

WASTE ANTIFREEZE CHARACTERIZATION STUDY

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ABSTRACT

Waste antifreeze was tested at six sites (3 generators and 3 recyclers) in Washington between February and March, 1991. Samples were collected in both eastern and western Washington and encompassed a broad range of vehicle types. Analyses included: metals; semi-volatiles and volatile organic compounds using the Toxicity Characteristic Leaching Procedure (TCLP); halogenated hydrocarbons; percent ethylene glycol; and two acute toxicity tests (static acute salmonid bioassay and acute oral rat bioassay). Barium, and lead were detected at low levels in the recycler samples. Barium was the only metal detected in the generator samples. Benzene was found at levels exceeding the TCLP regulatory limit at one of the generator sites and was present at non-regulated levels in two of the three recycler samples. Tetrachloroethylene exceeded the TCLP regulatory limit in two of the recycler samples. Halogenated hydrocarbons were present at concentrations below the regulatory threshold in all samples. Bioassay results indicated that waste antifreeze was not acutely toxic to salmonids or rats. The mean concentration of ethylene glycol was 37% by volume. High levels of tetrachloroethylene found in some of the recycler samples suggests that generators are not adequately segregating their waste-streams.

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INTRODUCTION

Ethylene glycol-based antifreeze is widely used in Washington State as a motor vehicle coolant. Strand and Uvelli (1986) estimated that annual antifreeze usage approached 3.36 million gallons in the state in 1980. Spent antifreeze therefore represents a substantial waste-stream that may be of concern from a regulatory and waste management standpoint.

Used antifreeze has been tested for metals, organics, and aquatic toxicity in several states (San Bernardino, California, Water Department, 1988; California Department of Health Services, 1986, 1987; Washington Department of Ecology, 1982a, 1990). Available data have suggested that waste antifreeze may sometimes contain elevated levels of lead and possibly other metals (California Department of Health Services, 1986, 1987).

Waste antifreeze with ethylene glycol concentrations greater than 10% is identified as a dangerous waste under Chapter 173-303-084 WAC. However, the limited data available have not been sufficient to fully characterize this waste-stream under the Washington State Dangerous Waste Regulations (Chapter 173-303 WAC), primarily because the methodologies, data collection, and sampling procedures used were either not recorded in sufficient detail, or were not standardized. In addition, extensive testing of waste antifreeze using the Toxicity Characteristic Leaching Procedure (TCLP) had not yet been conducted.

Clarification of the status of waste antifreeze under Chapter 173-303 WAC, and the Federal Toxicity Characteristic Rule (FTCR) rule is an important step in establishing a statewide waste antifreeze management policy. Ecology's Solid and Hazardous Waste Program, therefore, requested the Toxics Investigations Section to perform a study with the following objectives: 1) collect data to clarify the status of waste antifreeze under Washington State Dangerous Waste Regulations (Chapter 173-303 WAC), and the FTCR; and 2) evaluate whether waste management practices influence contaminant levels found in waste antifreeze.

COMPOSITION AND USE OF ANTIFREEZE

Ethylene glycol is by far the most common base for antifreeze, although propylene glycol and certain alcohols (methoxypropanol) are occasionally used in some antifreeze formulations. Typical automotive coolant, as purchased over the counter, contains between 80-95% ethylene glycol, with lesser amounts of diethylene glycol (0-10%) and triethylene glycol. Other constituents include: 1-5% water and a variety of additives (1-5%). Toxicities associated with diethylene and triethylene glycols are lower than those recorded for ethylene glycol (Brown, *et al.*, 1963). Additives function as corrosion inhibitors, dyes, anti-foaming agents, scale inhibitors, and surfactants. Table 1 lists some of the additives commonly found in antifreeze. The only metallic salts currently added to antifreeze are sodium and potassium salts. Neither mercury nor benzene are known to be incorporated into coolant additive packages. The pH of new antifreeze is typically basic, ranging between 7.5-11. As ethylene glycol breaks down over time into organic acids, the pH of the coolant tends to drop. Lower pH can facilitate engine

corrosion (particularly solder degradation). This is a likely explanation for the higher concentrations of dissolved metals found in coolant that has not been changed for a long period of time. Ethylene glycol breakdown products include various organic acids (acetic, formic, and glycolic acids). In Washington, antifreeze is typically used in a 50:50 mixture with water, however actual concentrations in vehicles may be highly variable.

Diesel engines may require different coolant usage and procedures than gasoline engines due to differences in engine construction, average annual mileage, loading, and other factors. As a result of these differences, some diesel fleets use heavy duty antifreeze and/or supplemental additive packages in their vehicles (Hudgens and Bugelski, 1990). Many of the additives used in heavy duty coolants are similar to those found in standard automotive coolants, but differ in the relative concentrations of some of the additives. Nitrites, polyacrylates, and detergents are commonly found in heavy duty coolants, but are generally missing from most automotive antifreeze (see Table 1). A 50:50 ratio of antifreeze and water is also generally used in diesel engines.

Table 1. Antifreeze additives commonly found in different types of regular automotive and heavy duty diesel antifreeze. (Hudgens and Bugelski, 1990; Hudgens, 1991).

Compound ¹	Function
benzoic acid	corrosion protection
benzotriazole	" "
mono and di-carboxylates	" "
sodium (or potassium) nitrate	" "
sodium (or potassium) nitrite*	" "
sodium silicate	" "
sodium molybdate*	" "
sodium mercaptobenzothiazole	" "
tolytriazole (sodium salt)	" "
triethanolamine phosphate	" "
sodium borate/ boric acid	buffer
sodium or potassium diphosphate/phosphoric acid	buffer, corrosion protection
sodium hydroxide	buffer component
organophosphate*	chelating agent, scale inhibitor
organophosphonate/ phosphino-carboxylate*	scale inhibitor
polyacrylates*	" "
detergents*	oil dispersant
xylene sulfonate*	surfactant
silicone	anti-foaming agent

¹Compounds marked with an asterisk are more commonly found in heavy duty diesel coolants than in standard automotive coolants.

METHODS

Sampling

To characterize waste antifreeze under Washington's Dangerous Waste regulations and the FTCR, representative samples were collected from a wide range of motor vehicle types in two regions of the state. Samples were analyzed for TCLP metals and organics, halogenated hydrocarbons, and percent ethylene glycol. A static acute fish toxicity test and an acute oral rat toxicity test were also run. The role of waste management practices in the potential contamination of waste antifreeze was assessed by sampling at two points in the waste-stream: 1) directly from the vehicles; and 2) at the point of delivery to recycling facilities.

Site Selection. A total of 6 sites were sampled during the course of the study. At three of the sites (generators), samples were taken directly from vehicle radiators. The remaining three sites (recycler sites) were all recycling facilities and samples were taken either from tanker trucks or 55 gallon collection drums. Generator sampling sites included: 1) an automobile service station; 2) a radiator repair shop; and 3) a diesel fleet facility. Two of the sites were located in western Washington and the third was located in the eastern part of the state. Two of the three recycling sites were also located in western Washington while the third was located in eastern Washington (Spokane). Sampling locations are shown in Table 2.

The following criteria were used in selecting vehicular (generator) sampling sites;

- sample a variety of business expected to produce waste antifreeze;
- facilities located in different regions of the state;
- high volume of business; and
- wide variety of models (foreign, domestic) and ages of vehicles available.

Facilities that used chelating agents to enhance radiator flushing, were eliminated from consideration. Where possible, vehicle owners were asked to fill out a questionnaire, which was used to help assess the history of the vehicles being sampled. Data on the sources of antifreeze sampled at each of the vehicle and recycle sites is included in Appendix A.

