

# Characterization of Air Toxics from an Oil-Fired Firetube Boiler

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## ABSTRACT

Tests were conducted on a commercially available firetube package boiler running on #2 through #6 oils to determine the emissions levels of hazardous air pollutants from the combustion of four fuel oils (a #2 oil, a #5 oil, a low sulfur #6 oil, and a high sulfur #6 oil). Measurements of carbon monoxide, nitrogen oxides, particulate matter, and sulfur dioxide stack gas concentrations were made for each oil. Flue gases were also sampled to determine levels of volatile and semivolatile organic compounds and of metals. Analytical procedures were used to provide more detailed information regarding the emissions rates for carbonyls (aldehydes and ketones), and polycyclic aromatic hydrocarbons (PAHs) in addition to the standard analyses for volatile and semivolatile organics. Metals emissions were greater than organic emissions for all oils tested, by an order of magnitude. Carbonyls dominated the organic emissions, with emission rates more than double the remaining organics for all four oils tested. Formaldehyde made up the largest percentage of carbonyls, at roughly 50% of these emissions for three of the four oils, and approximately 30% of the carbonyl emissions from the low sulfur #6 oil. Naphthalene was found to be the largest part of the PAH emissions for three of the four oils, with phenanthrene being greatest for the #2 fuel oil. The flue gases were also sampled for polychlorinated dibenzodioxins and polychlorinated dibenzofurans; however, inconsistent levels were found between repeat tests. For the boiler tested, no single hazardous air pollutant (HAP) was emitted at a rate which would

require control under Title III of the Clean Air Act Amendments of 1990. The fuel emitting the largest amount of HAPs was the high sulfur #6 oil, which had a total HAP emission rate of less than 100 lb (45 kg)/year, based on operation for a full year at a firing rate of  $1.25 \times 10^6$  Btu/hr (50% load of the unit tested).

## INTRODUCTION AND BACKGROUND

Emissions of air toxics, or hazardous air pollutants (HAPs), have become a problem of increasing concern over the last few years, particularly since the passage of the 1990 Clean Air Act Amendments (CAAA),<sup>1</sup> which under Title III mandated regulation of HAPs from a wide range of sources. Title III of the CAAAs lists 189 compounds and compound classes as HAPs, and requires application of maximum achievable control technology (MACT) to a nonutility source that emits over 10 tons/year<sup>1</sup> of any one HAP, or 25 tons/year of any combination of HAPs. (Note: a table converting English to metric units can be found in the Appendix.) In the case of sources such as chemical production facilities, characterization of HAP emissions is relatively straightforward, since they are primarily fugitive vapor emissions from the production of a single chemical compound. In other cases, characterization is more difficult. For instance, hydrocarbon combustion processes may emit trace quantities of benzene, toluene, and polycyclic aromatic hydrocarbons (PAHs), even during efficient combustion. Because of the large volumes of flue gas produced during the combustion process, even HAP concentrations on the parts per million (ppm) level can result in annual mass emissions that are greater than the limits specified under Title III.

Because of the wide variety of sources subject to HAP emission regulation under Title III, the regulations were to be promulgated over a 10 year period. EPA's Office of Air Quality Planning and Standards developed a list of HAP emission source categories based on relative risks to human health, and from that list assigned a date by which regulations for each source category would become effective.<sup>2</sup> Several of these source categories involve external combustion boilers for industrial, commercial, and institutional applications. Because of the large number of such units across

## IMPLICATIONS

This article provides practical information relating to emissions of hazardous air pollutants from combustion sources. These results may provide assistance in understanding the types and amounts of HAPs being emitted from the combustion of different fuel oils, and can be helpful in estimating such emissions from similar types of units. These results will be of particular interest to persons working on issues related to potential HAP emissions or regulatory compliance under Title III of the 1990 Clean Air Act Amendments.

the country, and because of the relatively small amount of quantitative information characterizing HAP emissions from these sources, a research project designed to provide such quantitative information was undertaken by the Air Pollution Technology Branch of EPA's Air Pollution Prevention and Control Division (APPCD) in Research Triangle Park, NC. In particular, this project sought to characterize emissions of HAPs from the combustion of different fuel oils in a firetube package boiler.

