Emissions of Organic Hazardous Air Pollutants from the Combustion of Pulverized Coal in a Small-Scale Combustor

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The emissions of hazardous air pollutants (HAPs) from the combustion of pulverized coal have become an important issue in light of the requirements of Title III of the 1990 Clean Air Act Amendments, which impose emission limits on 189 compounds and compound classes. Although previous field and laboratory studies have examined the emissions of some HAPs from coal combustion sources, no work has been done to evaluate the emissions of a broad range of these compounds, particularly in the case of organics. Therefore, a study was conducted at the U.S. Environmental Protection Agency's Air and Energy Engineering Research Laboratory to characterize emissions of 76 organic HAPs in the flue gases from the combustion of pulverized coal in a small-scale down-fired combustor. The combustor was operated under different conditions to simulate baseline, high excess air firing, and nitrogen oxide (NO_x) controls by combustion modifications. Samples were extracted near the combustor exit, upstream of any pollution control equipment. Data collected indicate that relatively low levels of organic HAPs are present in the flue gases for any of the combustion conditions; however, several compounds were present that have not been reported in previous studies. To the extent these small-scale tests accurately simulate full-scale units, estimates based on these experiments indicate that the total HAP emissions from a large utility power plant are not likely to increase significantly due to the installation of combustion modification techniques for NO_x control.

Introduction and Background

Title III of the 1990 Clean Air Act Amendments (CAAAs) identifies 189 compounds and compound groups as hazardous air pollutants (HAPs), and it requires regulation of any source which emits more than 9091 kg (10 t)/year of any one of the 189 HAPs, or a total of 22 727 kg (25 t)/year of any combination of two or more HAPs (1). These limits translate to very low threshold concentrations of HAPs when considering the large mass of flue gas released from full-scale combustion sources on an annual basis. As an example, a moderately sized boiler with an annual average firing rate of 470 MW (1.6×10^9 Btu/h) can emit over 9091 kg (10 t)/year of a given pollutant if the average annual emission rate of that pollutant is 6.02×10^{-4} g/MJ (1.4×10^{-3} lb/10^6 Btu). The emission rate of all listed HAPs would exceed the 22 727 kg (25 t)/year level with a total average annual emission rate of only 1.51×10^{-3} g/MJ (3.5×10^{-3} lb/10^6 Btu). Such low threshold concentrations highlight the need for precise information

concerning potential emissions of HAPs from combustion sources. This is particularly true for fuels that may be more prone to incomplete combustion and that may contain chlorine and/or nitrogen, since a significant portion of the listed HAPs are chlorinated or nitrogenated hydrocarbons. Because of the inherent presence of chlorine and nitrogen in most coals and the immense amount of coal utilized in this country, the emissions of HAPs from the combustion of pulverized coal is a topic of considerable interest.

The great majority of coal is used in utility generation of electricity, primarily in pulverized form. Although electric utility emissions of HAPs are not currently regulated under Title III, the CAAAs require the U.S. Environmental Protection Agency (EPA) to evaluate the contributions of utility boilers to the emissions of HAPs and to report to Congress on the health risk associated with these emissions (1). Unfortunately, data characterizing the emissions of most HAPs from the combustion of pulverized coal are sparse. While previous studies of coal combustion emissions emphasized criteria pollutants [such as sulfur dioxide (SO_2), oxides of nitrogen (NO_x), and particulate matter (PM)], some data on HAP emissions from coal combustion are available (2, 3). Since the primary purpose of these earlier studies was to evaluate the effect of combustion modifications on NO_x emissions, measurements of HAPs (particularly organic HAPs) were limited. The majority of studies in which HAP emissions from utility boilers were reported focused on the emissions of metals (4–6) and a limited number of organic compounds, primarily benzene, formaldehyde, toluene, and polyaromatic hydrocarbons (PAHs) (7–9). These data show that PAHs tend to increase as low NO_x combustion modifications are applied (2, 3). This is consistent with the increase in carbon monoxide (CO) and unburned carbon in the fly ash. The emissions of most other Title III-listed organic compounds have not been studied in detail for a variety of reasons, primarily because organic emissions have not been considered a significant problem due to the high temperatures and residence times typically found in utility boilers. Such conditions have traditionally been assumed adequate to destroy any significant levels of products of incomplete combustion. However, as noted above, in a high-volume gas stream typical of such systems, the 9091 kg (10 t)/year limit on HAP emissions can be exceeded by a very low concentration of a given compound. A figure of 9.091×10^9 kg (10^7 t)/year of flue gas is not unreasonable for a medium-sized utility boiler, leading to a concentration threshold of 1 part per million on a mass basis (ppmm) for exceeding the limit for a single compound or 2.5 ppmm for all 189 HAPs. It is therefore important to examine these pollutants previously characterized as "trace" in more detail.