Only two large-scale antifreeze recyclers currently serve Washington state. One of these (Clean Care Corp., Tacoma, WA) picks up antifreeze from both eastern and western Washington. At the time of sampling, the other recycler (Antifreeze Environmental Service Corp., Tacoma, WA) served only western Washington. Samples were collected from both western Washington (Tacoma) facilities, as well as at an eastern Washington (Spokane) collection location.

Table 2. Site Locations for Waste Antifreeze Study.

Type of Site	Site Name	Site Location	Date	# of vehicles sampled per site
Radiator Shop	Walt's Radiator & Muffler	517 E. 4th Ave. Olympia, WA	2/27/91	5
Diesel Fleet Service	Pacific Coast Truck Center	2312 Milwaukee Way, Tacoma, WA	2/28/91	6
Service Station	Firestone	W. 305 3rd Ave. Spokane, WA	3/7/91	6
Recycler	Antifreeze Environmental Service Corp.	1400 15th St. E. Tacoma, WA	3/6/91	4
Recycler	Clean Care Corp. Tacoma, WA	224 Port of Tacoma Rd. Tacoma, WA	3/5/91	6
Recycler	Clean Care Corp. Tacoma, WA	Spokane, WA	3/7/91	5

Collection Methods. All samples were collected within the two-week period from February 27, 1991 - March 8, 1991. At each location, samples were collected during a single day and were composited upon return from the field. Chain of custody procedures were followed for all collections. All samples were stored on ice at 4°C until being transported to the Ecology/EPA Environmental Laboratory at Manchester, Washington.

Vehicles were sampled as they came into the facility, without regard to model, age, or mileage. Preferentially, vehicles which had come in specifically to have their antifreeze changed were sampled. In other cases, samples were taken from vehicles which had come into the facility for other reasons. In the case of vehicles on site for reasons other than an antifreeze change, they were sampled if they met the following criteria: 1) they were not in the shop for an engine problem that could have contaminated the coolant system; and 2) the estimated time of the last antifreeze change was one year or more. All samples were grabs taken directly from the radiator petcock or radiator hose. Coolant was allowed to run out of the radiator briefly before a sample was collected. Samples were collected directly into priority pollutant cleaned glass containers with teflon-lined lids supplied by I-Chem, Hayward, California. Half-gallon jars were used for semivolatiles and 40 mL glass containers with teflon septa were used to collect volatiles. With the exception of the VOAs, composite samples (each representing equal aliquots

from 5-6 individual vehicles) were homogenized in a priority-pollutant cleaned one-gallon glass container. Homogenization was accomplished by stirring with a stainless steel spoon. The composite sample was then split into subsamples for analysis. Spoons used in compositing samples were pre-cleaned with sequential washes of: LiquiNox® detergent, hot tap water, 10% nitric acid, deionized water, pesticide-grade acetone, and air dried and wrapped in foil until used. Equal aliquots from the individual VOA samples were composited into 125 mL glass VOA containers with teflon septa. Mixing was achieved by inverting the sealed 125 mL VOA containers several times.

Recycler samples were collected directly from trucks that had just come in from making antifreeze collections. Trucks generally go out several times a week to pick up antifreeze from generators. Each truck-load includes waste antifreeze from an average of 3-5 generators. One of the recyclers (Antifreeze Environmental Service, Tacoma, WA) collects waste antifreeze in a tanker truck. The other recycler (Clean Care Corp., Tacoma, WA) picks up 55 gallon drums of waste antifreeze from generators. Samples were therefore collected either from a tanker truck or out of drums, using a 2-inch diameter bottom emptying teflon bailer, lowered to the bottom of the tanker chamber or drum. Each drum sampled represented a pick-up from a different generator. A single bailer was used to sample from all drums at any one site. Prior to sampling, solution from the drum being sampled was used to rinse out the bailer. Samples were composited and split as described above for the vehicle sites. All sampling equipment (bailers, spoons) used for homogenizing samples was pre-cleaned prior to use, as described above for vehicle samples. Sample storage and handling procedures were identical to those described for the vehicle samples.

Analyses

The following analytical tests were carried out on each composite sample: TCLP (metals, volatiles, and semivolatile organics), halogenated hydrocarbons, total solids, and percent ethylene glycol. No analyses were carried out for TCLP pesticides and herbicides. Two bioassays were also run on each composite sample: a static acute fish toxicity test (one concentration: 1000 mg/L, test organism: *Oncorhynchus mykiss*); and, an acute oral rat toxicity test (one concentration: 5000 mg/kg). A Beckman 21 pH meter with combination electrode was used to test the pH of individual samples in the field prior to compositing. A complete list of analytes, analytical methods and laboratories used in the study are listed in Table 3.

Quality Assurance

Quality control samples included field duplicates, method blanks, matrix spikes and spike duplicates, surrogate spike analyses, and reference standards.

Laboratory precision, calculated as matrix spike/matrix spike duplicate relative percent difference (RPD) values (range as percent of mean), was excellent for TCLP metals and VOAs being $\pm 7\%$ and $\pm 17\%$ respectively. In the case of semivolatile analyses, some percent recoveries and all

Table 3. Analytical methods for waste antifreeze.

Analysis	Method	Reference	Laboratory
<u>TCLP</u>			
Volatiles Benzene, carbon tetrachloride, chlorobenzene, chloroform, 1,2 dichloroethylene, methyl-ethyl-ketone, tetrachloroethylene, vinyl chloride, trichloroethylene	GC/MS purge-trap (EPA SW846-1311)	Fed. Reg. 1990	Ecology/EPA Manchester Lab Manchester, WA
Semivolatiles m-cresol, o-cresol, p-cresol, 1,4 dichlorobenzene, dinitrotoluene, hexachloro-1,3-butadiene, hexachloroethane, nitrobenzene, pyridine, pentachlorophenol, 2,4,5 trichlorophenol, 2,4,6 trichlorophenol	GC/MS (EPA SW 846-1311)	"	Ecology/EPA Manchester Lab
Metals arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver	ICP, CVAA (EPA SW846-1311)	"	Sound Analytical Services, Tacoma, WA
% Solids	pressure filtration (EPA SW 846-1311)	"	Ecology/EPA Manchester Lab
Halogenated Hydrocarbons	extraction/combustion ISE probe	Ecology, 1982b	North Creek Analytical Bothell, WA
% Ethylene glycol/ diethylene glycol	GC, FID detector	Manchester in-house	Ecology/EPA Manchester Lab
pH	pH meter	-	field

Table 3. (Continued)

Analysis	Method	Reference	Laboratory
BIOASSAYS			
Acute fish (1 conc./1000mg/L)	static acute 96-hr.	Ecology, 1981	Ecology/EPA Manchester Lab
Oral rat (1 conc./5000mg/kg)	14-day	Ecology, 1981	Bio-Technics Laboratories Los Angeles, CA

RPD values calculated for matrix spike/matrix spike duplicates exceeded Contract Laboratory Program (CLP) QC control limits for one set of matrix spike samples due to severe matrix spike interference. RPD values and percent recoveries for the other set of matrix spike samples exceeded CLP control limits for 1,4-dichlorobenzene, hexachloroethane, and hexachlorbutadiene only. Overall precision (sample collection + laboratory), calculated from field duplicates (a single sample homogenized and split in the field) was good for percent ethylene glycol (RPD = $\pm 27\%$). RPD values for field duplicates analyzed for halogenated hydrocarbons were quite variable and ranged from 9%-110% (see organics discussion below).

The quality of TCLP metals data was reviewed by Craig Smith of the Ecology/EPA Manchester Laboratory. In the opinion of the reviewer, all the metals data were acceptable for use without qualifications.

