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Project Summary

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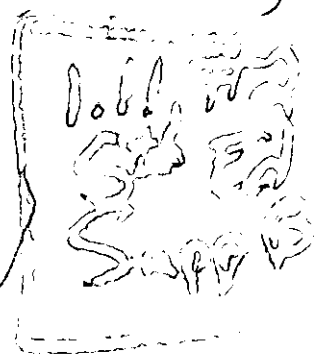

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PROJECT SUMMARY:

ENVIRONMENTAL CHARACTERIZATION OF DISPOSAL OF WASTE OILS BY COMBUSTION IN SMALL COMMERCIAL BOILERS

May 1984

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Office of Solid Waste and
Office of Research and Development

PROJECT SUMMARY

PURPOSE AND SCOPE OF THE PROJECT

In recent years the environmental impact of the disposal of used oils has been an area of growing concern. Numerous studies conducted by state and Federal agencies have documented the presence of contaminants such as polynuclear aromatics (PNAs), chlorinated hydrocarbons and heavy metals in samples of used motor oils. One of the more common and widespread practices for disposing of used oils is burning as a supplemental fuel. In some cases, waste oil is burned directly; in others, it is blended with other fuel feedstocks.

The disposal of waste materials in boilers is of particular interest because to date, there has been little documentation of the extent to which chemical contaminants in waste oil are destroyed during the combustion process.

In this project, tests were conducted on boilers in the size range of 0.4 to 25 x 10^6 Btu/hr. These are commonly classified as commercial sources, as opposed to industrial or electric utility sources. Commercial boilers are of particular interest with regard to waste oil disposal for several reasons. These units generally would use untreated or poorly characterized waste fuels. They could be expected to provide less efficient combustion because of the generally intermittent mode of operation. In addition, their widespread distribution and their low stack heights makes their emissions more proximate to the general population.

Seven boilers were designated for testing in the program. The units were selected so as to provide a representative cross-section of the commercial boiler population. A 4000 gallon lot of used automotive oil was obtained in

order to maintain a consistent supply of waste fuel for the program. Table 1 shows the composition of the base stock waste oil used throughout the program. Portions of the base stock oil was spiked with predetermined amounts of selected organic compounds which are typically found in waste oil and in some cases are considered hazardous waste materials. The selected compounds were as follows:

- chloroform
- 1,1,1-trichloroethane
- trichloroethylene
- tetrachloroethylene
- trichlorobenzene
- 1-chloronaphthalene
- 2,4,5-trichlorophenol
- chlorotoluene

In Table 2 are shown data comparing a typical spiked waste oil feed in this project with data from a cross-section of representative waste oils.[1]

Measurements were conducted at each of the sites to determine the atmospheric emissions of particulate, inorganic compounds (principally lead and HCl), and volatile organic and semivolatile organic material. The destruction and removal efficiencies (DRE) for each of the spiked components were also determined. A listing of the boilers and a summary of the tests conducted at each site are presented in Table 3.

TEST RESULTS

Destruction and Removal Efficiencies

The principal atmospheric emissions for each of the test sites are presented in Table 4. In general, the data indicate that the emission rates of the principal inorganic components, lead and HCl, were substantially higher than the organic emissions from the six boilers tested. The average

TABLE 1. COMPARISON OF THE PROJECT'S BASE STOCK WASTE OIL WITH A NO.4 FUEL OIL

Component	Concentration (µg/g)	
	Base stock waste oil	Typical No. 4 fuel oil
Pesticides	ND (<10)	ND (<10)
PCBs	ND (<6)	ND (<6)
Sulfur	0.41%	0.62%
Chlorine	0.16%	0.02%
Metal Content		
Aluminum	10.2	3.3
Antimony	0.5	<0.5
Arsenic	14.0	<0.8
Barium	59.5	0.2
Beryllium	0.05	<0.01
Boron	0.3	1.2
Cadmium	2.18	<0.03
Calcium	760	4.7
Chromium	7.13	<0.08
Cobalt	0.16	0.4
Copper	45.8	<0.05
Iron	163	4.6
Lead	1520	0.8
Magnesium	201	3.5
Manganese	7.53	0.03
Molybdenum	3.79	0.05
Nickel	2.1	12.1
Selenium	<0.5	<0.5
Silicon	68.5	1540
Silver	<0.03	<0.03
Sodium	133	23.4
Strontium	1.08	0.09
Thallium	<1	<1
Tin	9.1	1.1
Titanium	1.29	0.15
Vanadium	2.2	18.1
Zinc	743	0.83