## EXPERIMENTAL SETUP

### Equipment

The tests were performed on APPCD's North American Scotch marine-type package boiler (NAPB) capable of firing natural gas, or #2 through #6 fuel oils. This unit was chosen due to its ease of operation as a test unit to provide initial information on emissions of HAPs from different fuels, and because it is similar to many package boilers in use at small industrial, commercial, and industrial locations. The boiler is of a three-pass firetube design built in 1967, model 5-360H-D, and shown schematically in Figure 1. The burner is a North American model 6121-2.5H6-A65 rated at  $2.5 \times 10^6$  Btu/hr, and has a ring-type natural gas burner and an air-atomizing center nozzle oil burner capable of firing #2 through #6 oils. The main firetube has a diameter of 18 in, and each of the 24 second pass tubes and 20 third pass tubes has an inside diameter of 2.5 in. The boiler has 300 ft<sup>2</sup> of heating surface, and generates up to 2400 lb/hr of saturated steam at gauge pressures up to 15 psig. Heat is extracted from the steam through a heat exchanger to an industrial cooling water system that simulates the boiler load. Oil temperature can be adjusted using an electric oil heater to maintain proper viscosity, and both fuel and atomizing air pressures are variable to ensure proper oil atomization. The NAPB is fully instrumented, with continuous emission monitors (CEMs) for carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), nitrogen oxides (NO<sub>x</sub>), oxygen (O<sub>2</sub>), sulfur dioxide

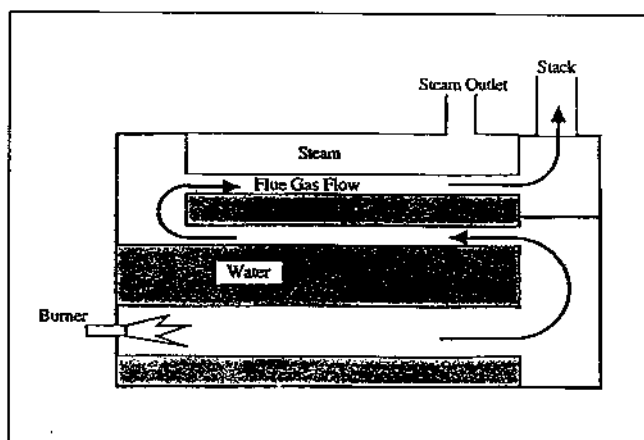
(SO<sub>2</sub>), and total hydrocarbons (THCs). A computerized data acquisition system was used to continuously record CEM measurements as well as steam and flue gas temperatures.

The flue gases from the unit pass through a manifold to an air pollution control system (APCS) consisting of a natural-gas-fired secondary combustion chamber, an acid gas scrubber, and a fabric filter to ensure proper removal of pollutants generated when tests mimic poor combustion conditions. During the tests reported here, the APCS was operated to provide a constant draft to the NAPB to minimize changes in the induced draft. Although this type of boiler normally operates only under forced draft, the imposition of an induced draft due to the APCS was not felt to introduce any significant effects on boiler emissions.

### Test Matrix

The test matrix was chosen to focus on the effects of changing fuel on HAP emissions. Four fuels were chosen for testing: a #2 fuel oil, a #5 fuel oil, a low sulfur #6 fuel oil, and a high sulfur #6 fuel oil. Although the boiler is also capable of firing natural gas, tests were not conducted using natural gas due to the extremely low HAP emissions from natural gas measured in a previous series of tests.<sup>3</sup> The low sulfur #6 oil had a sulfur concentration of 0.49% by weight, compared to a concentration of 1.66% by weight for the high sulfur #6 oil. The ultimate analyses of the oils are given in Table 1, and Table 2 presents the trace element concentrations of the four oils. The majority of tests were conducted at a single baseline test condition: a firing rate of  $2 \times 10^6$  Btu/hr, a nominal stoichiometric ratio of 1.2, an outlet steam pressure of 5 psig, and an atomizing air pressure of 48 psig. The oil temperatures and pressures were adjusted for the different oils to ensure adequate flow and atomization. In addition to the tests measuring the effects of changing oils, tests were conducted using the #5 oil under different firing conditions to evaluate the impact of combustion conditions on HAP emissions. The different firing conditions consisted of: (1) firing at a lower stoichiometry of 1.05 compared to the baseline of 1.2; (2) using a lower atomizing air pressure of 26 psig, compared to 48 psig for the baseline; and (3) using a lower fuel temperature of 83 °F compared to the #5 oil baseline temperature of 170 °F.

