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Project Summary

Comparative Analysis of Contaminated Heating Oils

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An exploratory investigation was conducted of the possible contamination of virgin heating oils by hazardous waste in the New Jersey/New York area. Twenty oil samples, including some that were suspected to be contaminated, were analyzed for 39 volatile organic compounds. In addition, total chlorine and water extractable chlorides were measured in 13 samples. A statistically valid sampling program was developed to determine the extent of heating oil contamination in New York City.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The report gives results of an investigation of the potential contamination of virgin heating oil by hazardous waste. Residual oils (No. 5 and 6) and No. 4 oil are more likely to be contaminated than light distillate oils (No. 1 and 2). The heavier oils tend to mask contaminants, and the contaminants may not create any gross deterioration of burner performance.

New York and New Jersey account for 42.8 percent of U.S. deliveries of residual and No. 4 heating oils to the commercial sector (apartments, offices, general retail, etc.). Much of this oil is used in the winter heating season. In addition, the northeastern New Jersey and New York metropolitan areas are very densely populated. The presence of major hazardous waste generators in the area and consideration of the above factors indicate the potential for more severe problems in the New Jersey/New York area than in most other areas.

A sampling strategy was developed to determine, in a statistically valid manner, the extent of heating oil contamination in New York City. Because it was suspected that only a few percent of the heating oil may be contaminated and there were more than 30,000 sites (heating units or storage tanks), many samples would have been required. Specifically, if the true fraction of contaminated oil was 1 percent, there were 32,400 sites, and a relative error of ±30 percent (a result of 1±0.3 percent) was acceptable, then 5,774 random samples would have been required. The many samples required for a statistically valid sampling program precluded its implementation.

Therefore, program objectives were redefined to conduct an exploratory analytical program using samples that had been previously collected by the states of New Jersey and New York and the city of New York. A primary objective of the final program was to analyze a collection of virgin oil samples for 39 selected volatile organic compounds. No concentration data for these volatile organic compounds in virgin oils were available. A second, equally important, objective was to investigate chlorine speciation (organic vs. inorganic forms) in selected virgin oil samples. Unexpectedly high levels of chlorine had been recently found in some samples, but no data were available to indicate if the high chlorine levels were caused by salts (possibly from salt water) or contamination by chlorinated organic compounds. In addition, analyses of the samples for total bromine and fluorine were planned.

Results and Discussion

Twenty samples (13 virgin oils and 7 waste oils) were selected for analysis of volatile organic compounds. Selection of the samples was based on the type of oil (No. 2, No. 4, No. 6, or waste), the source (terminal, refinery, apartment house, industry), the state or city where the sample was collected (New York, New Jersey, New York City), and preliminary indications of contamination or noncontamination.

Any general conclusions drawn from the exploratory analyses of such a limited collection of samples should only be made with extreme caution. In addition, some loss of volatile organic compounds may have occurred between the time that the samples were collected by the states in the fall of 1982 and the analysis by GCA in the spring of 1983. During this period, the samples were opened and analyzed under a separate program conducted by EPA Region II. When received at GCA, the sample containers were typically less than 50 percent full.

In this study, "contamination" means that the sample was found to contain at least one compound at a relatively high concentration compared to other oils of the same type. It does not imply any harmful environmental effect which must depend on toxicity, the effects of combustion, the extent of exposure, etc. Similarly, statements that an oil is not contaminated imply that it is similar to other oils of the same type but not necessarily that the normal components of an uncontaminated oil are not harmful. The ultimate impact of the volatile organic compounds found in contaminated and uncontaminated oil was not intended to be assessed in this study.

Selected examples of volatile organic compounds that were detected in the 13 virgin oil samples are presented in Table 1. Samples E, F, and N clearly appear to be contaminated. These three samples contain chlorinated organic compounds that are not found in other samples while sample E also contains relatively high concentrations of benzene, ethylbenzene, toluene and xylene. Note that samples E, F, and N were supplied as samples that were suspected to be contaminated. Sample K shows some slight evidence of contamination: it contains detectable concentrations of methylene chloride and 1,1,1-trichloroethane. Although Sample B appears to contain unusually high levels of ethylbenzene, toluene, and xylene, the data base (consisting of only two samples of No. 2 oil) is too small to develop any firm conclusions.