TABLE 2. CONCENTRATIONS OF SELECTED CONTAMINANTS IN 24 REPRESENTATIVE WASTE OILS--COMPARED WITH A TYPICAL SPIKED OIL USED IN THIS PROJECT

Contaminant	Concentration (μg/g)		
	Representative oils[a]		Typical "spiked oil," (this project)
	Average	Range	
Elements			
Aluminum	45	1 - 640	10.2
Arsenic	12	<1 - 100	14.0
Barium	66	10 - 160	59.5
Cadmium	1	<1 - 2.8	2.2
Chlorine	2260[b]	50 - 27,000	12,000
Chromium	6	<1 - 37	7.1
Iron	240	60 - 980	168
Lead	1100	350 - 2060	1,520
Magnesium	260	5 - 590	200
Vanadium	3	<1 - 13	2.2
Zinc	800	90 - 1550	743
Volatile Organics			
Trichlorotrifluoroethanes	410	<20 - 1900	-
1,1,1-trichloroethane	700[b]	<20 - 14,800	3,500
Trichloroethylene	600	<20 - 4900	50
Tetrachloroethylene	400[b]	<20 - 13,000	3,100
Toluene	3100	380 - 12,000	2,800
Chloroform	-	-	2,500
Semivolatile Organics			
Phenol	25	<5 - 70	10
2,4,6-trichlorophenol	<5	<5 - <10	1,000
N-nitrosodiphenylamine	<5	<5 - <10	<10
Benz(a)anthracene	20	<5 - 40	16
Benzo(a)pyrene	<5	<5 - 30	-
4,4'-DDE	<5	<5 - <10	-
PCBs	<5	<0.1 - 65	<6
Trichlorobenzene	-	-	1,800
1-chloronaphthalene	-	-	1,500

[a]Taken from Ref. 1.
[b]Average value does not include maximum value shown in range.
- Denotes data not available or not investigated.

TABLE 3. BOILER DESCRIPTIONS

Site description	rated capacity 10^6 Btu/hr	Boiler type	Method of atomization	Site description	Spike level of each component (ppm)	Total number of test runs
A	0.5	Cast iron	Mechanical	Office building	1,500, 3,000	3 3
B[a]	1.0	Scotch firetube 2 pass	Rotary cup	Dairy complex		
C	2.4	Horizontal return tube	Rotary cup	Greenhouse	3,000	3
D	2.7	Scotch firetube 3 pass	Air	Office building	3,000, 10,000	3 3
E	3.4	Scotch firetube 4 pass	Rotary cup	Greenhouse	3,000, 5,000	3 3
F	4.2	Scotch firetube 3 pass	Air	Greenhouse	3,000 5,000	3 3
G	12.5	Scotch firetube 4 pass	Air	Greenhouse	3,000 10,000	3 1

[a]Boiler not available for testing in the program due to problems with the burner assembly and fuel feed system.

TABLE 4. AVERAGE ATMOSPHERIC EMISSIONS (gram/hr)

Site[a]	A[b]	C	D[b]	E	F	G
Particulate	32	544	277	312	367	508
Inorganic Components						
HCl	150	550	337	1050	600	1510
Lead	3.7	112	9.8	48	69	85
Zinc	2.0	52	5.7	29	37	45
Organic Components						
Volatile						
Chloroform	0.04	0.2	0.06	0.07	0.13	0.1
Trichloroethane	0.03	0.1	0.03	1.2	0.6	0.2
Trichloroethylene	0.06	0.1	0.10	0.1	0.05	0.3
Tetrachloroethylene	0.06	0.3	0.3	0.5	0.3	0.1
Semivolatile						
Trichlorobenzene	0.02	0.03	0.10	0.13	0.07	0.2
1-chloronaphthalene	0.01	0.02	0.03	0.05	0.06	0.2
Trichlorophenol	0.003	0.01	NA	0.04	0.01	NA
Chlorotoluene	NA	NA	0.02	NA	NA	0.3

[a]Waste oil feed rates used throughout the program generally ranged from 3-30 gal/hr, depending on the size of the facility.

