



WMRC Reports

Waste Management and Research Center,
A Division of the Illinois Department of
Natural Resources

Pollution Prevention Products for Illinois Dry Cleaners:

Testing and Recommendations of Chemicals for Wetcleaning

A Report of
The Center for
Neighborhood Technology

By
Anthony Star
William Eyring

RR-106
April 2004
<http://www.wmrc.uiuc.edu>



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The Center for Neighborhood Technology
Chicago, Illinois

By:

Anthony Star
and
William Eyring

April 2004

Submitted to the
Illinois Waste Management and Research Center
(A Division of the Illinois Department of Natural Resources)
One Hazelwood Dr.
Champaign, IL 61820

The report is available on-line at:
http://www.wmrc.uiuc.edu/main_sections/info_services/library_docs/RR/RR-106.pdf

Printed by the Authority of the State of Illinois
Rod R. Blagojevich, Governor

Acknowledgments

This project was supported by funding from the Illinois Waste Management and Research Center, a Division of the Illinois Department of Natural Resources. We would like to acknowledge the assistance of Marvin Piwoni, Dan McGinness, Robbi Farrell, and Julie Hafermann.

We would also like to thank Ann Hargrove for providing the testing facilities and wetcleaning technical assistance as well as the suppliers of the wetcleaning chemicals for making their products available for this study.

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Introduction

As drycleaners prepare for the 21st century, one key component of new business models is the adoption of cleaning processes that are environmentally friendly. The dominant process used in the second half of the 20th century, cleaning with the solvent perchloroethylene, has proven not to be sustainable or good for business. The industry, already facing pressure from low margins, and the growth in casual wear and washable garments, has also been burdened with the liability and compliance costs associated with the use of highly regulated solvents. The late 1990s provided hope to cleaners in the form of new technologies that offered the promise of reducing or eliminating those costs and risks. Wetcleaning, liquid carbon dioxide, glycol ethers, and siloxates have all been researched and to varying degrees commercialized.

Wetcleaning is the most established of these methods, carefully researched in a number of studies, in use in thousands of shops, and well supported by a number of equipment and detergent suppliers. Wetcleaning offers cleaners a way to reduce the use of perc and to provide better service to customers. Given the growing use of the process, there is an interest in ensuring that it will not have its own set of environmental issues. Perc on the other hand, has been linked to numerous environmental, health and safety problems. Increased regulation, fear of ground and water contamination, and the fears of landlords and insurance companies of working with the cleaning industry necessitate the search for new cleaning processes.

This report examines the wastewater from nine different products typically used in the wetcleaning process. While several previous studies have indicated few or no problems with the wastewater associated with the wetcleaning process, those studies have all examined single types of wetcleaning setups (e.g., machines, detergents). This study analyses the wastewater from nine of the most commonly used wetcleaning products to provide a broader overview of the characteristics of the effluent.

Wetcleaning is a range of techniques and technologies that use water as the primary solvent to clean clothes labeled “Dry Clean Only.” Wetcleaning is performed in a commercial setting with a system that utilizes water, specially formulated detergents, and precise control (either manual or computerized) over the mechanical action, water temperature and level, and carefully regulated drying. Wetcleaning spotting is done by using products designed for the process that can be safely discharged to sewer systems. Pressing of wetcleaned garments may be done either with conventional professional pressing equipment, or with tensioning finishing equipment and/or drying cabinets for greater productivity.

Framing the Question

In 1999, the Center for Neighborhood Technology surveyed 57 wastewater agencies in Illinois to provide a snapshot of their likely concerns regarding wetcleaning. Nine agencies responded to the survey (a 16% response rate), and most of their responses indicated low levels of concerns regarding the likely make-up of wetcleaning wastewater. Metals and phthalates were of most concern. (See Appendix A for the survey and summary of responses)

While this survey indicated that wetcleaning wastewater was not of major concern to the likely regulatory agencies, the Center for Neighborhood Technology continued to find concern among cleaners about the process. This concern grew out of several issues. First, cleaners who use perc operate in a highly regulated environment. As a result, cleaners are very aware of environmental issues, although the industry as a whole has struggled to be in compliance with those regulations. Therefore, cleaners are likely to wonder about and ask what are the environmental regulations that they assume any cleaning process will have. Second, the industry has been disappointed in the past. A CFC-based solvent called Valclean was introduced in the 1970s, and the industry was not properly warned about the coming phase-out of CFCs. Many cleaners who pursued this new technology suffered greatly or lost their businesses as a result. The cleaning industry has rightly placed a high barrier of acceptance on any new process as part of an attempt to avoid such wrong turns.

Wetcleaning appeared to have many positive environmental benefits, eliminating the use of chlorinated solvents was an obvious improvement. The main concern about wetcleaning was the fact that it did use water, and that water was typically discharged into sewer systems, although the amount of water used per garment is less than if that garment were washed in a conventional home top loading washing machine. One analysis of wetcleaning (UCLA/PPERCC) found that if every cleaner in the Los Angeles area were to convert to wetcleaning, it would be the equivalent of 3,106 new people moving into a region of 16 million people. That same study found that wetcleaning used less electricity and more natural gas than drycleaning, but that the net environmental trade-offs of that energy usage were about equal. Water and other resource usage issues appear to be insignificant for wetcleaning according to the UCLA study.