Selected examples of volatile organic compounds detected in the waste oil samples are presented in Table 2. These waste oil samples included automotive and industrial wastes that are apparently used as fuels. Some of the samples contain percentage levels of chlorinated organic compounds.

Thirteen of the 20 samples analyzed for volatile organics were analyzed for total bromine, fluorine, and chlorine, and investigated for chlorine speciation. Total bromine concentrations in all samples were below the detection limit of 600 mg/kg. Except for two waste oil samples which contained 96 and 182 mg/kg, fluorine concentrations were below the detection limit of 50 mg/kg.

The results of the halogen analyses are summarized in Table 3. Many of the virgin oil samples do contain inorganic chlorides (water extractable chlorides), but these do not appear to account for the total chlorine. The unaccounted for chlorine may be attributable to the precision of the analytical methods, or some of these samples may contain inorganic chlorides that are not extractable, semivolatile chlorinated compounds, or volatile chlorinated organics for which analyses were not performed.

Conclusions

A small group of virgin fuel oil and waste oil samples were analyzed for 39 selected volatile organic compounds, chlorine, bromine, and fluorine. There may have been significant loss of volatile organic compounds prior to analysis by GCA because the samples were opened, partially analyzed under another project, and not maintained at 4°C in a headspace-free condition. Many of the samples were selected for analysis because they were suspected or known to be contaminated. The results provide examples of the types of compounds and indications of the

Table 1. Selected Examples of Compounds Detected in Virgin Oil Samples, mg/kg[a]

Sample Identification	A	B	C	D	E	F	G	H	I	J	K	L	M	N
Oil Grade	2	2	4	4	4	4	6	6	6	6	6	6	6	4
Compound / Oil Source	Terminal	Refinery	Terminal	Terminal	Terminal	Terminal	Terminal	Terminal	Terminal	Terminal	Terminal	Refinery	Refinery	Apartment
Benzene	<20	110	46	45	590	140	23	<2	15	30	37	28	15	<100
Ethylbenzene	240	970	160	120	2,500	240	94	<2	47	30	230	110	21	580
Toluene	440	910	230	110	7,900	490	87	<2	49	40	330	110	100	730
Xylene (isomers)	590	4,100	110	79	7,900	160	67	22	47	36	180	50	20	1,900
Methylene chloride	<20	<2	<1	<1	10	180	<1	<2	<0.9	<1	11	<1	<0.9	<20
Tetrachloroethene	<20	<2	<1	<1	140	140	<1	<2	<0.9	<5	<1	<1	<0.9	<20
1,1,1-trichloroethene	<20	<2	<1	<1	950	1,900	<1	<2	<0.9	<1	8	<1	<0.9	3,900
Trichloroethene	<20	<2	<1	<1	40	26	<1	<2	<0.9	<1	<1	<1	<0.9	<20

[a]*All samples are from New Jersey except N which is from New York City*

Table 2. Selected Examples of Compounds Detected in Waste Oil Samples, mg/kg[a]

Sample Identification	O	P	Q	R	S	T
Compound / Oil Source	NY	NY	NY	NY	NJ	NJ
Benzene	55	<3	520	100	<90	<80
Ethylbenzene	190	50	7,000	3,900	630	800
Toluene	480	<3	60,000	81,000	1,300	1,800
Xylene	110	93	35,000	19,000	2,700	3,300
Methylene chloride	15	<3	730	3,000	<20	<20
Methyl ethyl ketone	<700	<300	34,000	95,000	<2,000	<2,000
Tetrachloroethene	39	3,500	940	21,000	490	310
1,1,1-trichloroethane	970	17	1,400	28,000	270	420
Trichloroethene	5.6	440	450	14,000	<20	<20
Trichlorofluoromethane	510	<3	<40	<20	<20	<20
Methyl isobutyl ketone	<700	<2,000	17,000	18,000	<2,000	<2,000

[a]*These "waste oils" are not, in general, typical automotive waste oils. They are called waste oil because apparently they are burned as fuel.*

Table 3. Summary of Halogen Results, mg/kg[a]