TCLP organics data were reviewed by Dickey Huntamer of the Ecology/EPA Manchester Laboratory. Water surrogate spike recoveries for the semivolatiles were within normal CLP limits with the exception of d5-phenol and d10-pyrene. Surrogate recoveries for the VOAs were within CLP limits with the exception of 1-bromo-2-fluoroethane in one sample. CLP recovery limits are not intended for use with TCLP, and therefore should be considered to be only advisory in nature. Low levels of methyl-ethyl-ketone were found in the laboratory blanks for the VOA. The EPA "five times" rule was applied to all target compounds found in the blanks.

Poor recoveries and elevated detection limits obtained for several of the semivolatile organics are most likely related to preferential partitioning of the analytes between ethylene glycol and the extraction solvent (i.e. as the percentage of ethylene glycol increased extraction efficiency of the solvent decreased). Interferences from the oil and large amounts of benzoic acid in some samples also contributed to lower recoveries and higher detection limits. In addition, difficulties associated with homogenizing an oily matrix are probably responsible for the variable results noted above for duplicate analysis.

EPA Method 1311 (TCLP) Section 8.2.5 states that measured values should be corrected for analytical bias. Matrix spike recovery bias corrections are not shown for any of the TCLP data. In the opinion of the Manchester Lab Quality Assurance Section, recovery correction applied to samples with differing matrices may introduce significant error in the reported concentrations. For comparison when recovery corrections are applied to the data, no additional values were found to exceed the regulatory limits.

All samples were analyzed within the recommended holding times for TCLP metals and semivolatiles. In the case of the volatile analyses, re-analysis of two samples for high levels of tetrachloroethylene exceeded holding times. One set of matrix spikes were analyzed after the holding time, but since these values are used to determine matrix effects on the analysis, the additional holding time should have no significant effect on the spike recoveries. Volatile organics in sample 10-8081 were analyzed after the holding time. A "J" or estimated value qualifier was added to all data for which holding times were exceeded (Table 6).

Halogenated hydrocarbons were analyzed by North Creek Analytical of Bothell, Washington, using the method described in WDOE 83-13, "Chemical Testing Methods for Complying with the State of Washington Dangerous Waste Regulation." The quality of the data was reviewed by Stuart Magoon of the Ecology/EPA Manchester Laboratory. In the opinion of the reviewer, the results can reliably be used to assess whether the samples exceeded the regulatory limit of 100 ppm. Values below 100 ppm are considered estimates only, due to method blank contamination. In an attempt to quantify halogenated hydrocarbon levels below 100 ppm, Sound Analytical Services of Tacoma, Washington, performed a modified version of the test which uses a solvent extraction and coulometric titration. These results confirmed that halogenated hydrocarbon levels were below the 100 ppm regulatory level in all samples tested.

The LC_{50} for the reference toxicant used in the static acute fish toxicity test was within the normally expected range of values for the species used. Weight changes were comparable for control and test groups of Sprague-Dawley rats used in the acute oral rat toxicity bioassay.

Case narratives and quality assurance reviews of all data are included in Appendix B.

RESULTS

Samples taken at generator sites included vehicles ranging in age from 3-25 years, and with mileages ranging from 35,000 to 530,000 miles (diesel truck). Both domestic and foreign vehicles were represented, as well as both copper-brass and aluminum radiator types. Recycler samples included waste antifreeze collected from car dealers, fleets, heavy equipment, and marine transportation sources. Estimated quantities of new antifreeze used at vehicle sites ranged from 10-165 gallons per month. Recyclers reported collecting from 1000 to 15,500 gallons of waste antifreeze per month (Appendix C).

The results of halogenated hydrocarbons, percent ethylene/diethylene glycol and pH analyses are summarized in Table 4.

Table 4. Summary of halogenated hydrocarbons, percent ethylene glycol/diethylene glycol and pH analyses for waste antifreeze study.

Site Name/Sample #	Total Halogens (ppm)	% ethylene glycol	pH range*
Vehicle sites			
Walt's Radiator, Olympia 09-8083	20 JB	49	7.9-10.2
Pacific Coast Truck, Tacoma 09-8084	37 JB	43	8.5-9.8
Firestone, Spokane 10-8085	18 JB	51	7.8-9.3
Recycler Sites			
Antifreeze** Environmental, Tacoma 10-8080/8086	40 JB	19	7.4
Clean Care, Tacoma** 10-8081/8087	43 JB	36	8.0-9.0
Clean Care, Spokane** 10-8082/8086	52 JB	41	7.8-8.5

* pH values represent range of values found in waste antifreeze from the individual generators making up each composite sample.

** Halogenated hydrocarbon and percent ethylene glycol values for all 3 recycler sites reported as mean of field duplicates.

U = not detected at detection limit shown

J = Estimated value

B = Also detected in method blank

All values for organic chloride were below the regulatory limit of 100 ppm (.01%). While concentrations below 100 ppm are considered to be estimates only, some trends in the data may be observed. Halogenated hydrocarbons were lowest in the vehicle site samples. Among the recycler samples, the highest values were measured in samples from in the Clean Care, Spokane.

The mean percent ethylene glycol by volume for all samples was 37% (range: 17%-51%). Higher values were found in the vehicle samples (mean=48%) than in the recycler samples (mean= 31%). Samples from eastern Washington had slightly higher values (mean= 44%) than those from western Washington (34%). A sample of new (unused) Texaco antifreeze taken directly from a fresh container, yielded a concentration of 97% ethylene glycol.

pH values measured in the field ranged from 7.4-10.2 for all samples. Values did not appear to differ markedly between vehicle and recycler sites.

The results of TCLP metals analyses are presented in Table 5. Only lead, and barium were found at detectable levels in antifreeze samples. Barium occurred at low levels in all samples (range= 0.1-0.6 mg/L). The highest concentration of barium (0.6 mg/L, reported as the mean of duplicate samples) was found in one of the recycler samples (Antifreeze Environmental Service). Lead levels in recycler samples ranged from <0.5-2.8 mg/L, while lead was not detected in any of the vehicle samples (0.1 mg/L detection limit). The highest levels of lead were present in samples from Clean Care Corp., (Tacoma and Spokane samples). Mean concentrations for Clean Care were 2.7 mg/L and 2.8 mg/L for Tacoma and Spokane sites respectively. All values for TCLP metals were at concentrations below the regulatory thresholds.

Results of TCLP organics analyses of waste antifreeze samples are shown in Table 6. Four TCLP organic compounds were detected in waste antifreeze samples. These included o-cresol, benzene, methyl-ethyl-ketone, and tetrachloroethylene. o-Cresol and methyl-ethyl-ketone were each detected in 1 out of 9 samples (490 $\mu\text{g/L}$, 520 $\mu\text{g/L}$, respectively). Benzene was found in 3 out of 9 samples (range=2.5-630 $\mu\text{g/L}$) and tetrachloroethylene occurred in 2 of 9 samples (2300 and 2600 $\mu\text{g/L}$). Benzene was found at one of the vehicle sites and in two of the recycler samples. Tetrachloroethylene and methyl-ethyl-ketone (both solvents) were only detected in recycler samples. Only one sample exceeded the TCLP regulatory limit for benzene (630 $\mu\text{g/L}$, Walt's Radiator and Muffler, Olympia). Two samples exceeded the TCLP regulatory limit for tetrachloro-ethylene (Clean Care, Tacoma and Spokane sites; 2300 and 2600 $\mu\text{g/L}$, respectively). The remaining two analytes detected were well below regulatory limits.

No mortality was observed in the trout bioassay for any of the vehicle samples and none occurred in two of the recycler samples. 26.7% mortality was observed in the Clean Care, Spokane sample (8 deaths out of 30). These results indicate that the LC_{50} was greater than 1000 mg/L for all samples. The samples therefore do not designate as a dangerous waste under Chapter 173-303-101 WAC as determined by this test.