[b]Waste oil diluted 50:50 with No. 2 oil to improve combustion for test purposes.

NA - Not analyzed, compound not spiked into fuel.

particulate emissions for the six boilers tested was determined to be 0.7 lb/hr (0.3 lb/10^6 Btu heat input). Combustion efficiencies, calculated for each of the boilers, ranged from 99 to greater than 99.9 percent.

The flue gas emissions of the organic compounds of interest correspond to destruction and removal efficiencies of 99.4 to 99.99 percent as indicated in Table 5. There were no strong correlations between destruction efficiency and boiler size or firing technique. One trend that is apparent from the data is that the destruction efficiencies for the semivolatile compounds are consistently higher than those of the volatile compounds. The fact that generally higher DRE's were achieved for the semivolatile components, trichlorobenzene, 1-chloronaphthalene and trichlorophenol, is consistent with the ranking of the spike compounds on the EPA Hierarchy of Waste Incinerability.[2]

Generally the lowest DRE's were found in site A, the only boiler rated at less than 1 x 10^6 Btu/hr. This unit normally fires a No. 2 fuel oil and its adaption to firing waste oil proved difficult. Eventually dilution of the waste oil on a 1:1 basis with No. 2 oil was required for acceptable operation. Even with this modification, the combustion efficiency and destruction efficiencies were significantly lower than the other units.

Concentrations of Contaminants in Combustion Gases

In Table 6 are shown the concentration ranges in the stack gas of the compounds studied within the program. In general, concentrations ranged from 40 to 400 $\mu g/m^3$ for the volatile compounds and from about 10 to 50 $\mu g/m^3$ for the semivolatile compounds. On a volume/volume (v/v) basis, these are very low concentrations. As an example, a range of 40 to 400 $\mu g/m^3$ for a compound such as trichloroethylene corresponds to a concentration of 7.4

TABLE 5. CALCULATED DESTRUCTION AND REMOVAL EFFICIENCIES (PERCENT)

	A	C	D	E	F	G	Average by compound
Volatile Compounds							
Chloroform	99.65	99.91	99.96	99.90	99.94	99.95	99.88
Trichloroethane	99.78	99.95	99.97	99.37	99.80	99.93	99.80
Trichloroethylene	99.45	99.92	99.89	99.85	99.92	99.87	99.82
Perchloroethylene	99.74	99.91	99.86	99.73	99.85	99.96	99.84
Semivolatile Compounds							
Trichlorobenzene	99.84	99.98	99.96	99.90	≥99.96	99.89	>99.92
1-chloronaphthalene	99.95	99.95	99.95	>99.94	99.98	99.92	>99.95
2,4,5-Trichlorophenol	>99.97	>99.99	---	≥99.92	≥99.98	---	>99.97

TABLE 6. AVERAGE FLUE GAS CONCENTRATIONS OF THE VOLATILE AND SEMIVOLATILE SPIKE COMPONENTS

	($\mu g/m^3$)					
	A	C	D	E	F	G
Volatile Components:						
Chloroform	110	120	44	53	88	153
Trichloroethane	90	88	22	580	400	140
Trichloroethylene	160	94	66	62	70	200
Tetrachloroethylene	160	200	180	220	170	100
Semivolatile Components:						
Trichlorobenzene	48	20	75	51	48	89
1-chloronaphthalene	16	12	22	23	36	89
Trichlorophenol	10	9	--	16	6	--

to 74 parts per billion (ppb) on a volume/volume basis. Conducting emission tests at these low concentrations required extensive refinement of available emission source testing techniques.