It may never be possible to absolutely determine that there are no risks from the wastewater of wetcleaning (or for that matter any other process that could be developed). However, developing a body of evidence from multiple tests under different conditions, coupled with recommendations of good operating practices, can provide cleaners with a strong degree of confidence that wetcleaning is an environmentally preferable method of garment care. This is ultimately the purpose of this report.

In 1999, the Center for Neighborhood Technology received funding from the Waste Management and Research Center, a division of the State of Illinois Department of Natural Resources to conduct the study described in this report. CNT had extensive experience in research and outreach with the professional fabricare industry and had conducted a previous wastewater study at the Greener Cleaner demonstration shop. WMRC's Hazardous Materials Laboratory is a state-sponsored research laboratory that helps businesses and citizens reduce and manage solid and hazardous wastes released to air, water or land.

This research used nine different wetcleaning products and tested them under similar conditions to examine the question of what is the variation among products currently available. This is a departure from the methods of previous tests, and helps to build the body of diverse evidence of wetcleaning environmental impact.

Summary of Previous Research

There have been four major studies of wetcleaning wastewater, EnvironmentCanada (1995), CNT (1996), UCLA (1997), and CAMP (1999). A summary of these studies is in Appendix B. The U.S. EPA also assessed two wetcleaning detergents that were on the market in the early 1990s as part of the 1998 Cleaner Technologies Substitutes Assessment.

The EnvironmentCanada study was the most limited and found no problems. The CNT study, as part of the broader case study of the Greener Cleaner demonstration shop, turned up a few minor issues. First, in one sample on which a drycleaning spotting agent had been used on one of the garments, a small amount of trichloroethylene was found. This led to the recommendation that when wetcleaning, only spotting agents designed for the process should be used. The report concluded that:

“This wastewater should be acceptable to most municipal wastewater treatment systems, most often without the need for any on-site pretreatment by the cleaning establishment. Metal concentrations in the wastewater were not found to be significant. Concentrations of toxic organic chemicals in the wastewater were generally below regulatory concern. There may be environmental concerns, including BOD and suspended solids levels, with discharges to small municipal systems and direct discharges to streams and other waterways.”

The most recent analysis of wetcleaning wastewater was conducted at Reehorst Cleaners in Cleveland by CAMP, Inc. Their study found that one specific conditioner had high phosphorus levels. Because this product is not used in all cleaning cycles this concern appeared to be more cautionary than a negative finding. The EPA’s Cleaner Technologies Substitutes Assessment included an analysis of the constituent chemicals in two wetcleaning detergents. Based upon theoretical models of release amounts, the report concluded that of the two detergents, one contained two components (lauric acid diethanolamide and sodium lauryl isothionate) that exceeded the concern concentration for aquatic life if the wastewater were directly released to surface water rather than to a municipal sewer system.

Study Design

It is important to know whether there would be contaminants in wastewater introduced by the detergents or conditioners that are used in wet cleaning. Since the contaminants that would be introduced by the apparel being cleaned in actual cleaning operations could mask those due to the wet cleaning chemicals, it was decided to conduct a controlled series of tests under rigorous test conditions.

The formulation of the research question and study protocol was developed by two staff members from CNT, Anthony Star, Research/Outreach Associate, and William Eyring, P.E., with assistance from the technical staff at Bill Eyring had previously directed the experimental work conducted at The Greener Cleaner in 1995 to 96. The test facilities and operational oversight of the cleaning process were provided by Anne Hargrove of Ann Hargrove and Associates, who is also the Executive Director of the Professional Wetcleaning Network and

former manager of the Greener Cleaner. The laboratory analysis was designed and conducted by the staff of WMRC. The actual testing was performed on three days, September 20, 1999, November 23, 1999 and February 21, 2000.

The study design was intended to simulate the conditions that would be found in a commercial wetcleaning process. Therefore a standardized load of linen and wool fabrics was run through a typical wetcleaning process. Due to the high cost and lack of easy availability of a full size wetcleaning washer, a cleaning protocol using a conventional home laundry machine was developed that provided an acceptable simulation.

The wetcleaning process uses the same sequence of operations as home laundry. The dry clothing, after being sorted by color and fabric, is washed in cold/room temperature water with a detergent. After an initial rinse, a conditioner is added to the water during final rinsing. The machine uses approximately eight gallons of water for washing and approximately eight gallons during the rinse cycles. For this test, a load consisted of four pounds of unbleached muslin fabric and a small swatch of wool fabric which had been soiled with one teaspoon (7 grams) of simulated soil. The soil used in each case was taken from a specially prepared mixture of 6 ounces of vacuum cleaner bag contents, 3.6 ounces of salt, 1.2 ounces of starch and 1.2 ounces of mineral oil. The 12 ounces of this mixture than were diluted with the addition of 6 ounces of water. The soil was ground into a small piece of wool fabric prior to each test.