No mortality was observed in the oral rat bioassay for any of the samples. Physical and behavioral changes in the test animals were also not observed for any of the samples. Gross pathological abnormalities were not evident. The acute LD_{50} for all samples was greater than 5g/Kg body weight. The samples would, therefore, not be considered to be a dangerous waste under Chapter 173-303-101 WAC, as determined by this test.

Table 5. Results of analyses for TCLP metals in waste antifreeze (mg/L).

Vehicle Sites				
Site Sample #	WR 09-8083	PT 09-8084	FS 10-8085	Regulatory Limit
Arsenic	0.2 U	0.2 U	0.2 U	5.0
Barium	0.2	0.2	0.1	100.0
Cadmium	0.1 U	0.1 U	0.1 U	1.0
Chromium	0.1 U	0.1 U	0.1 U	5.0
Lead	0.1 U	0.1 U	0.1 U	5.0
Mercury	0.02 U	0.02 U	0.02 U	0.2
Selenium	0.3 U	0.3 U	0.3 U	1.0
Silver	0.1 U	0.1 U	0.1 U	5.0
% solids	0.5 U	0.5 U	0.5 U	-

Recyclers			
Site Sample #	AE* 10-8080/8086	CCW* 10-8081/8087	CCE* 10-8082/8088
Arsenic	0.2 U	0.2 U	0.2 U
Barium	0.6	0.2	0.4
Cadmium	0.1 U	0.1 U	0.1 U
Chromium	0.1 U	0.1 U	0.1 U
Lead	0.5 U	2.7	2.8
Mercury	0.02 U	0.02 U	0.04 U
Selenium	0.3 U	0.3 U	0.3 U
Silver	0.1 U	0.1 U	0.1 U
% Solids	0.5 U	0.5 U	0.5 U

* = Reported as mean of duplicate analyses.
 U = Not detected at detection limit shown.

Key to site names:

- WR = Walt's Radiator, Olympia
- PT = Pacific Coast Truck, Tacoma
- FS = Firestone, Spokane
- AE = Antifreeze Environmental Service, Tacoma
- CCW = Clean Care, Tacoma
- CCE = Clean Care, Spokane truck

Table 6. Results of TCLP Organics Analyses for Waste Antifreeze Study. All values in µg/L.

Site Sample #	Vehicle Samples			Recycler Samples			Detection Frequency	TCLP ¹ Limit	No. of Exceedences	
	Walt's Radiator Repair 09-8083	Pacific Coast Truck Center 09-8084	Firestone 10-8085	Antifreeze* Environmental 10-8080/10-8086	Clean Care* Tacoma 10-8081/10-8087	Clean Care* Spokane 10-8082/10-8088				
Compound										
<u>Semivolatiles</u>										
m-Cresol	50 U	50 U	500 U,J	150 U,J	380 U,J	380 U,J	0/9	200,000	0	
o-Cresol	40 U	490 U	400 U	120 U	300 U	300 U	1/9	200,000	0	
p-Cresol	40 U	40 U	400 U	120 U	300 U	300 U	0/9	200,000	0	
1,4 Dichlorobenzene	40 U	40 U	400 U	110 U,J	300 U	300 U	0/9	7,500	0	
2,4 Dinitrotoluene	100 U	100 U	1,000 U	300 U	750 U	750 U	0/9	130	0	
Hexachloro-1,3-Butadiene	100 U	100 U	1,000 U	300 U	750 U	750 U	0/9	500	0	
Hexachloroethane	40 U	40 U	400 U	120 U	300 U	300 U	0/9	3000	0	
Nitrobenzene	40 U	40 U	400 U	120 U	300 U	300 U	0/9	2000	0	
Pentachlorophenol	200 U	200 U	2,000 U	600 U	1,500 U	1,500 U	0/9	100,000	0	
Pyridine	25 U	25 U	250 U	70 U	190 U	190 U	0/9	5,000	0	
2,4,5 Trichlorophenol	200 U	200 U	2,000 U	600 U	1,500 U	1,500 U	0/9	400,000	0	
2,4,6 Trichlorophenol	100 U	100 U	1,000 U	300 U	750 U	750 U	0/9	2,000	0	
<u>Volatiles</u>										
Benzene	630	50 U	50 U	30 U,J	370 J	190	5/9	500	1	
Carbon Tetrachloride	50 U	50 U	50 U	35 U	30 U,J	50 U	0/9	500	0	
Chlorobenzene	50 U	50 U	50 U	35 U	30 U,J	50 U	0/9	100,000	0	
Chloroform	50 U	50 U	50 U	30 U,J	30 U,J	50 U	0/9	6,000	0	
1,2 Dichloroethane	50 U	50 U	50 U	35 U	30 U,J	50 U	0/9	500	0	
1,1 Dichloroethylene	50 U	50 U	50 U	35 U	30 U,J	50 U	0/9	700	0	
Methyl Ethyl Ketone	280 U,J	180 U,J	50 U	150 U,J	70 U,J	520	3/9	200,000	0	
Tetrachloroethylene	50 U	50 U	50 U	60 U	2,300 J	2,600 J	5/9	700	3	
Vinyl Chloride	50 U	50 U	50 U	35 U	30 U,J	50 U	0/9	200	0	
Trichloroethylene	50 U	50 U	50 U	35 U	30 U,J	50 U	0/9	500	0	

1 = Values in bold print exceed the regulatory limit for that analyte.

Data Qualifiers

J = Estimated value.

U = Compound not detected at detection limit shown.

* Reported as mean of duplicate analyses.

DISCUSSION

Table 7 summarizes all TCLP analytes detected or exceeding regulatory levels in the present study including several additional waste antifreeze samples taken by the Department of Ecology's Southwest Regional Office (SWRO).

Of the nine samples analyzed during the present study, benzene in one vehicle sample (sample no. 09-8083) and tetrachloroethylene in three of the six recycler samples (sample nos. 10-8087 and 10-8082/8088) were the only TCLP constituents that exceeded regulatory limits in waste antifreeze. All values for halogenated hydrocarbons were below the regulatory limit. The LC_{50} was greater than 1000 mg/L for all samples, as indicated by the static acute fish toxicity bioassay. The LD_{50} exceeded 5gm/Kg body weight for the oral rat toxicity test. Waste antifreeze would therefore not be classified as a dangerous waste, based upon these two bioassays alone. The mean percent ethylene glycol for all samples was 37%. Percent solids as determined under TCLP were below 0.5% in all but one sample.

In December, 1990, Ecology's Southwest Regional Office (SWRO) took three waste antifreeze samples at a recycling facility located in Tacoma, Washington (Northwest Processing). In general, results from these samples confirm the results found in the present study. Benzene and tetrachloroethylene were the only two compounds that caused one of the three samples to designate as a dangerous waste under Chapter 173-303 WAC.

Barium and lead were detected at low levels (0.4-0.5 mg/l and <0.1-3.6 mg/l, respectively) in the SWRO samples, when analyzed under TCLP. Silver and chromium were also detected at low levels (<0.1-0.6 mg/l and <0.1-0.4 mg/l, respectively).

TCLP organics analysis found benzene (2600 ug/L) and tetrachloroethylene (950 ug/L) to be present at levels exceeding the TCLP regulatory limits (500 ug/l and 700 ug/l, respectively) in one of the samples collected by the SWRO. This sample (#507254) was taken from a 10,000 gallon waste antifreeze storage tank, that contained antifreeze which had been processed through an oil-water separator. Methyl-ethyl-ketone was also detected in sample #507254 at low levels (500 ug/l). Seven other organic compounds typically used as solvents but not on the TCLP organics list, were also detected in some or all of the SWRO samples. These included: acetone (1400-4800 ug/l), xylene (<250-7400 ug/l), 1,1,1-trichloroethane (750 - 50,000 ug/l), methylene chloride (<250-960 ug/l), toluene (<250-22,000 ug/l), ethylbenzene (<250-1200 ug/l), and 4-methyl-2-pentanone (<500-1900 ug/l). Halogenated hydrocarbons were detected at low levels in one of three SWRO samples (13 mg/l).