Lead and Other Metal Emissions

The samples of flue gas particulate collected at each site were analyzed for a total of 27 metals by ICAP techniques. Lead and zinc were present at concentrations substantially higher than any other trace metals. The lead concentrations in the flue gas samples ranged from 5,380 $\mu g/m^3$ to 72,400 $\mu g/m^3$ corresponding to an average emission rate of 0.12 lb/hr. Calculations based on simplified models have shown in some cases, lead emissions at these levels could cause violations of ambient air quality standards for lead. The concentrations of zinc in the flue gas ranged from 3,100 to 34,000 $\mu g/m^3$, corresponding to an average emission rate of 0.06 lb/hr. The ratio between lead and zinc emissions was generally 2:1, consistent with their concentration in base stock oil, which was 1,550 ppm and 760 ppm by weight, respectively. Lead and zinc compounds are commonly found in waste automotive oil and result from both gasoline and oil additives.

Other metals which received special attention were arsenic, cadmium and chromium. These were generally at low enough concentrations in the stack gas so that when diluted in the atmosphere they should not cause major problems, but the situation is still of some concern as the concentration of these metals could be substantially higher in other waste oil base stocks (e.g., see Table 2).

The results of metal emissions are summarized in Table 7.

TABLE 7. CONCENTRATIONS OF METALS IN FLUE GAS ($\mu g/m^3$)

Site	A	C	D	E	F	G
Arsenic	11.2	655	26.1	106	251	286
Cadmium	31.2	102	8.3	182	350	81
Chromium	62.2	166	112	230	205	263
Lead	9,680	72,400	5,390	20,300	49,800	51,000
Zinc	5,150	33,700	3,134	12,100	26,800	27,000

Particulate and Chloride Emissions

Particulate emission rates at the six sites ranged from 0.07 to 1.2 lb/hr with an average value of 0.73 lb/hr (0.34 lb/10^6 Btu heat input). This is significantly higher than the literature value of 0.09 lb/10^6 Btu for commercial boilers firing residual oil,[3] but the higher value is consistent with the much higher ash content of waste oil, which can range from 0.15 to 1.5 percent. Particulate sizing measurements conducted at four of the test sites indicated that 80 to 90 percent of the particulates containing lead are submicron in nature and would be readily inhalable.

The flue gas emissions of HCl from the six boilers averaged 2.6 lb/hr. This is a relatively high emission rate for such small units, but it is below the 4.0 lb/hr air emission standard established for hazardous waste incinerators, which would typically burn large quantities of chlorinated compounds similar to those used in this program.

Mass flow calculations indicate that 50 to 60 percent of the lead and chloride introduced into the boilers exits from the system in the flue gas

streams. The analysis of samples of firetube ash collected at a single site indicates concentration levels of lead and chloride in the ash on the order of 1 to 2 percent. Data from the stack gas emissions coupled with the chemical analysis of the firetube fly ash and the waste oil provide for material balance closures at about 65 percent for the total system. This was considered a reasonable closure for the purpose of this project and further investigative work on the remaining 35 percent was not performed.

Products of Incomplete Combustion

The flue gas samples from each site were screened by GC/MS for additional organic components, considered to be potential products of incomplete combustion. The types of compound which were identified are shown in Table 8. In general, the components were nonchlorinated in nature and were representative of the types of compounds that result from the combustion of traditional fossil fuels.[4] These compounds were also very typical of contaminants sometimes found on the blank sample adsorbing medium, XAD-2 resin. The extent to which these compounds, when detected, resulted from combustion byproducts or from resin contaminants could not be determined; hence, the concentrations in Table 8 could be viewed as upper limits for many of the nonchlorinated products of incomplete combustion. During the course of this program, there were some baseline runs done on conventional No. 4 fuel oil. As expected, no chlorinated hydrocarbons were detected in the stack gas, with detection limits being 8 $\mu g/m^3$. With conventional No. 4 oil, combustion products such as naphthalene and similar PAH compounds were 100 $\mu g/m^3$ or less.