Wet cleaning materials are marketed by vendors who design and recommend specific combinations of their products. Nine brands of detergent and conditioner were selected for the testing. Table 1 contains the nine combinations of detergent and conditioner.

Table 1: Wetcleaning Products Tested

Company	Detergent	Conditioner
Adco	Detergent	Conditioner
Aquatex	Detergent	Retex
Bufa	Odopal Basic	Pre Finish
Gurtler	Easiclean	Softfab
Kreussler	Aktiv	Apret
Laidlaw	Soft N' Brite	SoftenAll
R.R.Street	Hydrocare	Conditioner
Sanitone	Elegant Care	Revitalize
Seitz	P1	Top Size

Each of these products consists of a proprietary formula, and the makeup of them was not available. Material Safety Data Sheets for the products were of little assistance in identifying unusual components. This complicated the tests, since there are a virtually limitless combination of ingredients that could be searched for in the tests. One method that was attempted to define the analytes to be analyzed for was to survey people in the sewage treatment plants to determine which compounds would be priorities. The results of this survey are shown in Appendix A.

Testing Procedures

The collection of the samples for analytical testing was standardized. The machine was filled with cold water and the detergent was added. Then the soiled fabric samples were added. After 30 seconds of agitation in the wash cycle, eight ounces of the water was dipped out and temperature and pH were measured. At the end of the wash cycle, an eight-ounce sample was dipped from the wash water, from which two 40-milliliter vials were filled, with care taken to eliminate any air bubbles in the vials. Also, a 1-liter sample was collected of the discharge from the washer. The samples were sealed and chilled on ice. Cleaned sample containers were obtained from WMRC. The 40-ml samples were used to analyze for volatile organic compounds and the 1-liter samples were used for semi-volatile organic compounds and, in some cases, for total suspended solids and metals.

The same procedure was followed during the rinse cycle. The machine was automatically filled with cold water and the conditioner was added. The temperature and pH were measured after 30 seconds of agitation. Two 40-ml vials and a 1-liter bottle were collected and chilled.

On September 20, 1999, the first sampling was done in the presence of two staff members of the WMRC. Four different quantities of soil were tried and the 7-gram amount was selected for further testing. One and two ounces of detergent were tried and one ounce was chosen as the standard quantity. These trial samples were used by WMRC staff to refine their procedures for sample collection and analysis.

The first sampling for analysis was done on October 11, 1999. Ten runs were conducted. The first was a blank – there were no detergents, fabrics, soil or conditioners added to the water. The other nine runs simulated the effects of washing for the nine product combinations in Table 1, using the procedures described above.

Additional sets of tests were conducted on November 23, 1999 and again on February 21, 2000. The conditions and procedures were identical, except that the order of the products being tested was changed in each case.

The water temperature changed considerably from day to day. The wash water was as high as 32° C on October 10th and as low as 22° C on February 21st. The rinse water was as high as 20° C on October 10th and as low as 5° C on February 21st. (This can be explained, since the source of the water is Lake Michigan and not groundwater, which would be much more consistent.) The temperature may have had an effect on the pH. On October 10th, the wash water pH was between 7.18 and 7.63, while on February 21st it was between 7.42 and 8.03. On October 10th, the rinse water was between 6.57 and 7.92, while on February 21st it was between 7.94 and 8.90. On November 23rd, both the temperatures and the pHs were in the mid-points of these ranges.

Study Results

Tables 2 through 4 contain the results of the tests for phosphorus and metals, combined volatile organic materials, and semivolatile organic materials, respectively. All of the results shown are in parts per billion, which is equivalent to nanograms per milliliter or micrograms per liter.

Each of the tables shows regulatory standards, if any standards were located, for each material. Table 5 shows the sources of the standards, which could differ in different localities, states, or water bodies. Note that the regulations of the Metropolitan Water Reclamation District of Greater Chicago (MWRDGC), the operators of the local sewage treatment plants, are for concentrations in waters being discharged either to the treatment plants or streams. In contrast, the federal standards are for concentrations in the water of streams – concentrations that are considered acceptable in healthy streams. These are generally much lower than the allowable concentrations in discharges.

The analyses were complicated and extremely challenging for the laboratory staff. Detergents contain a wide variety of proprietary compounds, and are designed to dissolve any materials not a part of a fabric. The analyses, in comparison, depend upon measuring individual compounds and thus require that they be separated, at least in part, from the solution so that their concentrations are high enough to be detected. By reporting results in parts per billion, these analyses are 1,000 times more sensitive than the parts per million that are usually reported for all but the most hazardous substances in wastewater.

Total Suspended Solids

One of the tests that had been planned was for total suspended solids (TSS). This is a measure of the material in wastewater that can be caught on a filter. A total of eleven tests were conducted on samples taken on September 20 and October 11, 1999. All of the values were between 21 mg/L and 85 mg/L. There were no discernible differences between different products. This is the range that might be expected due to the quantity of soil that was placed on the fabric during the tests.

Phosphorus

The samples with detergent from October 10th were analyzed for phosphorus and a wide variety of metals, as shown in Table 2. The analysis was conducted by Inductively Coupled Plasma Mass Spectrometry.

