

Contaminants in Used Lubricating Oils and Their Fate during Distillation/Hydrotreatment Re-Refining

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Used oils are an excellent example of a high-volume recyclable commodity that can be turned from a waste into valuable products. Debate concerning the degree of hazard posed by improper management of used oils relates to the typical contaminants one might find. Samples were taken for this study at every step within a used oil management system, including re-refining. Concentrations of chlorinated solvents, three metals (Cd, Cr, and Pb), and polynuclear aromatics are compared for each step and with past studies.

Introduction

On September 23, 1991, the U.S. Environmental Protection Agency (EPA) again presented information on contamination found in used lubricating oils (1). While this data had many similarities to that published in 1984 (2), at least one area was given special attention. This was the polynuclear aromatics (PNAs) content. This broad grouping of compounds includes both known and suspected mutagens and carcinogens (3). As such, their presence in a waste stream that ends up in the environment in large volumes through improper disposal is a concern.

One of the problems with the 1991 EPA data was the attempt to cover a large variety of types and uses of oils, which resulted in very few samples of any one category being tested. Since the primary volumes of used oils can be broadly categorized as "automotive" or "industrial", this study focused on those sources. In addition, this study includes a significant number of samples from an oil re-refinery, representing the actual used oil stream as it occurs in commerce.

The primary objective of this study was to focus not only on the principle sources of used oil but also on the main contaminants found by the EPA and others. Secondly, the fate of representative components of each type of contaminants were monitored as they are processed through a distillation/hydrotreating re-refining system.

This paper is limited to contaminants that have been addressed by the EPA and others. These are key metals (cadmium, chromium, and lead), halogenated solvents, and polynuclear aromatics.

Sampling

Used Oils. There were two types of used oil samples studied. The first population involved samples taken specifically for this study. They were immediately chilled, placed in coolers, and shipped by overnight courier to the laboratory. The samples were preserved at 4 °C in refrigerators until subsampling was completed. These are designated as "preserved" throughout this paper.

A second population of samples was obtained from the wide variety of industrial waste streams received routinely at this lab for screening. These samples were obtained at customer sites around the country by company personnel, placed in clean 1-L containers and shipped in individual cartons to the lab by 2-day carrier. These samples received no special preservation procedures and are designated as "unpreserved".

Preserved Used Oil Samples. Within this designation were several types of samples:

(1) *Vehicle Crankcase Oil.* Lubricating oil was taken directly from the crankcase of 24 vehicles (from five locations, see Table 1). One-gallon glass containers were used in order to obtain essentially the entire contents of the crankcase. Only gasoline engines were included to reduce the number of variables.

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TABLE 1
Sampling Locations

vehicle crankcase oil	Elgin, IL Glen Burnie, MD Johnstown, PA Altamonte Springs, FL Charlotte, NC
quick-lube shops	Westchester, PA Brunswick, OH Davenport, IA
industrial lube generators	Indianapolis, IN Saginaw, MI Kaukauna, WI Greer, SC Malvern, PA

(2) *Quick Lube Oil.* Sixteen samples were taken from the used oil storage tanks of service facilities offering rapid lube oil changes (see Table 1 for locations). One-gallon glass containers were used to provide enough volume to allow full-length coliwasa sampling.

(3) *Industrial Oil.* Twenty-five samples were taken from used industrial oil generators by directly sampling their storage tanks (see Table 1 for locations). A clean coliwasa was used to obtain a full-depth sample. Generator applications included gear oils, metal-working, and hydraulic fluids.

(4) *Used Oil Tankers.* Twenty-two samples were obtained from truck and railroad tankers as they arrived at a re-refinery in East Chicago, IN. These samples were obtained during transfer operations using a sampling valve in the pump line. The valve was flushed before the sample was taken. These samples represent a cross-section of all types of used oils collected.

(5) *Used Oil Feedtank.* Nine samples were obtained over a period of several weeks from the primary feedtank (2.2 million gal capacity) to a 75 million gallon/year re-refinery. Even more than the tanker samples, these provide an average understanding of the composition of the used oil collected over a wide portion of the country.

All of these samples were immediately capped and placed in a cooler with ice packs. Paper work was completed by Safety-Kleen personnel to provide a detailed history of each sample. Samples were sent by overnight express courier to the laboratory for immediate processing and storage at 4 °C. The data accompanied the samples.