The combustion condition variation tests were designed to evaluate the changes only in organic emissions, since it was assumed that the relatively small changes in conditions would not significantly affect the total emissions of metals. The combustion condition variation tests included sampling of only volatile and semivolatile organics and carbonyls. Metals and polychlorinated dibenzodioxin (PCDD) and polychlorinated dibenzofuran (PCDF) emissions were measured only under the baseline conditions for the four oils. The #5 oil was chosen for the combustion condition tests because it is easier to handle than the #6 oils, allowing a relatively simple evaluation of the impacts of combustion condition variations.



**Figure 1.** Schematic of the North American package boiler. The boiler is a three-pass firetube boiler capable of burning natural gas or fuel oils.

**Table 1.** Ultimate analysis results of the oils used in the test program. Concentrations are given in percent by weight on a dry basis (except for water), and viscosity values are in centistokes.

	#2 Oil	#5 Oil	Low Sulfur #6 Oil	High Sulfur #6 Oil
Water	0.01	0.80	0.60	0.60
Carbon	85.84	85.26	82.35	85.29
Hydrogen	11.98	10.58	11.02	10.53
Nitrogen	0.03	0.54	0.41	0.54
Sulfur	0.41	1.42	0.49	1.66
Chlorine	0.03	0.02	0.03	0.05
Ash	0.01	0.05	0.06	0.23
Oxygen <sup>1</sup>	1.69	1.33	5.04	1.10
Viscosity, cSt				
@ 100I °F	NM <sup>2</sup>	58	215	334
@ 210I °F	NM	9	20	25

<sup>1</sup> Oxygen values are calculated by difference.<sup>2</sup> NM = Not measured.

### Sampling and Analysis

Title III of the 1990 CAAAs lists 189 compounds and compound classes as HAPs. In the case of a combustion source, many of these compounds may be emitted at trace levels as a result of the combustion process. However, it is not known a priori which compounds will be emitted or at what level they will be emitted. It was therefore decided to sample and analyze for as many of the non-chlorinated and non-nitrogenated listed organic compounds as possible. The current program used different methods to sample and analyze for five major categories of HAPs: volatile organics, semivolatile organics, polychlorinated dioxins and furans, carbonyls, and metals. Table 3 lists the sampling and analytical procedures used in the test program. Duplicate samples were collected during each test run to provide an indication of emissions measurement reproducibility. Sample probes were colocated in the stack, using the same axial location, and with the radial location being determined by the point of average duct velocity. In addition, field and laboratory blanks were collected for each type of emissions sample to allow evaluation of potential contamination of the samples by laboratory procedures. Reported emissions data take into account the field and laboratory blank

**Table 2.** Trace element content of the four oils used in the test program, in 10<sup>-6</sup> lb/lb.

Element	#2 Oil	#5 Oil	Low Sulfur #6 Oil	High Sulfur #6 Oil
Arsenic	<1	<1	<1	<1
Antimony	<1	<1	<1	<1
Beryllium	<0.5	<0.5	<0.5	<0.5
Cadmium	0.01	0.08	0.09	0.26
Chromium	0.05	0.40	0.43	1.06
Lead	0.04	1.04	4	21
Manganese	0.01	0.40	0.30	0.91
Mercury	0.11	0.02	0.02	0.02
Nickel	0.05	29.0	15.7	43.0
Selenium	<1	<1	<1	<1
Vanadium	0.06	132	7	146

results. No data were reported for compounds that exhibited excessive blank levels.

The test program was conducted using APPCD Quality Assurance (QA) Level IV procedures. However, the major difference between this test program and those conducted using more stringent QA procedures is the level of audits and reviews required. The sampling and analytical procedures used in these tests were exactly as described in the published methods,<sup>4-6</sup> and the use of field blanks, duplicate measurements, and CEM calibration procedures have resulted in data quality that is much higher than required by QA Level IV.