The results for phosphorus need explaining. Phosphates are commonly found in detergents. Often an analysis of water quality shows the concentration of phosphate rather than phosphorus (to obtain the concentration of phosphate, which is an ion containing one phosphorus atom and four oxygen atoms, multiply the concentration of phosphorus by 3.06). Note that there is no MWRDGC standard for phosphorus, while the federal standard for streams is much lower than any of the sample concentrations, including the blank. The City of Chicago adds phosphates to its water supply in order to reduce scale buildup in its water pipes. Thus, there is a background phosphorus concentration in all of the samples. It also appears that seven of the nine detergent products contain phosphorus. This is not surprising; many home detergents also contain phosphorus. (Note that seven out of ten of the phosphorus analyses were obtained by a semi-quantitative determination. Quantitative results are considered accurate to within +/- 20% of true values, while semi-quantitative data should be within a factor of two times true values.)

Metals

The list of metals that were analyzed is long and contains many rare metals that are seldom considered. They are included because they could be readily analyzed and because we were curious about whether any were detectable.

There are a number of metals that are not in the table. Alkali metals (Sodium, Magnesium, Potassium and Calcium) are normal constituents in most water supplies at concentrations in the ppm range. They are not of concern, and the high concentrations in the water would mask any contribution from the detergents. The elements Lithium, Scandium, Indium and Yttrium were used as internal standards for the quantitative analysis, and therefore could not be reported as analytes in the samples.

Of the metals in Table 2 for which significant concentrations were measured, the following conclusions can be drawn:

- Aluminum is a common component of water supplies. It is not regulated by the MWRDGC. The most stringent federal stream standard is 87 ppb. While many of the samples measured more than this standard, the concentrations are not higher than for many wastewaters containing detergents or other common household agents.
- Iron, Manganese, Copper, Lead and Zinc are all well below the MWRDGC standards.
- Mercury is tricky – if it’s there at all, it was below the detectable limit. Yet the standard, even for MWRDGC, is two orders of magnitude less than the detectable limit. Unless mercury is actually used in a manufacturing process, the detectable limit is an acceptable concentration.
- Zirconium was detected in one of the tests, but there is no zirconium standard. The metal may be an ingredient in the detergent, or the result may be due to an anomaly in the test.

Table 2: Phosphorus and Metals

Material	MWRD Sewers	MWRD Streams	Federal Streams	Blank	Adco	Aquatex	Bufo	Gurtler	Kreussler	Laidlaw	RR Street	Sanitone	Seitz
Phosphorus			50 (4)	700	5500	4300	3800	600	1600	4900	6500	4000	600
Aluminum			87 (3)	48	172	134	157	59	61	136	186	211	55
Chromium	25000	1000	74 (1)	-	11	10	-	-	-	12	11	11	-
Iron	250000	2000	1000 (4)	-	69	36	50	18	42	55	62	79	20
Manganese		1000		-	31	32	24	-	-	40	27	36	-
Copper	3000	500	9 (1)	-	36	22	25	-	-	24	16	31	10
Lead	500	200	2.5 (1)	-	11	-	11	-	-	-	16	11	-
Zinc	15000	1000	118 (1)	-	55	41	54	-	13	55	61	56	-
Barium		2000		20	18	16	16	17	17	19	16	17	23
Zirconium				-	-	-	-	-	-	-	-	-	34
Mercury	0.5	0.5	0.77 (1)	<100	-	-	-	-	-	-	-	-	-

All measurements are in parts per billion.

- Indicates less than 10 parts per billion (For mercury less than 0.1 parts per billion.)

See the “Explanation of Standards”, below.

The following metals were also searched for and all results were below detection limits: Antimony, Arsenic, Beryllium, Bismuth, Cadmium, Cerium, Cesium, Cobalt, Dysprosium, Erbium, Europium, Gadolinium, Gallium, Germanium, Gold, Hafnium, Lanthanum, Lutetium, Molybdenum, Neodymium, Nickel, Niobium, Palladium, Platinum, Praseodymium, Rhenium, Rhodium, Ruthenium, Samarium, Selenium, Silver, Tantalum, Tellurium, Terbium, Thallium, Thulium, Tin, Tungsten, Uranium, and Vanadium.

Volatile Organic Compounds

The screening for volatile organic materials looked for 29 substances (1,1,1-Trichloroethane, 1,1,2,2-Tetrachloroethane, 1,1,2-Trichloroethane, 1,1-Dichloroethane, 1,1-Dichloroethene, 1,2-Dichlorobenzene, 1,2-Dichloroethane, 1,2-Dichloropropane, 1,3-Dichlorobenzene, 1,4-Dichlorobenzene, 2-Chloroethylvinyl Ether, Benzene, Bromodichloromethane, Bromoform, Bromomethane, Carbon Tetrachloride, Chlorobenzene, Chloroethane, Chloroform, Chloromethane, cis-1,3-Dichloropropene, Dibromochloromethane, Ethylbenzene, Tetrachloroethene, trans-1,2-Dichloroethene, trans-1,3-Dichloropropene, Trichloroethene, Trichlorofluoromethane, Vinyl Chloride).