For this reason, the EPA's Office of Air Quality Planning and Standards (OAQPS), the U.S. Department of Energy (DOE), and the Electric Power Research Institute (EPRI) are cooperating to conduct a series of field tests to more completely characterize HAP emissions from full-scale utility boilers. The EPRI Power Plant Integrated Systems: Chemical Emission Studies (PISCES) program was begun as an integrated database (10–12) and has developed into a field test program that will sample toxic air emissions from 45 utility sites with a variety of boiler designs and pollution control equipment. The DOE's field tests will sample up to 15 other plants for as many of the 189 HAPs as possible, and the OAQPS tests will validate the results of both EPRI and DOE as well as expand the field test database by sampling emissions from additional plants.

However, this program is limited in its scope, and many of the field tests will sample for a limited number of the 189 listed HAPs. A further limitation is a low number of tests on the potential effect of combustion modification control strategies for NO_x such as overfire air (OFA) or low NO_x burners (LNBs) on the emissions of HAPs. The CAAAs require the Electric Utility Study (the basis for the Report to Congress noted above) to evaluate the potential emission of HAPs from utilities "after the imposition of the requirements of this Act"; i.e., after utilities have applied controls for the reduction of acid rain and ozone precursors, primarily SO_2 and NO_x (1). With LNBs specified in the Act as the minimum NO_x control technology for a large percentage of the boiler population, the effect of such combustion modifications on HAP emissions is an issue which could have considerable influence on the future of utility regulations.

To provide additional information concerning the potential emissions of a fuller range of organic HAPs, the Air and Energy Engineering Research Laboratory (AEERL) of the EPA's Office of Research and Development undertook a project to characterize the emissions of HAPs from a small-scale combustor burning pulverized coal. Several combustion conditions were chosen to simulate the combustion modification NO_x controls noted above, with the aim of determining the effects of changing combustion conditions on the generation of HAPs. In order to provide information most useful to the ongoing field test program, the small-scale tests were planned to provide data in the form of emission factors, on a mass per unit energy input basis. In addition, it was recognized that many of the listed HAPs were unlikely to be present in the coal flue gases in levels above the detection capabilities of the analysis equipment. Rather than to assume zero concentrations in these cases, it was desirable to determine maximum possible concentrations based on the detection capabilities of the equipment. By taking this approach, maximum levels of HAP emissions can be estimated. Since, in general, the alteration of combustion conditions should much more strongly affect the concentrations of organic compounds than those of metal or particulate matter, the study focused on organic HAPs rather than metals.

Experimental Details

Equipment. Combustion tests were conducted on the AEERL's innovative furnace reactor (IFR), a down-fired, refractory-lined cylindrical furnace nominally rated at 29.6
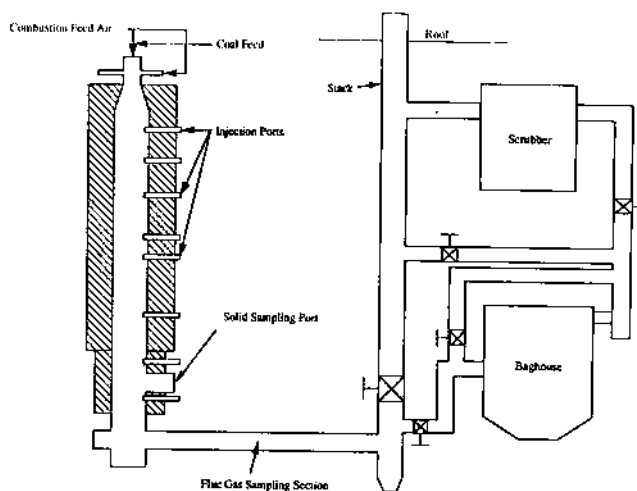