An acute oral rat bioassay performed on the SWRO samples determined that the acute LD_{50} greater than 5g/Kg body weight. The samples would therefore not be considered a dangerous waste under Chapter 173-303-101 WAC, based upon the results of this test alone.

Table 7. Summary of TCLP compounds detected in waste antifreeze samples.

Location/ Sample Number	Metals (mg/l)					Organics (ug/l)			Total Cresol
	Barium	Lead	Mercury	Silver	Chromium	Benzene	Methyl- ethyl- ketone	Tetra- chloro- ethylene	
Regulatory ¹ Limit	100	5.0	0.2	5.0	5.0	500	200,000	700	200,000
I. Vehicles									
Walt's 09-8083	0.2	0.1 U	0.02 U	0.1 U	0.1 U	630	280 UJ	50 U	40 U
Pacific Truck 09-8084	0.2	0.1 U	0.02 U	0.1 U	0.1 U	50 U	180 UJ	50 U	490
Firestone 10-8085	0.1	0.1 U	0.02 U	0.1 U	0.1 U	50 U	50 U	50 U	400 U
II. Recyclers									
Antifreeze Environmental* 10-8080/8086	0.6	0.5 U	0.02 U	0.1 U	0.1 U	30 UJ	150 UJ	60 U	120 U
Clean Care Tacoma* 10-8081/8087	0.2	2.7	0.02 U	0.1 U	0.1 U	370 J	70 U	2300 J	300 U
Clean Care Spokane* 10-8082/8088	0.4	2.8	0.04 U	0.1 U	0.1 U	190	520	2600 J	300 U
SWRO Samples- Northwest Processing, Tacoma									
507251	0.5	3.3	.009	0.3	0.1 U	250 U	500 U	400	200 U
507252	0.4	0.1 U	.006	0.6	0.1 U	250 U	500 U	250 U	200 U
507254	0.4	3.6	.005	0.1 U	0.4	2600	500	950	310

¹ = Values in bold print exceed the TCLP regulatory limit for that analyte.

U = not detected at the detection limits are not shown here.

* = Reported as mean of field duplicates.

J = Estimated value.

Previous studies have suggested that elevated levels of metals (particularly lead) might be present in waste antifreeze (California Department of Health Services, 1986, 1987; Hudgens, 1991). Our results indicated that although lead was detectable in waste antifreeze, it was not present at concentrations exceeding regulatory thresholds. Similar results were found in the samples taken by SWRO. Trace amounts of barium were also found in some samples. Interestingly, no lead was detected in samples of antifreeze taken directly out of vehicle radiators, although lead was detected in samples taken at recycling facilities. A sample taken by SWRO from a 10,000 gallon waste antifreeze storage tank and analyzed using TCLP, contained lead at concentrations below regulatory limits (3.6 ppm). This sample presumably represented a broad cross-section of the waste-stream, and confirmed the results of the present study. These data suggest that waste antifreeze may not generally designate as a dangerous waste for metals. At the present time, most radiators are constructed of copper and brass, with a lead-based solder. As the production and use of aluminum radiators and welded (rather than soldered) copper-brass radiators increases, the amount of lead getting into used antifreeze should decrease correspondingly.

Benzene was present at concentrations exceeding the TCLP regulatory limit at one of the three generator sites (sample #09-8083), but was not detected at the remaining two sites. Hudgens (1991), has found benzene in samples taken directly out of diesel truck radiators by Fleetguard Corp. an estimated 15% - 20% of the time. Since benzene is not an additive in antifreeze, it is probable, that the source of benzene in sample #09-8083 was an engine or oil cooler problem in one or more of the cars included in the composite sample. Cars were screened to insure that they were not at the shop for an engine-related problem, but this would not have precluded the inclusion of some vehicles with engine or oil cooler problems unknown to the owner. Benzene was present in all three recycler samples, although not at regulated levels. Engine difficulties in the contributing vehicles and poor shop management practices probably were both factors in these findings. Incidental observations made at service stations during the study, indicated that oily pans were sometimes used to catch antifreeze. With the exception of benzene, no other TCLP organics occurred at regulated levels in any of the samples taken directly from vehicles.

Tetrachloroethylene, a solvent, was found at regulated levels in two of the three recycler samples. Since tetrachloroethylene is not an antifreeze additive, solvents were probably getting into the antifreeze as a result of poor waste management practices. This interpretation is supported by handling practices observed during sampling. A thick layer of oil was visibly present on all of the recycler samples, although no oil was visible on any of the samples taken directly from vehicle radiators. Although oil can end up in antifreeze from an engine or oil cooler problem, this again strongly suggests the existence of poor waste management practices. Waste management practices followed at each site are described in Appendix D.

None of the samples designated on the basis of the halogenated hydrocarbon or bioassay results. Results obtained by SWRO concurred with these findings.

CONCLUSIONS

1. Barium and lead were detected in waste antifreeze at levels below TCLP regulated levels.
2. Benzene and Tetrachloroethylene were the only two organic compounds found to exceed TCLP limits in waste antifreeze. Benzene exceeded TCLP regulatory limits in one vehicle sample, while tetrachloroethylene exceed TCLP limits in three of the six recycler samples. Consequently, 44% of the samples tested designate as a dangerous waste, based on TCLP organics results.
3. The presence of solvents in recycler samples and the lack of these compounds in vehicle samples suggests that waste management practices are, in fact, influencing contaminant levels found in waste antifreeze. Thick layers of oil found in the recycler samples also tends to support this conclusion.

RECOMMENDATIONS

1. Segregate spent antifreeze from other waste streams to reduce contaminant levels.
2. The samples collected included a broad range of vehicle types and ages and are probably representative of the antifreeze waste-stream as a whole. Results indicate the status of used antifreeze, but fall short of full characterization of the entire waste-stream due to limitations in the number of samples. Additional studies with larger sample sizes would be required to answer specific questions including the actual proportion of waste antifreeze likely to designate as a dangerous waste based on concentrations of benzene and tetrachloroethylene or some other compound.

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Appendix A

Data on Sources of Antifreeze Sampled at Vehicle and Recyclers Sites

Appendix 1a. Sources of antifreeze making up vehicle samples.

Site Name/ Sample #	Av. Age of vehicles (yrs)	Av. mileage of vehicles	pH range of anti- freeze	Vehicle types	Radiator types
Walts Radiator, Olympia 09-8083	11 (range: 5-16)	100,000 (range: 40,000- 200,000)	7.9- 10.2	all domestic	all copper- brass
Firestone Spokane 10-8085	17 (range: 3-25)	90,000 (range: 35,000- 115,000)	7.8- 9.3	33% foreign 67% domestic	17% aluminum 83% copper brass
Pacific Coast Truck Ctr Tacoma 09-8084	11	230,000 (range: 100,000- 530,000)	8.5- 9.8	all domestic	all copper- brass

Appendix 2a. Sources of antifreeze making up Recycler samples.

Recycler Name	Sample No.	Sources	Vol. of antifreeze collected from each source (gal)	% of total
Antifreeze Environmental Tacoma	10- 8080, 10- 8086	marine heavy equipment fleet car dealer(foreign)	720 130 50 50 Total = 950	76 14 5 5
Clean Care Tacoma	10- 8081, 10- 8087	car dealer(domest.) car dealer (foreign)	110 495 Total = 605	18 82
Clean Care Spokane truck	10- 8082 10- 8088	car dealer (foreign) fleet heavy equipment	480 65 115 Total = 660	73 10 17

Appendix B.

Case narratives and quality assurance reviews of data.