Unpreserved Used Oil Samples. As part of the normal screening of potential customer waste streams for various recycling programs, a number of used oil samples are received each day. These represent wastes usually stored at the generator site in drums or small tanks. Trained personnel use a coliwasa to obtain a representative 1-L sample, which is shipped to the lab for testing. Since the original waste containers are normally open to the air over fairly long periods of time, no special preservation techniques are used. Samples are placed in sealed jars, which are then packed into individual cardboard boxes and shipped by second-day carrier.

For this study, data from a 12-week time period are tabulated for all samples that had been designated as used oils. To avoid bias, no selection process was applied.

Testing

There were three categories of contaminants included in this study—chlorinated solvents, metals, and polynuclear aromatics.

TABLE 2
Halogenated Solvent GC/ECD Method Conditions

column	cross-linked 5% phenylmethyl silicone (RTX-5, DB-5) film thickness, 1.0 μ m i.d., 0.32 mm length, 50 m
injector inlet	225 °C
detector	300 °C
oven temperature profile	initial initial value, 40 °C initial time, 6.0 min level 1 (first ramp) program rate, 10 °C/min final value, 180 °C final time, 0.0 min level 2 (second ramp) program rate, 25 °C/min final value, 280 °C final time, 2.0 min
carrier gas	hydrogen
head pressure	8 psi (approx)
column flow	2.2 mL/min (approx)
split vent	50 mL/min (approx)
split ratio	23:1 (approx)
septum purge	2 mL/min
makeup gas	nitrogen
makeup gas	40–60 mL/min
sample injection	1.0 μ L

Chlorinated Solvents. Immediately upon receipt, a small subsample was taken for analysis by gas chromatography using an electron capture detector. The procedure is an adaptation of EPA Method 8120 with an internal designation of SK9209. The 10 chlorinated solvents included in the EPA waste codes F001 and F002 were the target compounds, although other peaks were identified, if found. GC conditions are listed in Table 2. The method detection limit for most compounds is about 1 ppm.

Metals. Cadmium, chromium, and lead determinations for the preserved samples were done by atomic emission using acid microwave digestion preparation and inductively coupled argon plasma for analysis. The key instrument parameters are presented in Table 3. The method detection limit for lead is 5 ppm and for cadmium and chromium is 2 ppm. For the unpreserved samples, the lead data were obtained as part of a larger analysis program using the same techniques as for the other samples.

Polynuclear Aromatics. This analysis was only performed on the preserved samples. The approach used here was to look for 16 target PNAs designated by EPA Methods 8310 and 610. High-performance liquid chromatography using a UV detector was the primary instrumentation. System parameters are presented in Table 4. Confirmation of any possible co-elution was performed using a GC/MSD. The method detection limit for most compounds is about 1 ppm.

Re-Refining Process

The vacuum distillation/hydrotreating process evaluated for contaminant removal has been discussed in detail elsewhere (5). It is the predominant re-refining technique being installed around the world. Made up of several distillation stages followed by a high-pressure hydrogen treatment over a fixed catalyst bed, it has the added advantage of producing byproducts that can be used as commercial products, so that nothing needs disposal other

TABLE 3
Metals Analysis Conditions

Microwave/Acid Digestion Conditions		
sample weight, 1 g vessel, 120 mL of Teflon (PFA) 7.5 mL of concentrated nitric acid 5.0 mL of concentrated hydrochloric acid oven conditions (assuming 12 samples)		
stage	power (%)	time (min)
1	100	2
2	0	2
3	100	5
4	0	2
5	100	23

ICAP Instrument Operating Conditions		
nitrogen	15 psi	
argon	70 psi	
vacuum meter	10 or <10 mTorr	
power and forward power	on/max	
load control turning	automatic	
automatic power control	locked	

TABLE 4
HPLC Conditions for PNA Analysis

Apparatus			
reverse-phase column (LC-PAH, 15 cm × 4.6 mm i.d., 5 μm) Sep-pak florisisil cartridge detector, UV (490 nm) 200 μL injection loop 25 μL injection volume			

Eluant			
time (min)	flow (mL/min)	%A ^a	%B ^b
0	1.5	30	70
25	1.5	100	
35	1.5	30	70
50	0		

Calibration	
16 PNA standards diluted to 1, 5, 10, 25 and 50 μg/mL	

^a A = acetonitrile. ^b B = water.

than water generated in the initial dehydration step. This water undergoes a three-stage treatment to meet local POTW discharge requirements. In the United States alone, over 100 million gal of used oil are recovered each year using this type of process.