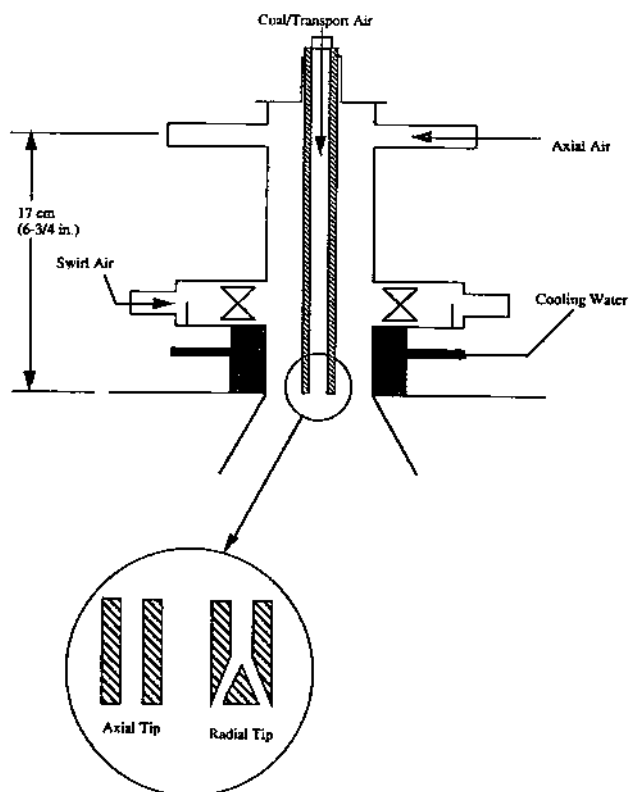**Figure 1.** Schematic of innovative furnace reactor.

Figure 2. Schematic of coal burner used on IFR.

kW (100 000 Btu/h). Figure 1 shows a schematic of the furnace and exhaust ducting. The IFR burner provides for fully adjustable swirl, and air may be staged by adjusting the primary, secondary, and tertiary airflows. The burner is illustrated in Figure 2. Ports are available along the furnace exhaust duct axis for the introduction of additional staging air or for the introduction of sorbents or extractive sampling. The locations of these ports are shown in Figure 3. Pulverized coal is fired by introducing the fuel into the center port of the burner and adjusting the tangential airflow rates to create a stable flame with the desired degree of swirl. Several previous test programs conducted on the IFR burning pulverized coal have resulted in combustion conditions within the furnace similar to those found in full-scale units (13). Since the IFR cannot precisely recreate the full time/temperature profile of a full-scale utility boiler, the aim of the test program was to determine relative trends in HAP emissions
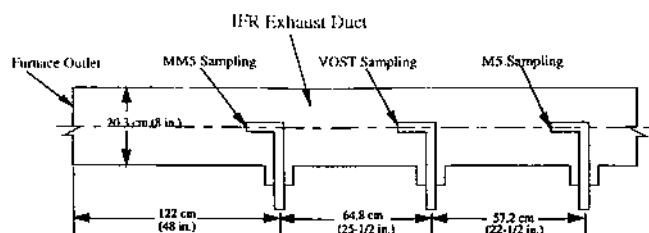
Figure 3. IFR exhaust duct showing sampling locations.