Compound	Sample Identification	B	C	D	E	H	I	J	L	M	N	O	Q	T
	Oil Grade	2	4	4	4	6	6	6	6	6	4	Waste	Waste	Waste
	Oil Source	Refinery	Terminal	Terminal	Terminal	Terminal	Terminal	Terminal	Refinery	Refinery	Apartment	---	---	---
TOTAL CHLORINE		--	99	81	1,360	768	149	81	86	74	5,560	2,760	13,400	1,300
Water extractable chloride		<8	44	20	187	936	101	44	27	44	140	580	1,620	72
Chlorine detected in volatiles		<2	<1	<1	915	<2	<4	<5	<1	<0.9	3,100	1,260	3,300	690
TOTAL FLUORINE		<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	96	182	<50
Fluorine detected in volatiles		<2	<1	<1	<40	<2	<0.9	<1	<1	<0.9	<20	71	112	<20

[a]Total bromine was below 600 mg/kg in all samples. Volatile brominated organic compounds were not detected (less than 600 mg/kg).

concentrations that may be found in contaminated oil. Any generalizations about the extent of contamination or the concentrations of contaminants in virgin fuel oil or waste oil are not appropriate.

Thirteen virgin fuel oil samples were analyzed for 39 selected volatile organic compounds. Three samples from terminals (E, F, and K) and one from an apartment house (N) were contaminated with volatile organic compounds. Contaminants that were identified in one or more of these samples are acetone, benzene, chloroform, 1,1-dichloroethane, ethylbenzene, methylene chloride, methyl ethyl ketone, tetrachloroethane, toluene, 1,1,1-trichloroethane, trichloroethene, trichlorofluoromethane, 1,1,2-trichloro-1,2,2-trifluoroethane, and xylene. Concentrations were in the range of 10 to 10,000 mg/kg.

Seven waste oil samples were also analyzed for volatile organic compounds. These samples may have included automotive waste oils and industrial chemical wastes that are apparently burned as fuel in New York. All the waste oil samples were contaminated with volatile organic compounds. Seventeen compounds with concentrations in the 6 to 95,000 mg/kg range were identified in one or more samples.

Ten of the previously discussed virgin fuel oil samples were analyzed for total chlorine, bromine, and fluorine. Bromine concentrations were below 600 mg/kg, and fluorine concentrations were below 50 mg/kg in all samples. Two samples, previously identified as being contaminated with volatile organic compounds, contained 1,366 and 5,560 mg/kg total chlorine. Seven samples, not contaminated with volatile organic compounds, contained 72 to 146 mg/kg total chlorine, and one sample contained 768 mg/kg total chlorine. Extraction of these 10 samples with water typically demonstrated that a significant fraction, but not all, of the total chlorine appeared to be present as inorganic chloride. The unaccounted for chlorine may reflect the precision of the analytical methods, semivolatile chlorinated organic compounds, unanalyzed volatile chlorinated organic compounds, or inorganic chlorides that were not extracted from the oil.

Three of the previously discussed waste oil samples were also analyzed for halogens. Total bromine was below 600 mg/kg in all samples. Two samples contained fluorine, 96 and 182 mg/kg. Total chlorine concentrations were in the 1,300 to 13,000 mg/kg range. Extractable inorganic chloride represented 5 to 25 percent of the total chlorine in these samples.

Recommendations

Further investigation of contaminated heating oil would be of value. The statistically and technically limited data set developed in this study provides new and interesting data, but does not allow substantive conclusions with respect to environmental/health effects. More information on the extent of contamination, the identity of all contaminants, the destruction efficiencies and emission rates, atmospheric dispersion, population exposure and health effects would facilitate consideration of possible environmental/health effects. Specific information would include:

1. Further investigations and validation of the apparently useful procedures used in this study to differentiate between inorganic-chloride- and organic-chlorine-containing compounds in virgin heating oil.
2. Further work on method development and validation, depending on the importance of the determination of bromine- and fluorine-containing compounds in heating oil.
3. Definition (in a larger, statistically valid sampling and analysis program) of the extent of virgin heating oil contamination, with samples collected from storage tanks at their points of use.
4. Determination (by reviewing theoretical analyses and current EPA waste oil investigations or additional tests) of the destruction of the identified organic compounds in small boilers, as well as evaluations (in a similar manner) of trace metal emissions.
5. Predictions of human exposure, based on emission estimates derived from the results of items 3 and 4 (above), used with dispersion models and population data.
6. Evaluations of the health effects of the predicted human exposures to determine if environmental problems exist and (if they do) their severity.

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The complete report, entitled "Comparative Analysis of Contaminated Heating Oils," (Order No. PB 84-190 990; Cost: $19.00, subject to change) will be available only from:

National Technical Information Service
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