Chlorinated dibenzofuran (PCDF) or chlorinated dioxin (PCDD) species were detected in 15 of the 25 samples analyzed as shown in Table 9. The

TABLE 8. EXAMPLES OF CONCENTRATION RANGES FOR POSSIBLE PRODUCTS OF INCOMPLETE COMBUSTION ($\mu g/m^3$)

	A	C	D	E	F	G
Naphthalene[a]	--	30	70	10	40	50
Benzaldehyde[a]	10-60	--	20-70	30	40	20
Chlorobenzene isomers	--	20	--	10	40	--
Dibenzofuran	70	5	2	10	20	5
Ethylbenzene	--	--	2-20	--	--	--
Chlorotoluene	9[b]	--	70[b]	--	--	--
Benzoic acid[a]	70	--	20-200	200	300	90
Alkyl benzene[a]	60	--	10-100	100-600	--	300

[a]This compound is a known contaminant of XAD-2 resin and could be a sampling and analysis artifact as well as a product of incomplete combustion.

[b]At sites A and D, chlorotoluene was not spiked into the waste oil; hence, its appearance here is as a product of incomplete combustion.

Note: The symbol -- means the compound was not detected by mass spectrometric computer matching scan. In such cases the detection limit is generally 100 $\mu g/m^3$ or less.

TABLE 9. AVERAGE CONCENTRATIONS IN STACK GAS OF DIBENZOFURAN AND DIOXIN SPECIES FROM TESTS EXHIBITING DETECTABLE LEVELS ($\mu g/m^3$)

	A[a]	C[b]	D[a]	E[a]	F[a]	G[c]
Dibenzofuran	62(5)	5.4(2)	3.4(5)	8.0(5)	16(3)	2.7(3)
Chlorodibenzofuran	0.8(3)	0.52(1)[d]	0.7(3)	0.4(2)	2.1(1)[d]	
Dichlorodibenzofuran	1.9(2)	0.07(1)		0.24(1)		
Trichlorodibenzofuran		0.43(2)				
Tetrachlorodibenzofuran				0.17(1)		
Dibenzodioxin	1.3(3)			0.73(1)		
Chlorodibenzodioxin		0.27(1)				
Dichlorodibenzodioxin		0.18(1)		1.6(1)	2.4(1)	
Tetrachlorodibenzodioxin						1.4(1)
Octachlorodibenzodioxin		4.5(1)[d]			17(1)[d]	

[a]Samples from 5 tests analyzed.

[b]Samples from 2 tests analyzed.

[c]Samples from 3 tests analyzed.

[d]Quality assurance samples indicate potential loss.

( ) number of tests in which component was detected.

concentration of these compounds ranged from 0.07 to 17 $\mu g/m^3$. On a volume/volume basis, this corresponds to a range of 7 to 470 parts per trillion (ppt).

Bulk samples of firetube ash collected at one of the sites contained parts per billion levels of 11 PCDF and PCDD isomers on a weight by weight basis. This is summarized in Table 10. Because chlorinated dioxins and chlorinated dibenzofurans were found in the flue gas, tests were also conducted on the waste oil base stock, both spiked and unspiked to determine the extent to which these types of compounds might be present in the oil. No chlorinated dioxins or chlorinated dibenzofurans were found in either the spiked or unspiked oil; detection limits for the various isomers are shown in Table 11.

TEST METHODS

Waste Oil Analysis

Waste feed samples were analyzed for chloride, metals and the organic spike components. The chloride content of the fuel was determined by Parr Oxygen Bomb Combustion followed by Ion Chromatography (IC) analyses. Metals concentrations were determined by means of Inductively Coupled Argon Plasma Emissions Spectroscopy (ICAP). The samples were prepared for ICAP analysis by a controlled dry ashing procedure utilizing IR lamps.

The volatile organic analysis of the waste fuel was accomplished by extraction followed by purge and trap GC/MS techniques in accordance with EPA Method 624 procedures. Sample preparation followed procedures as given in Method A101B5, with the substitution of tetraglyme for the polyethylene glycol normally specified. Tetraglyme (tetraethylene glycol dimethylether) is similar in nature to polyethylene glycol, but was found to contain fewer potentially interfering contaminants.