Table 1. Matrix of Test Conditions

run no.	test condition	fuel	stoichiometric ratio	air staging
1	1 (background)	natural gas	1.2	no
2	1 (background)	natural gas	1.2	no
3	2 (baseline)	coal	1.2	no
4	3 (SR variation)	coal	1.4	no
5	4 (low NO$_x$)	coal	1.2	yes
6	3 (SR variation)	coal	1.4	no
7	4 (low NO$_x$)	coal	1.2	yes
8	2 (baseline)	coal	1.2	no

under different combustion conditions rather than absolute values of pollutant concentration.

Test Conditions and Sampling Methods. The test condition matrix was designed with the goal of creating several combustion conditions which would simulate combustion modification NO$_x$ controls such as overfire air and low NO$_x$ burners. To accomplish this, the combustion conditions chosen were baseline, high stoichiometric ratio (SR), and air staging (low NO$_x$). Initial tests were conducted using natural gas as a means of determining "background" levels of HAPs. For each combustion condition, a volatile organic sampling train (VOST) (14) was used to sample the flue gases for volatile organic compounds (VOCs). [Note that the term "volatile organic compounds" is used here to denote organic compounds which are recovered by the VOST sampling method. The VOST method is designed to sample compounds with boiling points between 30 °C and 100 °C, and the associated analytical method applies to compounds with a boiling point less than 200 °C. This differs from the definition of VOCs relative to ozone nonattainment, given in 40 CFR 60.2. The regulatory definition of VOC is more limited, and denotes a specific list of compounds.] The EPA Modified Method 5 (MM5) train (15) was used to sample for semivolatile organic compounds. VOST and MM5 are accepted stack-gas sampling methods typically used in full-scale stack sampling programs. Continuous emission monitors provided readings of the pollutants most likely affected by modification of the combustion process, namely NO, CO, and O$_2$. Organic compounds were analyzed according to approved EPA methods. Instrument detection levels for all compounds were verified based on calibration standards for each compound. The full test matrix is shown in Table 1.

The stoichiometric ratio was varied by increasing the secondary and tertiary air streams. The low NO$_x$ condition was achieved by lowering the burner airflows to a sub-stoichiometric level (SR ≈ 0.9), with additional staging air introduced downstream of the primary combustion zone to bring the overall SR to the baseline value of 1.2. Natural gas was used in the initial two runs as a "background" to provide a relatively clean basis to which the coal combustion results could be compared. A pulverized Illinois

Table 2. Proximate and Ultimate Analyses and Trace Metal Contents of the Illinois Bituminous Coal Used in Tests[a]

moisture (%)	6.60 (wet)
volatile matter (%)	35.90 (dry)
fixed carbon (%)	56.10 (dry)
ash (%)	8.00 (dry)
carbon (%)	74.72
hydrogen (%)	5.06
nitrogen (%)	1.77
oxygen (%)	9.32
total sulfur (%)	1.17
heat content	31 425 kJ/kg
	13 295 Btu/lb
antimony (ppm)	<10
arsenic (ppm)	<10
beryllium (ppm)	<5
cadmium (ppm)	<5
chromium (ppm)	9.6
lead (ppm)	13.1
manganese (ppm)	19.5
nickel (ppm)	10.0
selenium (ppm)	<10

[a] Proximate and ultimate analysis percentages and trace metal concentrations are on a per weight basis. Moisture is as a percentage of the total as-received coal; volatile matter, fixed carbon, and ash are measured on a moisture-free basis.
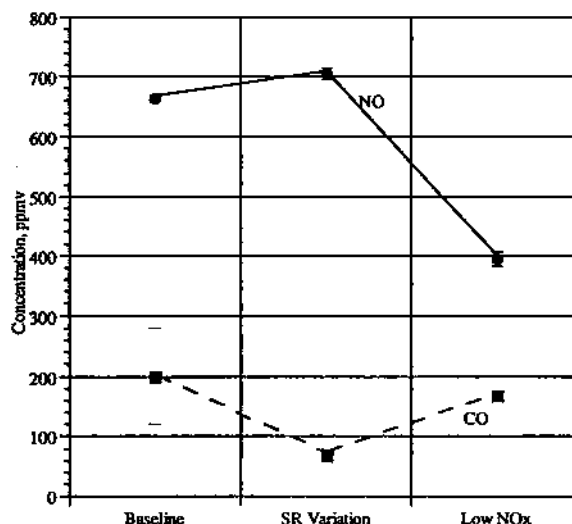