## RESULTS

### Criteria Pollutant Emissions

Two criteria pollutants and two other commonly measured emissions components closely related to criteria pollutants were measured during each test. Criteria pollutants are specifically defined under 40 CFR 50, and include CO, NO<sub>2</sub>, SO<sub>2</sub>, and PM<sub>10</sub> (particulate matter less than 10 µm in diameter). The measured criteria pollutants were SO<sub>2</sub> and CO. NO emissions were used as an indicator of oxides of nitrogen emissions, and total particulate emissions were

**Table 3.** Sampling and analytical methods used in the test program.

Compound Class	Sampling Method <sup>1</sup>	Analytical Method
Volatile Organics	SW-846 Method 0030 (VOST)	SW-846 Methods 5040 and 8240
Semivolatile Organics	SW-846 Method 0010 (Modified Method 5)	SW-846 Method 8270
PAHs		CARB Method 4296
Polychlorinated Dioxins and Furans	40 CFR Part 60 Method 235	Modified SW-846 Method 8280
Carbonyls	SW-846 Method 0011 (Draft)	SW-846 Method 0011 (Draft)
Metals	40 CFR Part 60 Method 29 (Draft Multi-Metals Train)	40 CFR Part 60 Method 29 (Draft Multi-Metals Train)

<sup>1</sup> All SW-846 methods are found in Reference 4.

**Table 4.** Emissions of criteria pollutants from the four oils tested under baseline conditions. CO, NO, and SO<sub>2</sub> values are in ppm corrected to 3% O<sub>2</sub>, dry conditions. PM is in g/m<sup>3</sup>.

	CO	NO	SO <sub>2</sub>	PM
#2 Oil	1.24	124	184	0.0061
#5 Oil	3.55	242	793	0.0527
Low Sulfur #6 Oil	1.30	254	226	0.0148
High Sulfur #6 Oil	5.34	271	740	0.1074

**Table 5.** Emissions of criteria pollutants from #5 oil tested under different combustion conditions. CO and NO values are in ppm corrected to 3% O<sub>2</sub>, dry conditions. O<sub>2</sub> is percent of dry flue gas. Baseline conditions are oil temperature of 170 °F, stoichiometry of 1.2, and atomizing air pressure of 48 psig. Low oil temperature is 83 °F, low excess air is a stoichiometric ratio of 1.0, and low atomizing air pressure is 26 psig.

	O <sub>2</sub>	CO	NO
Baseline	3.38	3.55	242
Low Stoichiometric Ratio	1.16	18.15	207
Low Oil Temperature	3.44	6.15	233
Low Atomizing Air Pressure	3.46	12.31	225

measured as a surrogate for emissions of PM<sub>10</sub>. These results are shown in Tables 4 and 5. Table 4 compares results for all four oils under baseline conditions, and Table 5 compares four different operating conditions for the #5 oil. The results did not show any unusual behavior. SO<sub>2</sub> emissions tracked fuel sulfur content very closely, and NO emissions also followed fuel nitrogen content. Particulate matter (PM) emissions were highest for the high sulfur #6 oil and second highest for the #5 oil, with the #2 oil being an order of magnitude below the #5 oil. PM emissions from the low sulfur #6 oil were nearly an order of magnitude lower than the high sulfur #6 oil, which agrees with the significantly lower metals content in the low sulfur #6 oil compared to the high sulfur #6 oil.

The results presented in Table 5 also followed typical behavior, with NO decreasing as excess air decreases, coupled with an increase in the CO emissions. Slight increases in CO were noted for the low oil temperature case and for the low atomizing air pressure case, and NO decreased slightly for these cases as well. However, in no case were the emissions outside of expected ranges.

### Metal Emissions

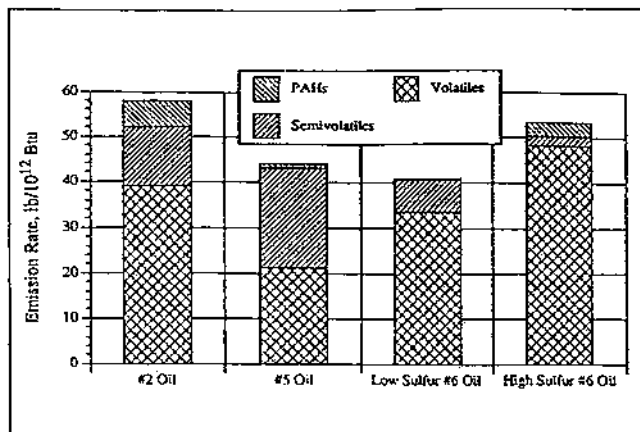
Emissions of metals from the combustion of fuel oils are typically estimated based on the amount of metals in the fuel oil. However, there are many complex processes that result in some of the metals being removed from the flue gases by mechanical means. As particulate sizes increase, metals in the particulate may fall to the bottom of the furnace and will not pass out the stack, reducing the amount

of metals emissions. Estimating emissions based on the assumption that 100% of the metals are emitted through the stack flue gases provides the upper limit of potential metals emissions. As seen from the trace metal concentrations in the fuel given in Table 2, the highest potential emissions are for nickel and vanadium, with the #5 and high sulfur #6 oils having the highest levels of these two metals. In the cases of antimony, arsenic, beryllium, and selenium, potential emissions must be based on the method detection levels for these metals in the oil, as the trace element measurements for these metals were below the detection levels.