TABLE 10. ANALYSIS FOR CHLORINATED DIBENZOFURANS AND DIBENZODIOXINS, SITE D - FLY ASH (μg/kg)

Component	First pass sample	Second pass sample	Third pass sample	Cleaning trap sample	Det. limit (NDI)
Dibenzofuran	250	170	24	230	0.5
Chlorodibenzofuran	ND	24	ND	ND	0.5
Dichlorodibenzofurans	ND	ND	ND	ND	0.5
Trichlorodibenzofurans	ND	ND	ND	ND	0.5
Tetrachlorodibenzofurans	350	170	11	160	0.5
Pentachlorodibenzofurans	1000	660	60	35	2
Hexachlorodibenzofurans	230	310	ND	250	2
Heptachlorodibenzofurans	580	340	ND	160	5
Octachlorodibenzofurans	40	26	ND	ND	10
Dibenzodioxin	ND	ND	ND	ND	0.5
Chlorodibenzodioxins	ND	ND	ND	ND	0.5
Dichlorodibenzodioxins	ND	ND	ND	ND	0.5
Trichlorodibenzodioxins	ND	ND	ND	ND	0.5
Tetrachlorodibenzodioxins	ND	ND	ND	ND	0.5
Pentachlorodibenzodioxins	120	58	ND	ND	2
Hexachlorodibenzodioxins	200	90	ND	ND	2
Heptachlorodibenzodioxins	230	130	ND	ND	5
Octachlorodibenzodioxins	33	150	ND	70	10

TABLE 11. DIOXIN AND DIBENZOFURAN CONTENT OF WASTE OIL BASESTOCK AND "SPIKED" WASTE OIL

Component	Sample ID	Oil[a]	Waste Oil Basestock	Typical "Spiked" Waste Oil	Detection Limit (mg/kg) (ND =)
		22033 W-BSB-1	22034 W-BS-1	290507-1 WO-C-3-WFC	
dibenzofuran	ND	ND	ND	ND	0.04
chlorodibenzofurans	ND	ND	ND	ND	0.08
dichlorodibenzofurans	ND	ND	ND	ND	0.10
trichlorodibenzofurans	ND	ND	ND	ND	0.20
tetrachlorodibenzofurans	ND	ND	ND	ND	0.20
pentachlorodibenzofurans	ND	ND	ND	ND	0.40
hexachlorodibenzofurans	ND	ND	ND	ND	0.40
heptachlorodibenzofurans	ND	ND	ND	ND	0.80
octachlorodibenzofurans	ND	ND	ND	ND	2.0
dibenzodioxin	ND	ND	ND	ND	0.04
chlorodibenzodioxins	ND	ND	ND	ND	0.08
dichlorodibenzodioxins	ND	ND	ND	ND	0.10
trichlorodibenzodioxins	ND	ND	ND	ND	0.20
tetrachlorodibenzodioxins	ND	ND	ND	ND	0.20
pentachlorodibenzodioxins	ND	ND	ND	ND	0.40
hexachlorodibenzodioxins	ND	ND	ND	ND	0.40
heptachlorodibenzodioxins	ND	ND	ND	ND	0.80
octachlorodibenzodioxins	ND	ND	ND	ND	2.0

[a]Provided for reference purposes.

The analysis of the waste oil for the semivolatile components of interest was performed using a gas chromatograph equipped with an electron capture detector (GC/ECD). Initial analysis of the waste oil employing silica gel chromatographic cleanup and GC/MS techniques was determined to be inappropriate due to the unacceptable sample recoveries for trichlorobenzene and trichlorophenol.

Combustion Gas Sampling and Analysis

The determination of volatile organic concentrations in the flue gas was carried out using a gas chromatograph equipped with an electron capture detector (GC/ECD). Duplicate, integrated samples of flue gas were collected in nonreactive Tedlar bags and injected into the instrument using a heated gas sampling loop. Each of the samples were analyzed in duplicate, with replication sample values to within $\pm$10 percent as the criterion for acceptance. The accuracy of the calibration standards developed for the analysis were verified by comparison of NBS traceable standards.

A modified Method 5 train equipped with an XAD-2 resin trap was used to collect particulate, semivolatile organic compounds, metals and HCl components from the flue gas of the boilers. The particulate, XAD-2 resin and flue gas condensate samples from the train were combined and solvent extracted; analysis of solvent extracts was conducted using capillary gas chromatography/ mass spectrometry (GC/MS). Aliquots of these sample aliquots were further concentrated for subsequent analysis for polychlorinated dibenzofuran and polychlorinated dibenzodioxin species. The analysis was conducted using a quadrupole Hewlett Packard 5985 GC/MS system fitted with a fused silica capillary column.