These compounds were identified as those most likely to be in the samples, based upon initial screenings of the products themselves and screening that was done following the pre-testing of September 20th. Both the wash and rinse waters were analyzed. The wash water test is shown in the table as Det. and the rinse water as Cond., since detergents or conditioners would be the source of these compounds at any concentration above those found in the blank.

Sample analysis was performed using a purge and trap sample introduction system hooked to a gas chromatograph with photoionization and Hall detectors. Details of the analysis are discussed in Appendix C. Techniques discussed in the appendix include the addition of four surrogate compounds to most samples and use of analytical duplicates, instrument blanks, and sample matrix spikes.

Three analyses were performed on each discharge stream using samples from the tests of October 11th, November 23rd and February 21st. All samples were analyzed down to an estimated quantification limit of 10 ppb. Three volatile organic compounds were found in some of the samples. Two of them, chloroform and bromodichloromethane, are trihalomethanes and are often found in chlorinated tap water. Benzene was found in one sample, but two subsequent tests of the same product found no evidence of benzene. Table 3 provides results for the three out of 29 compounds that were detected.

Table 3: Detected Volatile Organic Materials

Material	Federal Stream	Blank	Adco		Aquatex		Bufa		Gurtler		Kreussler		Laidlaw		RR Street		Sanitone		Seitz			
			Det	Cond	Det	Cond	Det	Cond	Det	Cond	Det	Cond	Det	Cond	Det	Cond	Det	Cond	Det	Cond		
Chloroform	470 (1)	19	17	<10	<10	11	20	<10	11	<10	<10	<10	12	14	12	<10	<10	12	10	<10		
			13	12	27	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	10	
			<10	<10	12	<10	<10	<10	<10	<10	<10	<10	<10	<10	10	<10	10	<10	<10	<10	<10	<10
Bromodichloromethane	46 (1)	10	11	<10	<10	12	12	<10	<10	<10	<10	<10	10	11	<10	<10	10	<10	<10	<10		
			<10	<10	17	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
			<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Benzene	71 (1)	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	23	<10	<10		
			<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	
			<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10

All measurements are in parts per billion

Semivolatile Organic Compounds

The only compound present at anything like the limits is bis(2-ethylhexyl)phthalate. The blank also has measurable amounts of this compound, which is used in many processes. The standards, however, are for streams. Sewage treatment and dilution will lower concentrations in treatment plant discharges to insignificant levels. Table 4 summarizes of the screening.

Table 4: Semivolatile Organic Materials

	Federal Stream	Blank	Adco		Aquatex		Bufa		Gurtler		Kreussler		Laidlaw		RR Street		Sanitone		Seitz	
			Det	Cond	Det	Cond	Det	Cond	Det	Cond	Det	Cond	Det	Cond	Det	Cond	Det	Cond	Det	Cond
2,4,6-Trichlorophenol	6.5 (1)		0.9	-	-						1.7	0.6								
2,4-Dichlorophenol			-	-							1.3	0.7								
4-Chloro-3-Metholphenol											1.6	0.6								
4-Nitrophenol											1.5									
Acenaphthene	2700 (1)					3.8								0.6	0.6					
Acenaphthylene				5.2							9.8	0.24						4.0		
				0.7							2.1									
Anthracene	110,000 (1)	0.6	0.3		0.1	0.2	0.7		0.23	0.2	0.3			0.3		0.2	0.2	0.6	0.6	
			0.6		0.6	0.7					0.5			0.6			0.3			
Bis(2-Ethylhexyl) Phthalate	5.9 (2)	20.0	13.0	3.8	24.0	18.0	42.0	18.0	3.3	3.8	2.3	2.1	17.0	13.0	13.0	5.9	14.0	2.6	3.2	3.6
		6.6	4.5	3.6	12.0	1.9	15.0	3.4	2.0	2.8	4.8	2.5	7.0	19.0	8.9	4.9	12.0	1.9	6.7	3.5
		1.7	11.0	9.2	9.9	2.5	3.8	31.0	3.9	2.0	4.4	3.5			16.0	18.0	6.6		26.0	13.0
		3.1					30.0		11.0								11.0			
									20.0											
Butyl Benzyl Phthalate			1.0	0.5	1.2	0.4	0.8	0.03		1.0	0.3		0.9	0.1	1.1		1.0	0.4	0.8	0.5
			0.8		0.6	0.5	29.0	0.47		0.7	0.8			0.1	1.0		1.3	0.2		
									0.8								1.6			
Diethyl Phthalate	120,000 (2)	0.7	0.7	0.7	1.8	0.3	1.9	0.9	1.9	11.0	1.8	1.1	34.0	4.4	47.0	110.0	0.6	0.6	0.92	0.8
		1.1	1.4	1.4	1.4	0.8	1.3	0.4	1.3	7.1	3.7	0.5	5.2	2.4	43.0	55.0	1.4	0.8	1.8	0.8
		0.8	1.9	0.5	1.3		1.4	1.5	2.5	7.3	4.3	1.4	7.4	4.9	75.0	130.0	1.7	0.8	2.1	1.2
		0.9			1.4				1.7								1.4			
									1.8											
Dimethyl Phthalate	2,900,000 (2)		0.6		0.6	0.2	2.7	6.3	0.6	0.4	0.7	0.2	0.6	0.1	0.2	0.5	0.6		0.7	
						0.7	1.3	2.0				0.5		0.7						
							1.1	6.3												
							2.2													
Di-N-Butyl Phthalate	12,000 (2)	15.0	6.5	2.4	9.0	3.3	14.0	6.3	12.0	3.4	1.6	4.4	10.0	5.9	11.0	16.0	5.7	5.4	7.2	8.5
		2.8	6.8	13.0	6.8	5.8	31.0	2.1	0.9	2.4	4.0	12.0	6.1	7.8	8.6	11.0	7.0	5.3	1.1	2.4
		0.9			12.0		15.0	0.2	2.8	2.5							9.3			
Di-N-Octylphthalate											0.1				0.88		1.1		0.2	
																	0.2			
Flouranthene				0.6								0.2								0.6
Fluorene						1.0	1.7													
Indeno(1,2,3-CD) Pyrene											2.1									
Naphthalene		0.1	7.3		0.5	1.6					0.4			0.2			1.0			
																	1.5			
Phenanthrene		0.6	0.3				0.5	0.7		0.22	0.2	0.3		0.2			0.2		0.6	0.6
							0.7				0.5						0.4			