The actual emission rates of metals from these four oils are presented in Table 6. Again, the metals showing the highest emissions are nickel and vanadium, with the maximum emission rate being that of vanadium from the high sulfur #6 oil. The values in parentheses represent the percentage of each metal actually emitted, compared to the maximum amounts that entered the boiler in the oils. The percentages of potential emissions of chromium, manganese, and nickel actually emitted for the #2 fuel oil are greater than 100%, indicating that more metal was emitted than was input with the fuel, based only on the trace element contents of these metals and their measured emissions. However, both the potential and measured values for these metals (in lb/10<sup>12</sup> Btu) are relatively small. Because of the low levels in both the flue gas and input oil, small errors in the absolute magnitudes of the metals analyses can lead to very large values in the ratio. A comparison of the actual emission rates in Table 6 shows that the levels of emissions from #2 oil are of reasonable magnitude. For manganese, which showed the largest difference between measured and potential emissions, comparisons to other results show that the measured emissions in this study are close to previously reported results,

**Table 6.** Measured emissions of metals, in lb/10<sup>12</sup> Btu. The percentages of the metals input in the fuel that exit in the flue gases are given in parentheses. For manganese from the #2 oil, the emission level is consistent with previously reported values,<sup>6</sup> while the #2 oil's manganese content was much lower than previously reported, resulting in a much higher recovery percentage than for the other metals.

Metal	#2 Oil	#5 Oil	Low Sulfur #6 Oil	High Sulfur #6 Oil
Antimony	0 (0)	4.96 (9)	17.6 (33)	15.5 (28)
Arsenic	0 (0)	8.48 (16)	2.84 (5)	3.61 (7)
Beryllium	0 (0)	0 (0)	0 (0)	0.066 (0)
Cadmium	0 (0)	0 (0)	0.934 (20)	7.22 (51)
Chromium	3.80 (148)	6.61 (31)	9.57 (42)	22.6 (39)
Lead	1.15 (56)	25.4 (45)	102 (48)	513 (45)
Manganese	6.11 (1110)	9.33 (43)	11.0 (70)	39.4 (80)
Nickel	2.96 (115)	896 (57)	508 (61)	1570 (67)
Selenium	0 (0)	3.46 (6)	0.687 (1)	2.68 (5)
Vanadium	2.72 (88)	5870 (82)	401 (108)	6020 (76)
Total Metals	16.7	6820	1050	8190



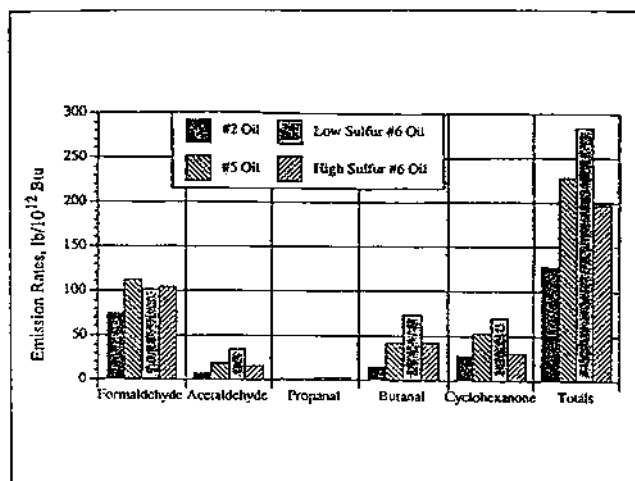
**Figure 2.** Total noncarbonyl volatile and semivolatile organic emission rates for the four oils tested, in lb/10<sup>12</sup> Btu. The plot shows the contribution of volatile organics, semivolatile organics (not including PAHs), and PAHs to the totals.

while the reported value of the measured manganese content of the oil used in this study is significantly lower than manganese content of distillate oils presented in the earlier study by Brooks.<sup>7</sup> Although no errors were found in measurement of either the #2 oil's manganese trace metal content or the stack sampling and analysis procedures, it is clear that both values cannot be correct. Based on the comparisons with the earlier study, it is likely that the measured emission value reported in Table 6 is close to the actual emission level, even though the ratio of measured to potential emissions indicates more metal is exiting the unit than is being input.