Figure 4. NO and CO concentrations for the three coal combustion conditions. Values are in parts per million by volume, corrected to 3% O$_2$. The dash marks above and below each point indicate the maximum and minimum readings for that condition.

bituminous coal was used in the coal combustion tests. Properties of the coal are shown in Table 2.

Results

(A) NO$_x$ and CO. The test conditions outlined in Table 1 were designed to create significant variations in the combustion environment for the purpose of changing NO$_x$ emissions. Continuous measurements of NO$_x$ [measured as nitric oxide (NO)] and carbon monoxide (CO) were taken during each test. Figure 4 shows the average NO and CO levels for the three coal combustion cases. The CO levels were higher than desired, particularly for the baseline condition. However, this was primarily due to the high CO value of the initial test run. As seen in Figure 4, the two baseline runs yielded CO values of 284 ppmv during the first run and 124 ppmv during the second

Table 3. List of Volatile Organic Substances for Which Flue Gases Were Analyzed

non-Title III compounds		Title III compounds	
acetone	1,1-dichloroethane	acetonitrile	ethylbenzene
bromoacetone	1,2-dichloroethane	benzene	hexane
bromodichloromethane	1,1-dichloroethene	bromoform	methylene chloride
bromomethane	1,2-dichloropropane	carbon disulfide	1,1,2,2-tetrachloromethane
2-butanone	fluorobenzene	carbon tetrachloride	tetrachloroethylene
chloroethane	heptane	chlorobenzene	toluene
chloromethane	2-hexanone	chloroform	1,1,2-trichloroethane
dibromochloromethane	iodomethane	cumene	trichloroethylene
1,2-dibromoethane	4-methyl-2-pentanone	1,2-dibromo-3-chloropropane	styrene
dibromomethane	pentachloroethane	1,4-dichlorobenzene	vinyl acetate
1,2-dichlorobenzene	1,1,1-trichloroethane	cis-1,3-dichloropropene	vinyl chloride
1,3-dichlorobenzene	trichlorofluoromethane	trans-1,3-dichloropropene	total xylenes
1,4-dichloro-2-butene	1,2,3-trichloropropane	1,4-dioxane	
dichlorodifluoromethane	trans-1,2-dichloroethene		

run. In order to maintain flame stability with the desired SR, it was not possible to further decrease the CO values for reasonable periods of time during the initial test run. Despite the CO values' being higher than desired during this run, the presence of organic species did not increase significantly, and the results from the initial test were deemed acceptable. The combustion modification technique (air staging) applied clearly lowers NO_x emissions from a baseline average of 668 ppmv to a low NO_x average of 400 ppmv. This is accompanied by a slight decrease in CO from 204 ppmv in the baseline case to 172 ppmv for the low NO_x condition. If the lower CO value is taken as the baseline condition, there is an increase in CO under low NO_x conditions of approximately 40%.

(B) Volatile Organic Compounds. VOST samples were analyzed using a gas chromatograph/mass spectrometer (GC/MS) system to determine the concentration of 53 separate VOCs, 25 of which are listed under Title III of the CAAAs (16, 17). These compounds are listed in Table 3. As expected, the majority of these compounds were either very near to or below the detection levels of the equipment. The high frequency of concentrations below the detection limit (BDL) requires that the average concentrations not be reported as precise values. Concentrations below the equipment detection limits should not be arbitrarily assigned a value of zero, nor should they be given the value of the detection limit. Rather, the actual value likely lies between the two extremes, although it is likely that the value lies closer to zero than to the detection limit. This is because in several instances the equipment was able to detect concentrations slightly below the listed detection limit of the unit, making the actual detection level of the unit somewhat less than the listed value. Results will be given in terms of the range in which the concentration of a given compound can fall, using the detection limit as the upper limit of that range and zero as the lower limit.