Table 5: Explanation of Standards

<p>MWRD to sewers</p> <p>The Metropolitan Water Reclamation District of Greater Chicago is Chicago’s publicly owned treatment works. These standards are contained in Appendix B of the “Sewage and Waste Control Ordinance – Discharge to and Pollution of Sewerage Systems”. Those materials shown without a standard are not regulated by the MWRDGC under this ordinance.</p>
<p>MWRD to streams</p> <p>These standards are contained in Appendix A of the “Sewage and Waste Control Ordinance – Discharges to and Pollution of Waters.” Those materials shown without a standard are not regulated by the MWRDGC under this ordinance.</p>
<p>Federal to stream</p> <p>Four different sources of data were needed to locate standards for many of the materials. The sources for each are shown on the tables, as follows:</p> <ol style="list-style-type: none">1. 62FR42160 (Volume 62 of Federal Register – 1997) U.S. EPA 40 CFR Part 131 “Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants for the State of California”2. 57FR60848 (Volume 57 of Federal Register – 1992) U.S. EPA 40 CFR 131 “Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants; States’ Compliance; Final Rule”3. 53FR19028 (Volume 53 of Federal Register – 1988) [U.S. EPA , page 33178, Appendix A – Summary of Water Quality Criteria for Aluminum National Standard”]4. “The Gold Book” Section 304(a)(1) of the Clean Water Act requires the U.S. EPA to publish and periodically update ambient water quality criteria. “Quality Criteria for Water”, 1986 (EPA 440/5-86-001) – issued with a gold-colored paper cover – discusses the impact of almost 100 different pollutants (mostly chemicals) on the health and safety of humans and aquatic life. (Earlier editions were red, blue and green.)
<p>In cases where there is more than one standard, the standard shown in the table is that judged by CNT to be the most stringent other than for water for human consumption. The federal standards were gathered with reference to a table previously compiled by the Prairie Rivers Network, located in Champaign, Illinois. We are grateful for their work, which facilitated our own.</p>

Remaining Questions

The detergents and conditioners examined in this report were not found to produce any significant contamination problems. It appears that cleaners who wetclean using these and other similar detergents and conditioners can do so with confidence that they are not using a process

that is likely to cause environmental harm. There are a few issues that were outside the scope of this research project that still require consideration.

First, spotting agents used to remove stains from garments were not tested. While these products are used in small quantities, and are often flushed out of garments prior to cleaning, many of the traditional spotting agents used for drycleaning contain hazardous substances. However, there are now available spotting agents designed for the wetcleaning process that can be discharged to sewers. Cleaners need to be aware of the differences between the products for wetcleaning and for drycleaning, and should set up their spotting areas in ways that will avoid the accidental misuse of inappropriate spotting agents.

Second, while water use has been shown not to be a major issue for wetcleaning, in areas of limited water supply it could remain a problem, and in other areas, conservation is always a recommended practice. Some wetcleaning machines have water recirculation tanks, and CNT has seen an improvement in water use efficiency among other machines over the past several years. Manufacturers of wetcleaning equipment should continue to develop machines that further reduce the amount of water used per load.

Recommendations

Cleaners should continue to expand their use of wetcleaning. Many resources are now available to provide information, training and certification. Other reports by CNT and others provide resources to cleaners who are interested in the process, performance and equipment needed for wetcleaning. This report has addressed the concerns that have been raised about potential negative environmental effects of the process.

Wastewater agencies need not view increased wetcleaning by cleaners as an issue of concern. The total amount of wastewater generated will be insignificant, and the composition of that wastewater will not pose problems for wastewater treatment facilities.

