxic are "hydrocarbon" solvents?

- Mckee et al. (2015):
 - 64742-48-9: "...consists of hydrocarbons having carbon numbers predominantly in the 6–13 range and boiling in the range of approximately 65 to 230°C."
- US EPA (2010):
 - "The composition and physical properties of this substance can vary considerably, depending on the raw material and the production processes"
- Official Journal of the EU (2006):
 - "The classification as a carcinogen need not apply if it can be shown that the substance contains less than 0.1% w/w benzene"



Classifying products: CAS# vs. EC#





• CAS#

- Non-specific
- May reflect feedstock, not product
- EC#
 - Designed by API for EU REACH
 - Specific to final product
 - EC# 920-901-0 = Hydrocarbons, C11-C13, isoalkanes, <2% aromatics



Manufacturing Isoalkane Dry Cleaning Solvents (High Flash "Hydrocarbons")





Sales Specification



DF-2000™ Fluid Dry Cleaning Fluid

Properties	Minimum	Maximum	Unit	Test Method
Appearance	Pass		-	VISUAL
Aromatic Content		0.02	wt%	AMS 140.31
Odor, Bulk	Pass		-	BTQAL 018
Color, Saybolt	30		_	ASTM D6045 ASTM D156
Flash Point	60		°C	ASTM D56
Specific Gravity @ 15.6/15.6 C	0.760	0.775	-	ASTM D4052





Chevron Phillips Chemical Company Issued Sales Specification

Name of Product ECOSOLV DRY CLEANING FLUID

Revision Date 3/26/2012

Chevron Phillips Chemical Company LP
10001 Six Pines Drive
The Woodlands, TX 77380
800-858-4327
Technical Service: 832-813-4862

Chevron Phillips Chemicals International N.V.	Chevron Phillips Chemicals Asia PTE Ltd.	
Brusselsesteenweg 355	5 Temasek Boulevard	
B-3090 Overjise, Belgium	05-01 Suntec Tower Five	
+32 (0) 2 689 12 11	Singapore 038985	
	+65 6337 9700	

Test	Units	Method	Typical	Minimum	Maximum	Qualitative	Note
Acidity of Dist Residue		ASTM D-1093	Neutral			Neutral	
Appearance		Visual	Clear with no particulate matter			Clear with no particulate matter	
Aromatics	ppm	ASTM E-169	40	(100		
Distillation - DP	FAH	ASTM D-86	406		410		
Distillation - IBP	FAH	ASTM D-86	374	355			
Flash Point, TCC	FAH	ASTM D-56	145	142			
Odor		Smell	Pass			Pass	
Saybolt Color	SAY	ASTM D-6045	30	30			
Specific Gravity 60/60		ASTM D-4052	0.7635	0.7580	0.7680		





TECHNICAL DATASHEET: CALYPSOLV[™] HC

TECHNICHEM

SPECIFICATIONS

Property	Unit	Method	Value	Qualitative/Notes
Appearance		Visual		Clean with no particular matter
Paraffins	%	GC	>99	
Aromatics	ppm	ASTM E169	40	Typical
Benzene	ppm	GC	<3	
Sultur	ppm	ISO 20846	<0.5	
Bromine Index	mg Br/100g	ASTM D1159	0.01	
Corrosion (3hrs@ 100 °C)		ASTM D130	1A	
Distillation, Initial Boiling Point	°C/°F	ASTM D86	189/372	
Distillation, Dry Point	°C/°F	ASTM D86	210/410	
Flash Point	°C/°F	ASTM D56	61/142	
Aniline Point	°C/ °F	ASTM D611	85/185	
Odor		Smell		Pass
Color	Saybolt	ASTM D156	+30	
Relative Evaporation Rate (nBuAc=1)		ASTM D3539	0.08	
Vapor Pressure @20 °C	kPa	Calculated	0.11	
Kauri-Butanol Value		ASTM D1133	26	
Viscosity @ 25 °C	mm²/s	ASTM D445	1.9	
Specific Gravity		ASTM D4052	0.7632	Typical
Molecular Weight	g/mol	Calculated	171	



Chemical analyses (2018)



- Purchased multiple 5-gallon lots of DF-2000 and EcoSolv from local supplier
- One sample of Calypsolv donated
- EPA Method 624 GC/MS for VOCs
 - Determine presence of BTEX (MDL = $1 \mu g/L$)
 - Identify isoalkane peaks





Local Hazardous Waste Management Program in King County



Instrument: 7890i.i

Column diameter: 2,00

Operator: Lily K.

Date : 24-JAN-2018 11:17 Client ID: 421193-130

Purge Volume: 5.0 Column phase:

Sample Info: Dry Cleaning Ecosolv_17HPEC005-1 manual 10X

Page 4

The Good



- Sampled solvents BTEX-free
- Manufacturers specify low aromatic hydrocarbon content, including benzene
- Not toxic to fish
- Largely immiscible with water
- Separator water may be discharged to sewer in King County (with permit)
- Filtration (rather than distillation) available
- Cleans well less aggressive than PERC
- Low odor
- Very low airborne exposures
- Community acceptance



The Bad



- They are petroleum hydrocarbons
- Flammable (Class IIIA solvent)
 - Fire suppression systems may be needed
- Bacterial growth
- Used with PERC spot cleaning products
- Occasionally use PERC process chemicals
- Generate a hazardous waste (still bottoms)
- Volatile Chemical Products air quality impacts
- Expensive (compared to wet cleaning)
- Greenwashing



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- Industry representatives who requested anonymity



www.lhwmp.org/home/Health/drycleaners.aspx



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Fish bioassays: LC50s (2018)

- DF2000: >5,000 mg/L
- Ecosolv: >100 mg/L
- Calypsolv: >100 mg/L



(PERC: 3.6 mg/L) (Solvon K4: 46 mg/L)





Exposure monitoring with NIOSH (2013)



	Main tasks		DF-2	2000 concentration (mg/m³)
Owner/Operator	Unloading and loading	Day 1 Day 2		1.4 0.99
Table E5. Results	of personal air samples collected A, May 2–3, 2013	d during sh	nort-term work	tasks, DF-2000
		d during sh	nort-term work Duration of task (minutes)	tasks, DF-2000 DF-2000 concentration (mg/m ³)
	A, May 2–3, 2013 Main tasks Loading, washing cycle, and	d during sh	Duration of task	DF-2000 concentration
drycleaning Shop	A, May 2–3, 2013 Main tasks	_	Duration of task (minutes)	DF-2000 concentration (mg/m ³)

Occupational Exposure Limit: 300 mg/m³ (DFG MAK)



The Training Workgroup continues to plan additional webinars intended to inform and engage. Let us know if you have ideas for future webinar topics or presenters.

Please give us your feedback through the post-webinar survey.



Thank you for attending.