WASHINGTON STATE DEPARTMENT OF ECOLOGY
MANCHESTER ENVIRONMENTAL LABORATORY
Manchester, Washington 98353

DATA REVIEW

By: *Craig Smith* Craig Smith, Chemist
PROJECT: Waste Antifreeze
Lab Sample No: 098083-84, 108080-82, 85-88 Report 04-11-91
WAS Pac. Tr.

	Collected	To Manchester	Analyzed
HOLDING TIME:	02-27	03-04	
		preserved 03-04	04-03-91
	03-08	03-11	
		preserved 03-11	04-03-91

Metals

Digestion: TCLP - Ethylene Glycol

HOLDING TIME: Analysis for all parameters were performed within the holding time limits.

REAGENT BLANK: The method blank showed no analyte values above the reporting detection limit.

MATRIX SPIKE: The targeted accuracy of matrix spikes is +/- 25% of the true value. All values were within the targeted limits.

SPIKE DUPLICATE: The target limits are +/- 20%, or +/- 1 detection limit for samples less than 5 times the detection limit. All values were within the targeted limits.

LABORATORY CONTROL SAMPLE The target is a +/- 20% recovery control limit. All values were within the targeted limits..

The data is acceptable for use without qualifications.

The results for all samples submitted gave no values above the maximum allowable concentration for TCLP.

The only parameters observed above the reporting detection limit were Pb, Ba, and in one sample, Hg. The Pb concentrations in two samples, 108081 and 108082, were 3.2 mg/L and 3.7 mg/L, respectively.

State of Washington Department of Ecology
Manchester Environmental Laboratory
7411 Beach Dr. E Port Orchard, WA. 98366

Data Review
May 13, 1991

Project: **Waste Antifreeze**

Samples: 108080 108081 108082 098083 098084
108085 108086 108087 108088

Laboratory: Sound Analytical Services
North Creek Analytical

By: Stuart Magoon *sm*

Halogenated Hydrocarbons

These samples were collected on February 27 & 28 and March 8, 1991.

These analyses were reviewed for qualitative and quantitative accuracy, validity, and usefulness.

Sound Analytical Services analyzed these nine samples using an adaptation of the Washington Dangerous Waste procedure. The analysis utilizes the petroleum ether extraction solvent as required by the Dangerous Waste procedure. However, the sample was only extracted once instead of three times, and analyzed using coulometric titration.

North Creek analytical extracted these samples as per the Washington State Dangerous Waste Procedure and then analyzed then with an ISE probe.

The results from North Creek Analytical are unreliable because the method blank contained a significant amount of chloride in relation to the samples. Since only one method blank was performed it is not possible to determine whether or not this level of contamination is representative of the level of contamination that may be present in all the sample analyses.

Results from Sound Analytical Services are more reliable, however, they were not performed in strict accordance to the Dangerous Waste Procedure.

Both results adequately demonstrate that there is no organic chloride present in any of these samples above 100 ppm (.01%).

This data is can be used to determine that these samples do not classify as dangerous waste under chapter 173-303 WAC.

MANCHESTER ENVIRONMENTAL LABORATORY

7411 Beach Drive SE , Port Orchard Washington 98366

CASE NARRATIVE

June 5, 1991

Subject: Waste Antifreeze Project - TCLP

Samples: 91-098083, 098084, 108080, 108081, 108082, 1080885, 108086, 108087 and 108088.

Case No. DOE-268Z

Officer: Laurie Wunder
Dale Norton

By: Dickey D. Huntamer *(Signature)*
Organics Analysis Unit

TCLP-SEMIVOLATILE ORGANICS

ANALYTICAL METHODS:

The samples were prepared following the EPA SW 846 Method 1311 Toxicity Characteristic Leaching Procedure (TCLP). A 50 mL aliquot of the TCLP preparation was diluted with 450 mL of organic free water to enhance the separation of the methylene chloride and ethylene glycol mixture. The semivolatile TCLP compounds were extracted using the Manchester modification of the EPA CLP procedure with capillary GC/MS analysis of the sample extracts. All of the samples except 108086 contained less than <0.5% solids and therefore did not have to undergo the TCLP leaching. The 0.7 um filtrate was used for analysis. Sample 108086 was just over the 0.5% residue level after filtration due to the oil in the sample. Consequently it required the TCLP leaching procedure and was prepared, along with an extraction blank, B9082. Due to the small field sample provided, less than 2.0 liters, a proportional amount of extraction fluid was used for the TCLP leaching procedure. Normal CLP QA/QC procedures were performed on the samples.

HOLDING TIMES:

The TCLP holding times allow fourteen days from date of collection to preparation of the TCLP leachate. An additional seven days is allowed from TCLP leaching to analytical extraction, then forty days until analysis. All antifreeze samples, 098083 and 098084 and the waste antifreeze samples, 108080 to 108088 and associated matrix spikes were analyzed within specified holding times.

BLANKS:

No significant blank contamination was detected in the laboratory blanks or the TCLP extraction blank.

SURROGATES:

TCLP surrogate recovery limits have not been officially established. The recommended CLP surrogate recovery limits are used as guidelines.

Water surrogate spike recoveries were within normal CLP limits for samples 098083 and 098084 except for d5-Phenol in sample 098083 which was 98%, 4% over the limit. Surrogate recoveries for samples 108080 through 108088 were within CLP limits for all but d10-pyrene in samples 108081 and 108082, d5-phenol in samples 108081, 108087, 108088, 108085, and matrix spikes 108080Y and 108080Z. No additional data qualifiers were added due to surrogate recoveries since the high recovery was probably due to matrix interferences.

MATRIX SPIKE AND MATRIX SPIKE DUPLICATE:

Matrix spike and matrix spike duplicate recoveries for the TCLP compounds have not been officially established however the Contract Laboratory Program QC limits have been used as guidelines. The antifreeze matrix spikes, 098084Y and Z were affected by severe matrix spike interferences resulting in the wide variation in recoveries. Compounds 1,4-dichlorobenzene, hexachloroethane and hexachlorbutadiene were outside recommended CLP limits for both recoveries and relative percent differences (RPD). The presence of benzoic acid, an antifreeze additive, caused considerable interference with the cresol (methylphenols) recovery.

Seven out of thirteen percent recoveries exceeded the CLP limits for samples 098084Y and Z. All Relative Percent Differences (RPD) were also out of CLP control limits. The poor recoveries are probably due to the high ethylene glycol concentrations in the sample.

The waste antifreeze sample, 108080 was used for matrix spikes. Spike recoveries for three compounds, 1,4-dichlorobenzene, hexachloroethane and hexachlorbutadiene were outside recommended CLP limits for both recoveries and Relative Percent Differences (RPD). The cleanest waste antifreeze sample was selected for matrix spikes but it still contained significant oil residues but much less than was present in some of the other samples where good spike recoveries would be impossible.

All other compounds in the waste antifreeze were within acceptable CLP limits for both recovery and RPD for both sets of matrix spikes. No additional data qualifiers were added to the data based on matrix spike recovery.

The concentration of ethylene glycol in sample 098084 was greater than 42% while the waste antifreeze sample matrix spike, 108080 contained only 17% ethylene glycol. The remaining waste antifreeze samples ranged from <0.1% to 50+%. If the spike results above are any indication the concentration of ethylene glycol can significantly affect the matrix spike recovery. Under TCLP, however the spike recoveries for 108080 would be used to correct the recoveries for the other waste antifreeze samples. If the ethylene glycol does affect the spike recovery then it is obvious that significant error could be introduced in the reported concentrations. An additional factor is the presence of varying amounts of lubricating oil in some of the samples and the oil's effect on spike recovery. The solution is to analyze individual matrix spikes for each sample. Obviously making spike recovery corrections would end up introducing greater errors than it purports to correct.