For the other metals, the ratios between input and output are relatively constant for the four oils. This indicates that the behavior of most of the metals tested in this combustion environment is similar for all four oils. This is expected, since the metals in the oils are almost exclusively in the ash fraction. This is significantly different than for coal, in which the metals are included in different components for different coals.<sup>8</sup> For instance, if manganese is found primarily in the organic matrix of a coal, it is probable that a greater percentage of the metal will be in the fly ash fraction than if it is found primarily in the inorganic fraction, in which case it will more likely be contained in the bottom ash fraction. Because metals are not contained in the organic fraction of oils, it is more likely that the metals will behave similarly among the different oils than would be the case for different coals.

### Organic Emissions

**Total Organic Emissions.** The test program analyzed for a total of 195 individual organic compounds, of which 72 were volatile organics, 101 semivolatile organics (including 16 PAHs), 12 aldehydes and ketones, and 10 PCDD and PCDF congeners. Of this number, 58 are listed as HAPs by Title III of the CAAAs. The majority of the organic emissions were



**Figure 3.** Measured emission rates of carbonyls (aldehydes and ketones) from the four oils tested, in lb/10<sup>12</sup> Btu.

carbonyls (aldehydes and ketones). The low sulfur #6 oil had an organic emission rate of 326 lb/10<sup>12</sup> Btu, followed by the #5 oil at 272 lb/10<sup>12</sup> Btu, the high sulfur #6 oil at 250 lb/10<sup>12</sup> Btu, and the lowest organic emission rate was for the #2 oil at 187 lb/10<sup>12</sup> Btu. Of these emissions, carbonyls comprised 69% of the #2 oil organic emissions, 84% of the #5 oil organics, 87% of the low sulfur #6 oil organic emissions, and 78% of the high sulfur #6 oil organic emissions.

For the remaining organics, the major contributor to the total emissions of organics was the volatile organics, followed by semivolatile organics and PAHs. Figure 2 presents the total rate of organic emissions (not including carbonyls, which will be discussed in more detail below) of the four oils under baseline conditions.

**Carbonyls.** A separate analysis procedure (see Table 3) was used to evaluate emission rates of carbonyls for the four oils under baseline conditions, and results are presented in Figure 3. Formaldehyde was the major compound found in the organic emissions of all four oils, and contributed approximately 50% of the total carbonyls for all the oils except for the low sulfur #6 oil, for which formaldehyde made up just over 30% of the total carbonyl emissions. The low sulfur #6 oil had the highest emission rates of carbonyls, at 285 lb/10<sup>12</sup> Btu, more than twice the emission rate of 129 lb/10<sup>12</sup> Btu from the #2 oil.

**PAHs.** In addition to the standard procedures used for analysis of semivolatile organics, a more sensitive PAH-specific analysis was conducted to quantify 16 individual PAHs. The results of these analyses are presented in Tables 7 and 8, and in Figure 4. Table 7 compares PAH emissions from the four different oils under baseline conditions, and shows that the #2 oil had PAH emissions more than twice those of any other oil, followed in order by the high sulfur #6 oil, the #5 oil, and the low sulfur #6 oil. The PAH with the highest

**Table 7.** Measured emission rates of PAHs from the four oils tested, in lb/10<sup>12</sup> Btu. Totals may not add exactly due to rounding.

PAH	#2 Oil	#5 Oil	Low Sulfur #6 Oil	High Sulfur #6 Oil
Acenaphthene	0.019	0	0	0.036
Acenaphthylene	0.018	0.078	0	0.062
Anthracene	0	0.043	0.031	0
Benzo(a)anthracene	0.348	0.037	0.095	0.044
Benzo(a)pyrene	0.695	0	0	0
Benzo(b)fluoranthene	0.859	0	0	0
Benzo(g,h,i)perylene	0.042	0.0287	0.027	0.066
Benzo(k)fluoranthene	0.745	0	0	0
Chrysene	0	0	0	0.029
Dibenz(a,h)anthracene	0.430	0.093	0.038	0
Fluoranthene	0.882	0	0.052	0.049
Fluorene	0.098	0.042	0.041	0.072
Indeno(1,2,3-cd)pyrene	0.129	0.033	0.028	0
Naphthalene	0.420	0.640	0.218	2.36
Phenanthrene	1.10	0.056	0.118	0.132
Pyrene	0.148	0	0.022	0.052
Total PAHs	5.93	1.05	0.669	2.90