In the case of VOCs, at least two samples were analyzed for each run for a minimum of four samples per test condition. The presence of a given compound was considered to be significant when at least two samples indicated detectable levels of that compound. Emission factor values were calculated by averaging all samples for the test condition of interest. The maximum average values were calculated using the listed detection limit of 10 ng/sample in cases where a reading below the detection limit was obtained, whereas the minimum values were calculated by assuming zero concentration in those instances. Thus, the fewer the samples with detectable

quantities, the more conservative the maximum calculated emission factor. Table 4 lists the maximum and minimum average Title III VOC emission factors for compounds that were detected in at least two samples. Figure 5 illustrates the results tabulated in Table 4.

The difference between the maximum and minimum calculated emission factors can be illustrated by the following calculation. If under a given condition, three samples result in calculated emission factors of 5.6×10^{-7} lb/10^6 Btu, 6.0×10^{-7} lb/10^6 Btu, and 6.2×10^{-7} lb/10^6 Btu, and one sample which was below the detection limit (resulting in a value of 4.2×10^{-7} lb/10^6 Btu for the emission factor), the resulting minimum emission factor would be

$$[(5.6 + 6.0 + 6.2 + 0.0) \div 4] \times 10^{-7} \text{ lb/}10^6 \text{ Btu} =$$
$$4.5 \times 10^{-7} \text{ lb/}10^6 \text{ Btu, (1)}$$

and the maximum emission factor would be

$$[(5.6 + 6.0 + 6.2 + 4.2) \div 4] \times 10^{-7} \text{ lb/}10^6 \text{ Btu} =$$
$$5.5 \times 10^{-7} \text{ lb/}10^6 \text{ Btu (2)}$$

where the zero value used in eq 1 has been replaced by the emission factor calculated from the method detection limit concentration. Thus, if all samples were below the detection level for a given compound, the minimum emission factor would be zero, and the maximum would correspond to the detection level. This case is illustrated for acetonitrile in the baseline condition of Table 4. Conversely, if all samples were above the detection level for a given compound, the minimum and the maximum would be the same, as Table 4 shows for benzene.

The volatile HAPs accounting for the largest portion of the total are benzene and carbon disulfide. For all combustion conditions, both compounds as well as toluene were detected in all samples. For the baseline and low NO_x conditions, these three compounds comprised roughly 70% of the total volatile HAP emissions, while for the stoichiometric variation condition, they combined for only 40–50% of the total, depending on whether one is comparing the maximum or minimum totals. Total HAP emissions were lowest in the stoichiometric ratio variation condition, as would be expected, since additional combustion air was used during the test, allowing more complete burnout of the organic compounds. In this case, total xylenes and methlyene chloride made up the majority of the remaining total volatile HAP emissions.

Emission factors for non-Title III VOCs are not tabulated. The VOC that was found in the highest concentration was acetone, which yielded a calculated emission

Table 4. Calculated Emission Factors for Three Coal Combustion Conditions for Volatile Organic Substances[a]