Due to the controversial nature of matrix spike recovery correction none of the data presented has been corrected. If the project officer desires to apply recovery correction to the data the formula is given in the TCLP procedure; Federal Register/Vol. 55, No 126/Friday June 29, 1990/ Rules and Regulations Section 8.2.5.

SPECIAL ANALYTICAL PROBLEMS:

The following notes apply to the analysis for the indicated sample.

91- 108080Y	3- and 4-methylphenol co-eluted, therefore the values reported are one-half the total of the two.
91- 108080	Benzoic acid (very high concentrations), phenol and 1,2 - dichlorobenzene, (94 ug/L) was also detected in the sample.
91- 108081	Benzoic acid (massive amounts) and 1,2-dichlorobenzene (19 ug/L).
91- 108082	Benzoic acid (massive amounts) and phenol were detected.
91- 108083	Benzoic acid and Benzyl alcohol were detected.
91- 108084	Benzoic acid.
91- 108085	Benzoic acid (massive amounts)
91- 108086	Benzoic acid (high concentrations) and 1,2-dichlorobenzene (48 ug/L) and phenol were detected.
91- 108087	Benzoic acid (massive amounts) and 1,2-dichlorobenzene (21 ug/L)
91- 108088	Benzoic acid (massive amounts), phenol and benzyl alcohol.

Both the antifreeze and the waste antifreeze samples presented analytical challenges. The antifreeze, samples 098083 and 098084 contained about 50% ethylene glycol plus other additives such as benzoic acid and had to be diluted with organic free water before extraction. Without dilution the extraction solvent, methylene chloride, was too miscible and poor solvent recoveries resulted. The waste antifreeze samples, 108080 to 108088, in addition to the ethylene glycol also contained significant amounts of petroleum products including gasoline and lubricating oil. Some chlorinated hydrocarbons were also detected which along with the presence of the petroleum products reflects poor recycling technique and combining of wastes streams during recycling. The elimination of the oil from the waste antifreeze would also simplify the TCLP analysis. Very little particulate matter was found in the samples but the retention of the lubricating oil on the filters caused one sample to undergo TCLP leaching when the 0.5% residue limit was exceeded.

The type of samples represented by the antifreeze samples and waste antifreeze samples in which significant levels of TCLP compounds are unlikely to be found are prime candidates for total analysis as allowed in the TCLP procedure with subsequent TCLP analysis if warranted. The total analysis also provides the advantage of determining the TCLP compound concentrations and allow matrix spiking at appropriate concentrations, permitting better spike recoveries.

TCLP-VOLATILE ORGANICS

ANALYTICAL METHODS:

The samples were first prepared following the SW 846 Method 1311 TCLP procedure and the filtrates/leachates were then analyzed for volatile organics using Manchester modification of the EPA CLP purge-trap procedure with capillary GC/MS analysis. Normal CLP QA/QC procedures were performed on the samples.

BLANKS:

Low levels of 2-Butanone were detected in the laboratory blanks. The EPA five times rule was applied to all target compounds which were found in the blank. Compounds that were found in the sample and in the blank were considered real and not the result of contamination if the levels in the sample are greater than or equal to five times the amount of compounds in the associated method blank.

SURROGATES:

Surrogate recoveries were within CLP limits for all of the samples except for 1-Bromo-2-fluoroethane in sample 108083D (dilution) which exceeded the recommended CLP limits by 4%. Since the CLP limits are not intended for TCLP analysis the recovery limits should be considered advisory. No additional qualifiers were added to the data based on the surrogate recoveries.

HOLDING TIMES:

All samples were analyzed within the recommended 14 day holding time for water samples after the TCLP extraction except for 108082A, 108087A, reanalysis of samples, 108082 and 108087 for high levels of tetrachlorethene which were analyzed within holding times. Two other samples, the matrix spikes, 108082Y and 108082Z were analyzed, six days after the holding time but since these are used primarily to determine matrix effects on the analysis the additional holding time should have no significant effect on the spike recoveries. The TCLP extraction blank, AVW1119 and sample 108081 were also over holding times and the values reported have all been given the "J" qualifier indicating an estimated value. The "J" qualifier was also added to the tetrachlorethene concentrations in samples 108082 and 108087 since the values were taken from the diluted 108082A and 108087A samples which were analyzed past holding times.

MATRIX SPIKE AND MATRIX SPIKE DUPLICATE:

No spike recovery limits have been established for matrix spikes in TCLP analysis. Two sets of matrix spikes using samples, 098084 and 108082, were analyzed. All of the TCLP VOA compounds were added to the samples. The spike recoveries ranged from 74% to 136% and the Relative Percent Difference (RPD) ranged from 0% to 17%.

SPECIAL ANALYTICAL PROBLEMS:

No special problems were encountered in the VOA analysis. Several TCLP compounds were detected in the samples. These included 2-butanone, chloroform, benzene and tetrachloroethene along with traces of

several other compounds. None of these compounds would normally be expected to be present in antifreeze, particularly in sample 098083 which was a composite sample taken from several car radiators. This could indicate possible cross contamination between the engine coolant and gasoline (the most likely source). The presence of the compounds in the week ten (108080-108088) samples is probably the result of poor recycling technique, allowing different waste streams, antifreeze and oil/gasoline to be mixed. Several of the waste antifreeze samples had a noticeable gasoline odor.

ETHYLENE GLYCOL

ANALYSIS:

The ethylene glycol was analyzed by direct injection capillary Gas Chromatography using a Flame Ionization Detector. Concentrations (percent by volume) were calculated from a calibration curve prepared by analyzing ethylene glycol standards.

HOLDING TIMES:

No holding times have been established for this method.

SURROGATES:

Not applicable to this method.

MATRIX SPIKES:

Not applicable to this analysis.

SPECIAL ANALYTICAL PROBLEMS:

No special problems were encountered with this analysis. The results are presented as the percent (%) ethylene glycol by volume. Sample 91 8000EG was a sample of Texaco Antifreeze taken from a bottle and was 97% ethylene glycol.

<u>Sample Number</u>	<u>% Ethylene Glycol by Volume</u>
91 - 098083	49.4
91 - 098084	42.6
91 - 108080	17.0
91 - 108081	32.7
91 - 108082	46.7
91 - 108083	0.09U
91 - 108085	50.8
91 - 108086	20.7
91 - 108087	38.7
91 - 108088	35.5
91 - 8000EG	97.0

DATA QUALIFIER CODES:

- U - The analyte not detected at or above the reported value.
- J - The analyte was positively identified. The associated numerical value is an estimate.
- UJ - The analyte was not detected at or above the reported estimated value.
- D - Signifies that the associated value was derived from a secondary dilution.
- B - This qualifier is used when the concentration of the associated value exceeds the known calibration range.
- R - The data are unusable for all purposes. The presence of the analyte has not been verified.
- NAR - No Analytical Result.



STATE OF WASHINGTON
DEPARTMENT OF ECOLOGY

Post Office Box 307 • Manchester, Washington 98353-0346 • (206) 895-4740

March 27, 1991

TO: Laurie Wunder
FROM: Scott Noble ^{SN}
SUBJECT: Waste Antifreeze
Results of Salmonid Bioassay

SAMPLE IDENTIFICATION

Laboratory Reference Number: 09-8083 and 09-8084
Date Sample Collected: 2/27-28/91
Sample Description: 09-8083 "WR1; Waste Antifreeze;
2/27/91; 1500; LW"
Green liquid with yellow
sludge on bottom
09-8084 "CMNS-1; Waste Antifreeze;
2/28/91; 1800; LW"
Green liquid with yellow
brown sludge on bottom

METHODS

Testing for toxic properties was in accordance with the Department of Ecology procedure for "Static Acute Fish Toxicity Test." The test organism was rainbow trout (*Oncorhynchus mykiss*). The sample was tested at 1000 ppm (mg/L) by weight in water. Ten trout were added to fifteen liters of sample/water mixture in each aquarium. Dechlorinated Manchester city water was used for dilution of samples, and as a control. Three replicates were run at each concentration. Cadmium chloride (EPA/EMSL, Cincinnati) was used as a reference toxicant. Test duration was 96 hours. Length, weight, and loading data were based on measurements of control organisms at the end of the test.