individual emissions were of naphthalene for all oils except for the #2 oil. For the #5 and high sulfur #6 oils, naphthalene dominated the emissions of the PAHs, contributing 63% of the total PAH emissions for the #5 oil and over 80% for the high sulfur #6 oil. The #2 oil emitted detectable amounts of 14 of the 16 PAHs, and was the only case which showed benzo(a)pyrene at levels above the method detection level. These results compare with the measured PAH emissions of 2.2 lb/10<sup>12</sup> Btu for residual oil and 41.2 lb/10<sup>12</sup> Btu for distillate oil in a firetube boiler, cited in a comprehensive review of HAP emissions data from oil and coal combustion.<sup>7</sup> Although the data cited in the review are taken from a 30-year old report, they lend support to the current findings that the PAH emissions from the #2 oil can be higher than those from the combustion of heavier oils.<sup>9</sup>

Table 8 compares PAH emission results from the combustion condition variation tests, all conducted using the #5 oil. The baseline condition resulted in both the highest PAH emissions as well as in the highest number of detected PAHs of the four conditions. Naphthalene was the PAH with the highest emission rate in all four conditions, making up at least 50% of the total for all conditions. Of the remaining conditions, the low oil temperature condition resulted in the next highest level of PAH emissions, at 0.92 lb/10<sup>12</sup> Btu.

**Dioxins and Furans.** The flue gases were sampled and analyzed for PCDD and PCDF emissions from all four oils at baseline conditions. However, the results were inconsistent across duplicate tests. While some measurements were at levels well above method detection levels, further tests using the same oils under the same conditions measured all congeners at levels below the detection level. Although a

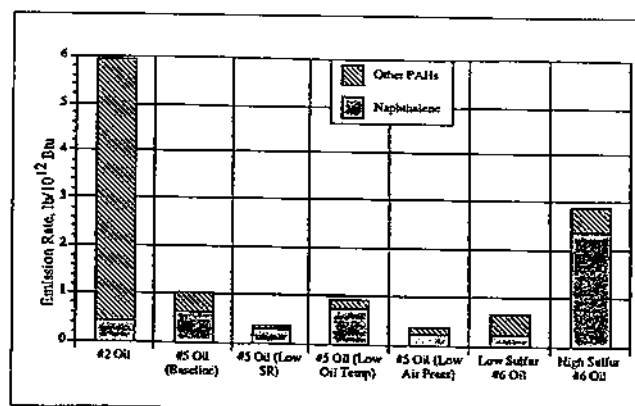
**Table 8.** Measured emissions of PAHs from the #5 oil tested under different combustion conditions, in lb/10<sup>12</sup> Btu. Baseline conditions are oil temperature of 170 °F, stoichiometry of 1.2, and atomizing air pressure of 48 psig. Low oil temperature is 83 °F, low excess air has a stoichiometry of 1.05, and low atomizing air pressure is 26 psig. Totals may not add exactly due to rounding.

PAH	Baseline	Low Oil Temperature	Low Excess Air	Low Atm Air Pressure
Acenaphthene	0	0	0	0.049
Acenaphthylene	0.078	0	0	0
Anthracene	0.043	0	0	0
Benzo(a)anthracene	0.037	0.062	0.044	0.022
Benzo(a)pyrene	0	0	0	0
Benzo(b)fluoranthene	0	0	0	0
Benzo(g,h,i)perylene	0.029	0	0	0
Benzo(k)fluoranthene	0	0	0	0
Chrysene	0	0.061	0	0
Dibenz(a,h)anthracene	0.093	0	0	0
Fluoranthene	0	0	0	0
Fluorene	0.042	0.028	0.020	0.021
Indeno(1,2,3-cd)pyrene	0.033	0	0	0
Naphthalene	0.640	0.739	0.296	0.227
Phenanthrene	0.056	0.034	0.031	0.044
Pyrene	0	0	0	0.026
Total PAHs	1.05	0.924	0.392	0.388

review of the collected data indicated the measurements were valid, it remains unclear whether one or more of the results were due to measurement and/or analytical errors. Additional tests are planned to further investigate the possible reasons for the different results.