Results and Discussion

The results from these studies are presented in a variety of formats, starting with two different summaries. Table 5 covers only the preserved used oil samples and provides the averages and ranges for each constituent. Table 6 covers the same samples, but breaks out the subcategories to provide average concentrations by sample type.

It is clear that there are both similarities and differences among the different data sets representing different origins, as well as within some of the sets. The first consideration was to determine whether there were any statistically

TABLE 5
Used Oil Analyses: Data Summary by Analyte^a

PNA compd name ^b	frequency				
	av	high	low	>MDL (%)	MDL
naphthalene	196	1443	0	92	1
acenaphthalene	2	134	0	3	1
acenaphthene	7	171	0	17	1
fluorene	21	304	0	85	1
phenanthrene	81	1387	0	96	1
anthracene	9	127	0	71	1
fluoranthene	308	2826	0	93	1
pyrene	357	1859	0	98	1
benz[a]anthracene and chrysene	65	726	0	96	1
benzo[b]fluoranthene	9	93	0	53	1
benzo[k]fluoranthene	6	111	0	38	1
benzo[a]pyrene	10	65	0	77	1
dibenz[a,h]anthracene	8	94	0	71	1
benzo[g,h,i]perylene	20	193	0	39	1
indeno[1,2,3-cd]pyrene	4	77	0	25	1
halogenated solvent (ppm)					
1,1,1-trichloroethane	78	887	0	46	0.04
perchloroethylene	63	881	0	39	0.07
trichlorofluoromethane	5	105	0	14	0.002
trichlorotrifluoroethane	3	66	0	19	0.09
trichloroethylene	2	59	0	15	0.04
o-dichlorobenzene	1	42	0	8	0.2
trichlorobenzenes	0	14	0	4	0.2
1,2,4-trichlorobenzene	1	60	0	3	0.2
methylene chloride	0	12	0	1	2.4
p-dichlorobenzene	0	14	0	1	0.2
n-dichlorobenzene	0	7	0	1	0.2
metals (ppm)					
cadmium	0	5	0	5	5
chromium	10	233	0	49	5
lead	29	265	0	75	5

^a Preserved samples: PNAs, metals, and chlorinated solvents.
^b Concentration in μg/mL.

significant differences among the various sources of used oil.

The PNAs show surprisingly similar results across sample types, including industrial oils for most components other than fluoranthene and pyrene. If one uses the criteria of twice the standard deviation on either side of the average, almost no differences can be identified for individual constituents. If one looks at the sum of PNAs, it is obvious that the industrial oils tend to have a lower level, probably due to less thermal stress.

The one PNA that stands out is fluoranthene, which is very low in industrial oils compared to the automotive sources (23 ppm versus around 400 ppm). A similar but less dramatic difference is seen for pyrene. It is possible that these have some crankcase oil additive origin. Thus, the fact the PNAs have not been analyzed for most of the oils within this and other studies is probably not significant, since they seem to develop similarly in many applications.

A larger variation is seen among the halogenated volatile organic compounds (HVOC). The automotive samples (repair shops, dealers, and quick-lubes) have almost no HVOC, while the industrial samples have low levels. However, used oil arriving at the re-refinery has substantially higher levels of 1,1,1-trichloroethane (TCA), perchloroethylene (PERC), and freon.

Further evidence of this is shown by comparing the oil taken directly from an automotive crankcase versus oil

TABLE 6

Used Oil Analyses Summary: Average Concentration by Oil Source

type ^a	PNAs														
	NAP	ANL	ACN	FLO	PHN	ANT	FLA	PYR	BAA	BBF	BKF	BAP	DBA	BOP	IDP
CCO/auto repair	196	0	0	8	48	6	369	248	25	11	3	14	9	32	2
CCO/dealer	328	0	2	15	79	20	495	458	62	7	6	21	13	24	0
CCO/feedtank	217	0	10	32	130	9	369	517	71	7	13	7	0	24	3
CCO/quick-lube	282	0	0	26	69	13	539	542	59	13	9	16	3	44	9
CCO/tanker	175	0	14	29	141	4	331	388	97	9	2	6	5	11	3
IND/oily waste	104	7	10	15	42	8	23	148	55	6	5	6	16	6	3
av	217	1	6	21	85	10	354	384	62	9	6	11	8	23	3
STD	72	2	5	9	38	5	166	143	21	3	4	6	6	13	3