Other government and public interest groups considering creating or promoting incentives or recognition for cleaners who increase their wetcleaning can feel confident that in doing so they are promoting environmental protection as well as better business practices.

Appendix A: Wastewater Survey

Survey sent to 57 Illinois wastewater agencies. Nine agencies responded to the survey (a 16% response rate).

1. Do you have drycleaning facilities in your service area who currently have NPDES permits?

0	Yes	9	No
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2. Is perchloroethylene from drycleaning facilities a problem for your treatment plant?

0	Yes	9	No
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3. Please assign a degree of importance to the following list of chemicals and types of chemicals. (1 not a problem, 10 serious problem)

Respondent	1	2	3	4	5	6	7	8	9
BOD	1	1	0	1	3	8	5	5	1
PH	5	1	0	1	4	6	5	3	1
SS	1	1	0	1	5	7	5	5	1
Nitrogen	5	1	0	1	2	1	8	8	1
Phosphorous	5	1	0	2	6	3	1	8	1
Metals	10	5	0	3	1	10	8	10	5
Phthalates	10	1	0	3	7	1	0	10	1

4. Does your plant have (or plan to have) guidelines for industrial releases of Endocrine Disrupting Chemicals?

0	Yes	9	No
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5. Given the process description of wetcleaning on the attached fact sheet, what parameter(s) would be of most concern to you?

Respondent	
1	Nitrogen, metals
2	None
3	None
4	Organics
5	BOD, Copper
6	BOD, FOG
7	TKn, Metals
8	BOD (high but manageable)
9	BOD, TKN, Zinc

Appendix B: References

Final Report for the Green Clean Project

Environment Canada, Toronto, 1995

Alternative Clothes Cleaning Demonstration Shop, Final Report [The Greener Cleaner]

Center for Neighborhood Technology, Chicago, 1996

Pollution Prevention in the Garment Care Industry: Assessing the Viability of Professional Wetcleaning

Occidental College/UCLA, Los Angeles, 1997

Cleaner Technologies Substitutes Assessment for Professional Fabricare Processes

Environmental Protection Agency, Washington DC, 1998

Wetcleaning Demonstration and Deployment Project at Reehorst Cleaners

CAMP, Inc., Cleveland, 1999

Appendix C: Previous Wastewater Studies

All values in mg/L [except pH]	<u>Environment Canada</u>	<u>CNT</u> <u>[Greener Cleaner]</u>			<u>UCLA</u>	<u>CAMP</u>
		<u>Day 1</u>	<u>Day 2</u>	<u>Day 3</u>		
pH:	7.3	-	-	-	6.6-7.4	7.07-7.84
BOD:	168.3	264	288	326	178	86-172
Suspended Solids	75.3	36	40	21	56	13-53
Fats, Oils, Grease	4.7-23.7	15	66	24	17.1	-
Ammonia Nitrogen	-	.31	1.13	0.65	-	.27-2.1
Total Kjeldahl Nitrogen	24.7	20.68	27.39	17.60	-	-
Phosphorous:	0.3	0.53	0.66	0.33	-	0.56-11.1
Arsenic	-	0	0	0	<0.001	-
Cadmium	-	0	0	0	<0.005	-
Copper	-	0.10	0.17	0.06	0.177	-
Iron	-	0.60	0.26	0.23	-	-
Lead	-	0	0	0	<0.01	-
Mercury	-	0.0002	0.0002	0.0001	-	-
Nickel	-	0.01	0	0	<0.015	-
Selenium	-	0.02	0	0	-	-
Silver	-	0	0.01	0	<0.015	-
Zinc	-	0.24	0.13	0.1	0.837	-
Acetone	-	0	0.147	0	0-0.716	-
Diethyl phthalate	-	0.020	0.025	0.021	0.0135, 0.0062	-
Di-n-butyl phthalate	-	0.011	0.011	0.010	0.0124, 0.0037	-
Butyl benzyl phthalate	-	0	0.010	0.013	-	-
Bis (2-ethylhexyl) phthalate	-	0.155	0.098	0.169	0.1920, 0.0320	-
Dodecanoic acid	-	1.10	0	1.30	-	-
Hexadecanoic acid	-	4.20	2.20	2.80	-	-
z-9-Octadecanoic acid	-	3.50	2.60	0	-	-
Octadecanoic acid	-	3.50	2.60	0	-	-
2-(2-Butoxyethoxy) ethanol	-	5.90	5.50	6.90	-	-
Trichloroethylene	-	0	0	0.287	-	-

Appendix D: Analytical Procedures

Analysis of the wastewater from a cleaning process is very challenging because the chemical makeup of the detergents and conditioners is similar to that of many of the regulated pollutants. Isolation of the chemicals is further complicated because detergents are designed to dissolve contaminants and resist their separation, in order to remove them efficiently from the fabric. The challenge was met by the laboratory scientists and technicians at the Waste Management and Research Center by using their state-of-the-art equipment combined with a variety of techniques that were designed specifically for this work.