TEST RESULTS

A full report of test data is attached. Mortality is summarized below.

09-8083 1000 ppm (mg/L) - 00/30 fish died = 00%mortality
09-8084 1000 ppm (mg/L) - 00/30 fish died = 00%mortality
Control - 00/30 fish died = 00%mortality

The LC50 for the cadmium chloride reference toxicant was estimated a 5.1 ug/L using the graphical method. This is within the range of values normally expected for this organism.



STATE OF WASHINGTON
DEPARTMENT OF ECOLOGY

Post Office Box 307 • Manchester, Washington 98353-0346 • (206) 895-4740

March 27, 1991

TO: Laurie Wunder
FROM: Scott Noble SN
SUBJECT: Waste Antifreeze
Results of Salmonid Bioassay

SAMPLE IDENTIFICATION

Laboratory Reference Number: 10-8080, 10-8081, 10-8082,
10-8085
Date Sample Collected: 3/8/91
Sample Description: 10-8080: "AE-1; waste antifreeze;
3/8/91; 1600; LW"
Cloudy yellow brown liquid
with rust colored sludge
10-8081: "CCW-1; waste antifreeze;
3/8/91; 2100; LW"
Cloudy green brown liquid
with rust colored sludge
10-8082: "CCE-1; waste antifreeze;
3/8/91; 1900; LW"
Dark green brown liquid with
light brown colored sludge
10-8085: "FS-1; waste antifreeze;
3/8/91; 1600; LW"
Bright green liquid with pale
yellow, fine precipitate

METHODS

Testing for toxic properties was in accordance with the Department of Ecology procedure for "Static Acute Fish Toxicity Test." The test organism was rainbow trout (*Oncorhynchus mykiss*). The sample was tested at 1000 ppm (mg/L) by weight in water. Ten trout were added to ten liters of sample/water mixture in each aquarium. Dechlorinated Manchester city water was used for dilution of samples, and as a control. Three replicates were run at

each concentration. Cadmium chloride (EPA/EMSL, Cincinnati) was used as a reference toxicant. Test duration was 96 hours. Length, weight, and loading data were based on measurements of control organisms at the end of the test.

TEST RESULTS

A full report of test data is attached. Mortality is summarized below.

10-8080	1000 ppm (mg/L)	- 00/30 fish died = 00 %mortality
10-8081	1000 ppm (mg/L)	- 00/30 fish died = 00 %mortality
10-8082	1000 ppm (mg/L)	- 8/30 fish died = 26.7%mortality
10-8085	1000 ppm (mg/L)	- 00/30 fish died = 00 %mortality
	Control	- 00/30 fish died = 00 %mortality

The LC50 for the cadmium chloride reference toxicant was estimated at 3.65 ug/L using the graphical method. This is within the range of values normally expected for this organism.

DATA REVIEW

BY: Margaret Stinson *MS*

FOR: Waste Antifreeze Study

DATE: April 12, 1991

BioTechnics Laboratories, Inc., has submitted the attached results of Acute Oral Rat Toxicity Tests on two samples from the Waste Antifreeze Study (Sample Numbers 09-8083 and 09-8084). The samples were tested at 5 gm/Kg body weight as defined by the Washington State Department of Ecology *Biological Testing Methods*, DOE 80-12 (1981). No physical or behavioral changes were noted during the fourteen day test. Necropsies conducted at termination of testing showed no evidence of gross pathological abnormalities. Weight changes in controls and test organisms were similar.

→ UACIS
→ Pacific Toxic

DATA REVIEW

BY: Margaret Stinson ^{MP}
FOR: Waste Antifreeze Study
DATE: April 24, 1991

BioTechnics Laboratories, Inc., has submitted the attached results of Acute Oral Rat Toxicity Tests on samples from the Waste Antifreeze Study (Sample Numbers 10-8080, -8081, -8082, and -8085). The samples were tested at 5 gm/Kg body weight as defined by the Washington State Department of Ecology *Biological Testing Methods*, DOE 80-12 (1981). No physical or behavioral changes were noted during the fourteen day test. Necropsies conducted at termination of testing showed no evidence of gross pathological abnormalities. Weight changes in controls and test organisms were similar.

Handwritten annotations: Arrows point from the words "submitted", "samples", "tested", and "Necropsies" to the handwritten labels "AE", "CCW", "CCE", and "451" respectively.

Appendix C.

Estimated Quantities of New Antifreeze Used at Vehicle Sites and
Waste Antifreeze Handled at Recycler Sites

Appendix 1c. Antifreeze usage at vehicle sites.*

Site Name	No. vehicles serviced/wk	Vol. (gal) of antifreeze used/mo.	Peak Months	Antifreeze dilution used
Walt's Radiator, Olympia	15-20	20-30	all yr.	50:50
Firestone Tire, Spokane	1-20	10**	Oct-Jan	50:50
Pacific Coast Truck Center, Tacoma	unknown	165	all year	50:50

* Information in this table represents a compilation of estimates made by store managers at each site.

** This store uses an on-site antifreeze recycling system.

Appendix 2c. Quantities of antifreeze handled at recycling sites.*

Site Name	No. of Pick-up Sites/wk	Volume of Antifreeze per month (gal)	Peak Months	Antifreeze Sources
Antifreeze Environmental Tacoma	3-5	2500-3000	all yr.	mainly fleets and car dealers; a few service stations, radiator shops, marine operations, airports
Clean Care, Tacoma	35	9000-15,500	Nov-Jan	car dealers, fleets, service stations
Clean Care, Spokane truck	5	1000-2500	Nov-Jan	car dealers, fleets, service stations

* Compilation of estimates made by recycling facility managers.

Appendix D

Waste Antifreeze Management Practices at Sampling Sites

Appendix 1d. Waste antifreeze management practices at sampling sites.

Vehicle Sites

Walt's Radiator and Muffler - According to the store manager, drainage pans were only used for antifreeze and not for used oil. Drainage pans observed at the site did not appear to have oil in them.

Pacific Coast Truck Center - The store manager stated that drained antifreeze was caught in pans, which they tried to keep separate from pans used for oil. However, pans used to drain antifreeze at the site were observed to be oily. Used antifreeze was stored at the site in 55 gallon drums, which were picked up and recycled by Clean Care Corp., Tacoma.

Firestone- This site used an "in-house" antifreeze recycling system (Wynn Oil Company Mark X Recycling System). Coolant is pumped out of the radiator and filtered and treated (with various additives) by the system. The processed antifreeze is then returned to the radiator. According to the store manager, any additional antifreeze that was collected at the site was put into a 55 gallon drum and stored on site. It was eventually picked up by a hazardous waste company. Shop workers stated that they mixed waste streams in the storage drum. Waste oil and transmission fluid thus probably contaminate this drum. Some of the pans used to collect drained antifreeze were coated with oil or had oil filters sitting in the pans.

Recycler Sites

A thick layer of oily material was visibly present on all the recycler samples.

Antifreeze Environmental Service- A tanker truck was used to pick up and deliver antifreeze. Many of their customers use a polyethylene container provided by the company to collect their waste antifreeze at the site. Customers were told to use clean drain pans to collect antifreeze and to segregate their waste streams.

Clean Care Corp.- Customers collected waste antifreeze in 55 gallon drums. Drums were picked up by Clean Care when they were full. Customers were told to keep their waste-streams separate.