	HVOC											
	TCA	PERC	FMF	FTF	TCE	ODCB	TCBS	TCB1	MECL	PDCB	MDCB	
CCO/auto repair	0	0	0	0	0	0	0	0	0	0	0	
CCO/dealer	0	0	0	0	0	0	0	0	0	0	0	
CCO/feedtank	244	165	53	20	12	3	0	0	1	0	0	
CCO/quick-lube	13	50	0	0	0	0	0	0	0	0	0	
CCO/tanker	197	124	1	3	4	4	1	0	0	1	0	
IND/oily waste	37	34	0	2	0	0	0	2	0	0	0	
av	82	62	9	4	3	1	0	0	0	0	0	
STD	100	62	20	7	4	2	0	1	0	0	0	

	Metals		
	CD	CR	PB
CCO/auto repair	0	4	51
CCO/dealer	1	1	15
CCO/feedtank	0	6	39
CCO/quick-lube	0	13	40
CCO/tanker	0	14	29
IND/oily waste	0	12	13
av	0	8	31
STD	0	5	14

^a CCO = crankcase oil; IND = industrial oil.

collected from storage tanks at auto service locations. While the concentrations of PNAs and metals are quite similar, the HVOC content is not. Perchloroethylene (PERC) is non-detectable in any of the direct-drain samples, but is as high as 880 ppm in one of the storage tanks, and is found in seven of 16 samples. Similarly, 1,1,1-trichloroethane (TCA) is found in seven tank samples (in all but one case, the same generators as for the PERC), but in none of the crankcase samples.

The most significant finding related to the metals content is that cadmium is almost nonexistent, while chromium is present at levels near those of regulatory interest when using the EPA Toxicity Characteristic Leaching Procedure (TCLP; 5 ppm), and lead is found frequently (75% of the samples) and at concentrations up to 265 ppm. This is well above the TCLP limit of 5 ppm.

As would be expected, most of the lead-free samples were from industrial customers. Used oil from car dealerships tended to have low levels of lead, which probably reflects the predominance of new cars they service.

To try to obtain some perspective, the data generated within this study were compared with that obtained by Franklin Associates in 1984 (2) and by the EPA in 1991 (1, 4). These comparisons are presented in Tables 7-9. It is important to note that, while the studies were published within the last 10 years, they are both compilations of data generated by others. Thus, some data included in the averages could be as much as 20 years old.

TABLE 7

Crankcase Oil at Generator: Comparison of Results with Past Studies^a

	Franklin Assoc.	SAI	SK data	
			direct	tank
1,1,1-TCA	73	nm	nd	16
trichloroethylene	1	nd	nd	nd
tetrachloroethylene	66	nd	nd	60
lead	2500	17	32	44
benzo[a]anthracene	nm	nm	35	75
benzo[a]pyrene	10	18	19	13
naphthalene	nm	nm	252	297

^a nm = not measured. nd = not detected. Franklin Assoc., ref 2, Table 19, pp 3-33; recalculated to average data over all samples. SAI, ref 4, Table 3-2 and 3-3, pp 3-5 and 3-6.

Table 7 shows the dramatic decrease in lead content over the last decade for crankcase oil taken at the generator location. On the other hand, there is little evidence of any change in halogenated solvents or PNAs, based on the TCE and B(a)P contents, respectively.

The industrial oil data comparison in Table 8 shows a similar decline in lead. The TCE levels are comparable. There is no PNA data available from the Franklin study for comparison, but our other data would suggest that the levels would be similar. It is likely that the "not detected" results within the SAI summary reflects more a lack of sensitivity in the methodology used, given the close agreement on those occasions where constituents were found.

TABLE 8**Industrial Oils: Comparison of Results with Past Studies^a**

	Franklin Assoc.	SAI	SK data
1,1,1-TCA	2300		37
trichloroethylene	2	nd	nd
tetrachloroethylene	57	nd	34
lead	238	88	13
benzo[a]anthracene	nm	nd	55
benzo[a]pyrene	nm	nd	6
naphthalene	nm	nd	104

^a nm = not measured. nd = not detected. Franklin Assoc., ref 2, Table 21, pp 3-35; recalculated to average data over all samples. SAI, metal working oils only, ref 4, Tables 3-35 and 3-36, pp 3-55-3-58.

TABLE 9**Composited Oil at Refiner: Comparison of Results with Past Studies^a**

	Franklin Assoc.	SK data	re-refined product
1,1,1-TCA	1860	244	<1
trichloroethylene	620	12	<1
tetrachloroethylene	1360	165	<1
lead	600	39	<2
benzo[a]anthracene	14*	71	<1
benzo[a]pyrene	nd*	7	<1
naphthalene	378*	217	<10

^a nm = not measured. nd = not detected. * = automotive only. Franklin Assoc., ref 2, Tables 20 and 22, pp 3-34-3-36; recalculated to average data over all samples.