## DISCUSSION

It is useful to place the emission rates reported here in the perspective of the requirements of Title III of the 1990 CAAAs. Title III requires regulation of any source if it emits over 25 tons/year of any combination of HAPs. The total HAP emissions here are well below this level for the small boiler tested. Summing the total metal and organic emissions results in a total emission of 2.2 lb/year from the #2 oil, 77.7 lb/year

**Figure 4.** Measured emissions of PAHs from the combustion of the four oils and from different operating conditions for #5 oil, in lb/10<sup>12</sup> Btu.

from the #5 oil, 15.1 lb/year from the low sulfur #6 oil, and 92.4 lb/year from the high sulfur #6 oil. These estimates are based on the boiler operating at 50% of its full load capacity of  $2.5 \times 10^6$  Btu/hr for 8,760 hours/year. These figures show the low levels of HAPs emitted from this single small source. However, this is not to say that these results should be discounted, since the risk factors associated with each compound were not considered. In addition, a source of this size may be considered an "area source," which may be subject to different regulatory requirements, under section 112(k) of the CAAAs.<sup>1</sup>

Although the study focused on the emissions of organics, the majority of HAP emissions from these four oils were from metals. Only for the #2 oil were the metal emissions lower than the organic emissions, and the metal emissions from the other three oils were at least three times greater than the organic emissions. Metal emissions made up only 8% of the total HAP emissions from the #2 oil, but were 96% of the #5 oil HAP emissions, 76% of the HAP emissions from the low sulfur #6 oil, and 97% of the high sulfur #6 oil HAP emissions.

For the organic fractions, several interesting results were noted from the measured data. First, the level of noncarbonyl organics from the #2 oil was higher than the emissions from the other tests, contrary to expectations. It is typically assumed that the #2 oil would result in lower organic emissions than the other oils because of its lower viscosity and higher level of refining. If all organics are compared, this assumption holds true; however, for particular classes of organics the #2 oil had the highest emission rate of the four oils tested. Because the carbonyl emissions were so much higher than any other organic emissions for all oils tested, the total organic emission rates depended strongly on the emission rates of the carbonyls. It is interesting to note that the ranking of total organic emissions from highest to lowest follows the order: low sulfur #6 oil, #5 oil, high sulfur #6 oil, and #2 oil. This is the exact opposite of the ranking for the noncarbonyl emissions, which follows the order, from highest to lowest: #2 oil, high sulfur #6 oil, #5 oil, and low sulfur #6 oil. This shows the impact that the carbonyl emissions have on the total organic emission rates.

Of the noncarbonyl emissions, the #2 oil had the highest emissions of PAHs and the second highest rate of volatile organics. The high sulfur #6 oil had the highest emission rate of volatile organics, but the lowest rate of non-PAH semivolatile organics. The low sulfur #6 oil had the highest level of total organic emissions, but the lowest rate of PAH emissions. In general, there seems to be little correlation between the emission rates of the different classes of organics to the oil type for the four oils tested.

## CONCLUSIONS

HAP emissions from four fuel oils tested in a firetube package boiler showed that the majority of HAP emissions were from the metals found in the oils, with the exception of the #2 oil, which had organic emissions higher than metals emissions. Formaldehyde made up the largest single organic HAP emitted for all the oils, with PAH emissions being

relatively low in comparison. Naphthalene was the PAH with the largest emission rate for the heavier oils, with phenanthracene being the largest contributor to PAH emissions for the #2 oil. For the size of the boiler tested, no single HAP was emitted at a rate which would require control under Title III of the CAAAs. The fuel emitting the largest amount of HAPs was the high sulfur #6 oil, which had a total HAP emission rate of less than 100 lb/year, based on 50% load operation for a full year.

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## APPENDIX

### English to Metric Conversion Table

$$\text{kW} = \text{Btu/hr} \div 3413$$

$$^{\circ}\text{C} = (^{\circ}\text{F} - 32) \div 1.8$$

$$\text{m}^2 = \text{ft}^2 \div 10.764$$

$$\text{cm} = \text{in} \times 2.54$$

$$\text{kg} = \text{lb} \div 2.2046$$

$$\text{kPa} = \text{psi} \times 6.893$$

$$\text{tonne} = \text{ton} \times 0.9072$$

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