Analyzing for Volatile and Semi-Volatile Organic Compounds

The tests for volatile organic compounds were performed using a purge and trap sample introduction system connected to a gas chromatograph with photoionization and Hall detectors. The purge and trap system operates by heating a sample of the water to drive the volatile compounds into the gas phase. An unreactive gas, such as nitrogen, is then used to sweep the gas phase volatile compounds into the gas chromatograph. The volatile compounds are separated while passing through a capillary chromatography column coated with adsorbent material. Each compound exits the column at a time specific to that compound (its retention time) under the operating conditions of the gas chromatograph. The detectors are calibrated for the compounds of interest. By analyzing the detector signals at predetermined retention times the concentrations of target compounds in the original water sample can be measured.

Semi-volatile organic compounds (SVOC) must first be extracted from the water matrix. Water samples are passed through a solid phase extraction disk on which the SVOCs are retained. A small amount of solvent is then used to extract the target compounds from the disk. The extract is reduced in volume to concentrate the SVOCs of interest. Then a small volume of the extract is injected via syringe into a heated injector where the SVOCs are volatilized. A nonreactive carrier gas moves the volatilized compounds from the injector through a capillary chromatography column where they are separated. The detector used for SVOC analysis was an ion-trap mass spectrometer. Retention time, compound structural information and the magnitude of the detector signal are used in the identification and quantization processes.

To monitor performance of the analytical system during testing for VOCs, 100 ng each of five surrogates (bromochloromethane, 2-bromo-1chloropropane, 1,4-dichlorobutane, 4-chlorotoluene, and pentafluorobenzene) were added (spiked) to most of the samples prior to purging. Surrogates are compounds of a chemical structure similar to the analytes of interest, but that are unlikely to be found in the environment. The measured amount of each surrogate is compared to the known amounts of the surrogate added to the sample in order to calculate the percent of the surrogate that is recovered by the analysis. Generally, surrogate recoveries in the range of 50 to 130% indicate that the analytical system is functioning adequately.

The three figures show gas chromatograms for the VOC tests. Figure C-1 shows a gas chromatogram of a blank sample (tap water with no additions). The time for the analysis was about 50 minutes. The peaks represent minute amounts of compounds in the water. Figure C-2 shows a chromatogram of one of the test samples containing detergents and contaminants. The more numerous and higher peaks result from the many compounds present in the water. Most of

the compounds are major components of the detergent or conditioner, or of the soil, and are not of interest, but some peaks represent regulated compounds. The challenge is to measure the amount of the regulated compounds as they are masked by much larger amounts of innocuous materials. Figure C-3 shows the chromatogram of a sample containing the five surrogate spikes. By measuring the spikes, the analyst can determine how well the analytical system is functioning.

A similar technique was employed during testing for SVOCs, except that the surrogates were 2-fluorobiphenyl and 2,4,6-tribromophenol. Surrogate recoveries for the 2-fluorobiphenyl were generally above 50% and acceptable. The tribromophenol recoveries were below 50%, but were reasonably consistent. Phenols, in general, can be difficult to isolate and chromatograph quantitatively. The sample matrix provided by some of these cleaners complicated measurement. WMRC is confident that the results presented in Table 4 reflects the actual concentrations to within a factor of 2 or 3.

Figure C-1: Blank Sample

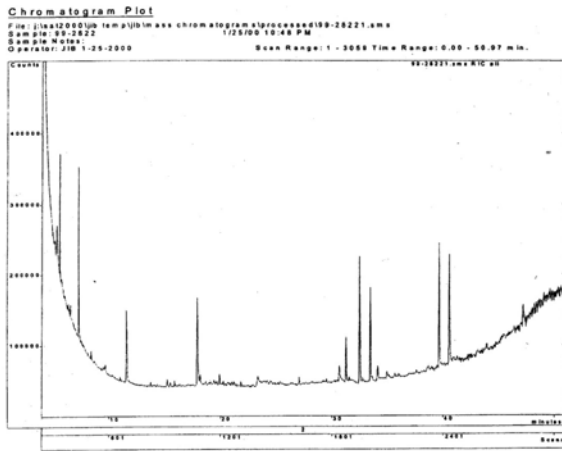


Figure C-2: Sample With Detergents and Contaminants

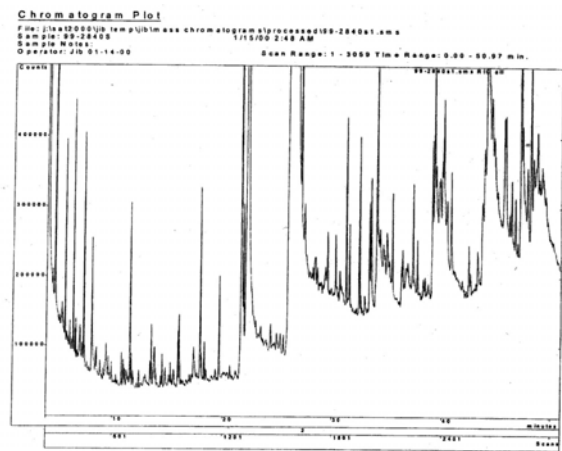


Figure C-3: Sample Containing Five Surrogate Spikes