It is interesting that the data from the re-refinery feedstock testing shows significant declines in both lead and halogenated solvents. The latter effect likely is due to the screening process used to select which oils will be accepted for re-refining. This facility does not accept wastes which include any of the F-listed halogenated solvents (i.e., wastes which have become listed hazardous wastes due to blending). Another probable contribution to the decline in halogenated solvents is the growing trend to remove chlorinated solvents from many automotive and industrial products.

As would be expected from all of the other data, there is no statistically significant change in PNA content. It seems obvious from all the data gathered during this study that the PNAs are generated during use in a wide variety of applications.

In Table 10, data are presented from analyses of industrial waste streams submitted for consideration as re-refinery feedstock components. All automotive used oils are exempt from this requirement. Thus, these data should be compared to the industrial samples in Table 6.

However, as shown in Table 11, the comparison is better for the used oil actually received at the re-refinery. This again implies that much of the halogenated solvent contamination occurs just before or during used oil collection when other wastes are incorporated into the used oil.

Data collected from finished stocks obtained after re-refining versus composited used oil are compared in Table 9. This is the most suitable point for comparison, since this information is more representative of a true feed for this process.

TABLE 10**Halogenated Solvents in Used Oils Submitted for Prequalification Analysis^a**

	FMF	FTF	MECL	TCA	TCE	PERC	DCBS	TCBS
av of positives	533	98	283	757	5	527	65	50
av of all	43	15	28	454	1	169	5	10
high concn	2945	1004	893	2060	15	2776	220	321
low concn	2	1	0	2	2	1	7	2
frequency found (%)	8	15	10	60	14	32	7	19

^a Compound codes: FMF, trichlorofluoroethane; FTF, trichlorotrifluoroethane; MECL, methylene chloride; TCA, 1,1,1-trichloroethane (111); TCE, trichloroethylene; PERC, perchloroethylene (tetrachloroethylene); DCBS, dichlorobenzenes (total); TCBS, trichlorobenzenes (total).

TABLE 11**Comparison of Prequalification Analyses to Actual Receipt and Generator Samples**

	FMF	FTF	MECL	TCA	TCE	PERC	DCBS	TCBS
av of all prequals	43	15	28	454	1	169	5	10
CCO/feedtank	53	20	1	244	12	165	3	0
IND/oily waste	0	2	0	37	0	34	0	2

The results indicate the effectiveness of the distillation/hydrotreatment process in the removal of lead and halogenated solvents and the significant reduction of PNAs. Lead and halogenated solvents are physically removed by distillation. PNAs are not affected by the front portion of the process, but are reduced to non-harmful levels through the hydrogen-addition stage.

This successful contaminant removal has been confirmed by many laboratory tests related to biological activity, such as DNA adduct screening. These will be presented in a subsequent publication.

Conclusions

While even 100 samples could be considered a rather small number by some, the consistency of the data is such that some obvious conclusions can be reached. Whether one is talking about used oil sampled directly at the point of generation or at the final recycling facility, polynuclear aromatics concentrations seem to be quite similar for most used oils. This is a significant and somewhat surprising finding given the wide variety of environments that these oils have experienced.

The metals analyses also show similarities now that leaded gasoline has been essentially eliminated as a contributor to the crankcase oil. On the other hand, the halogenated solvents, which rarely enter the oil during use, reflect a wide variation in concentration depending on the source of the samples. The fact remains that the used oil that is actually collected, transported, and processed continues to contain detectable quantities of chlorinated solvents. Until these solvents are eliminated from industrial and automotive applications, it seems unreasonable to assume they are not present. Having documented the current status of the presence and concentration of contaminants in used oils, it has been demonstrated that this potential waste can be recovered through conversion into a clean commodity when properly re-refined using vacuum distillation and hydrotreating.

Literature Cited

- (1) *Fed. Regist.* **1991**, No. 184, 48000.
- (2) *Composition and Management of Used Oil Generated in the United States*; U.S. EPA: Washington, DC, 1984; EPA/530-SW-013.
- (3) *LARC Monogr.* **1984**, No. 33.
- (4) Science Applications International (SAI). *Used Oil Characterization Sampling and Analysis Program: Final Report*; U.S. EPA: Washington, DC, 1991; EPA/UOLP-50073.

- (5) Brinkman, D. W. *Oil Gas J.* Aug 19, **1991**, 60.

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