A single set of Method 5 samples from each site was subjected to inorganic analysis for chloride and particulate metal determinations. Samples of the collected gas condensate were analyzed for chloride by direct injection on a Ion Chromatograph. Particulate samples from the train were prepared for metal determinations by a hot nitric acid leach followed by ICAP analysis.[6]

Additional samples of particulate were collected at four sites using an Andersen High Capacity Sampling System (HCSS) for particle size determinations. The size fractionated particulate (10 μm, 10-3 μm, 3-1 μm and 1 μm) were extracted using 3M nitric acid[7] and analyzed for lead using atomic absorption spectrophotometry.

Samples of firetube ash were collected for chloride, metals and semivolatile organic analysis. The methods for the trace metal and organic determinations are as described above. Aliquots of the samples were subjected to a hot aqueous leach to extract soluble chloride species followed by IC analysis. Additional samples were analyzed by EP Toxicity in accordance with the procedures outlined in §260.20 and §260.21.

Quality Assurance Procedures

Quality control checks were performed to ensure the collection of representative samples and the generation of valid analytical results. Blank samples including field biased blanks and method blanks, were used to assess the possible contamination of the samples. Duplicate and spiked samples were routinely employed during the program to verify the precision and accuracy of the analysis.

EPA quality control concentrates and NBS Standard Reference Materials were used where appropriate to assess the analytical work. A comprehensive

systems audit was conducted during the program to ensure that the project goals and requirements set forth in the Quality Assurance Plan were met.

CONCLUSIONS

Although a sample population of six boilers is very limited, there do seem to be several general conclusions which can be reached regarding the combustion of waste automotive fuels in boilers in this size range.

1. It is possible to achieve combustion efficiencies greater than 99.9 percent for small commercial boilers firing waste oils.

2. Destruction and removal efficiencies of greater than 99.9 percent can be obtained for chlorinated organic contaminants typically present in waste oils. For the volatile compounds studied (chloroform, trichloroethylene, trichloroethane and perchloroethylene), destruction and removal efficiencies were on the order of 99.9 percent. For the semivolatile compounds, (trichlorobenzene, 1-chloronaphthalene, trichlorophenol), destruction and removal efficiencies were on the order of 99.95 percent.

3. For boilers above 1 x 10^6 Btu/hr input, there were no apparent correlations between boiler size or firing method and destruction efficiency of organic contaminants.

4. Inorganic components, as opposed to organic components of waste oil, have substantially greater mass emission rates to the atmosphere as a result of the combustion of automotive waste oils. The principal inorganic components of concern are lead, hydrochloric acid and total particulate. Also of potential concern are arsenic, cadmium and chromium. The particulate lead emissions from a source may, during the peak heating season, affect the compliance with the primary ambient air standard for lead. A significant percentage of the particulate lead emissions is submicron in nature and would be readily inhalable.

5. Detectable levels of emissions of polychlorinated dibenzofurans and polychlorinated dibenzodioxins compounds were found in some of the boilers tested. These compounds, when present, were usually at levels less than 5 $\mu g/m^3$, which is less than 0.5 part per billion by volume in the stack gas. The extent to which these compounds pose a hazard at these low levels is undetermined.

   Tests were done on the base stock waste oil, with and without the spiked contaminants, to determine the extent to which the oil may have contained trace levels of dioxin. No dioxin or dibenzofuran compounds were detected in any of the oil samples; detection limits were 200 ppb by weight for TCDD and TCDF. If dioxin compounds were

present at or below their detection limits, such a quantity would not be large enough to account for the observed levels in the stack gas even with zero percent destruction. The conclusion is that dioxin and dibenzofuran found in the stack gas most probably was formed during the combustion process.

6. The fly ash deposited in the firetubes of the boilers may contain percent levels of lead and parts per billion levels of chlorinated dibenzofuran and dioxin compounds. The ash has the potential for being classified as hazardous on this basis, and may be subject to hazardous waste regulations for disposal.

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