compound	baseline coal (lb/10⁶ Btu)		SR variation (lb/10⁶ Btu)		low NO$_x$ condition (lb/10⁶ Btu)	
	max	min	max	min	max	min
acetonitrile	4.179×10^{-7}	0.000	6.056×10^{-7}	1.157×10^{-8}	2.165×10^{-6}	1.999×10^{-6}
benzene	8.625×10^{-6}	8.625×10^{-6}	2.444×10^{-6}	2.444×10^{-6}	8.817×10^{-6}	8.817×10^{-6}
bromoform	4.179×10^{-7}	0.000	4.274×10^{-7}	0.000	4.170×10^{-7}	0.000
carbon disulfide	6.456×10^{-6}	6.456×10^{-6}	3.368×10^{-6}	3.368×10^{-6}	7.939×10^{-6}	7.939×10^{-6}
carbon tetrachloride	4.206×10^{-7}	2.151×10^{-7}	4.274×10^{-7}	0.000	4.170×10^{-7}	0.000
chlorobenzene	3.356×10^{-7}	1.301×10^{-7}	3.727×10^{-7}	3.727×10^{-7}	2.919×10^{-7}	1.950×10^{-7}
chloroform	1.513×10^{-7}	5.744×10^{-8}	1.778×10^{-7}	6.207×10^{-8}	3.171×10^{-7}	5.270×10^{-8}
cumene	4.179×10^{-7}	1.252×10^{-7}	4.274×10^{-7}	0.000	4.170×10^{-7}	9.689×10^{-8}
1,2-dibromo-3-chloropropane	4.179×10^{-7}	0.000	4.274×10^{-7}	0.000	4.170×10^{-7}	0.000
1,4-dichlorobenzene	4.179×10^{-7}	0.000	2.806×10^{-7}	4.203×10^{-8}	4.170×10^{-7}	0.000
cis-1,3-dichloropropene	4.179×10^{-7}	0.000	3.958×10^{-7}	7.356×10^{-8}	4.170×10^{-7}	0.000
trans-1,3-dichloropropene	3.481×10^{-7}	1.746×10^{-8}	4.274×10^{-7}	0.000	4.170×10^{-7}	0.000
1,4-dioxane	4.179×10^{-7}	0.000	1.013×10^{-6}	3.641×10^{-7}	6.303×10^{-7}	3.716×10^{-7}
ethylbenzene	2.260×10^{-7}	2.260×10^{-7}	3.119×10^{-7}	1.962×10^{-7}	3.644×10^{-7}	2.255×10^{-8}
hexane	9.789×10^{-7}	8.851×10^{-7}	9.825×10^{-7}	8.668×10^{-7}	9.218×10^{-7}	6.574×10^{-7}
methylene chloride	8.411×10^{-7}	7.473×10^{-7}	4.275×10^{-6}	4.159×10^{-6}	4.380×10^{-6}	3.563×10^{-6}
styrene	5.882×10^{-7}	5.009×10^{-7}	3.843×10^{-7}	2.686×10^{-7}	3.291×10^{-7}	5.665×10^{-8}
1,1,2,2-tetrachloroethane	4.179×10^{-7}	0.000	4.274×10^{-7}	0.000	4.170×10^{-7}	0.000
tetrachloroethylene	7.434×10^{-7}	4.507×10^{-7}	4.274×10^{-7}	0.000	3.879×10^{-7}	6.782×10^{-8}
toluene	1.796×10^{-6}	1.796×10^{-6}	1.721×10^{-6}	1.721×10^{-6}	1.043×10^{-6}	1.043×10^{-6}
1,1,2-trichloroethane	4.179×10^{-7}	0.000	4.274×10^{-7}	0.000	4.170×10^{-7}	0.000
trichloroethylene	5.685×10^{-7}	4.747×10^{-7}	3.235×10^{-7}	2.078×10^{-7}	2.483×10^{-7}	1.732×10^{-7}
vinyl acetate	4.179×10^{-7}	0.000	4.274×10^{-7}	0.000	3.684×10^{-7}	2.081×10^{-8}
vinyl chloride	4.179×10^{-7}	0.000	4.274×10^{-7}	0.000	3.493×10^{-7}	7.516×10^{-9}
total xylenes	1.748×10^{-6}	1.748×10^{-6}	2.589×10^{-6}	2.473×10^{-6}	2.373×10^{-7}	1.404×10^{-7}
total Title III VOCs	2.884×10^{-5}	2.246×10^{-5}	2.395×10^{-5}	1.663×10^{-5}	3.296×10^{-5}	2.522×10^{-5}

[a] Maximum values assume compounds not detected are at the instrument detection level; minimum values assume compounds not detected are at zero concentration. Emission factors are in lb/10⁶ Btu.
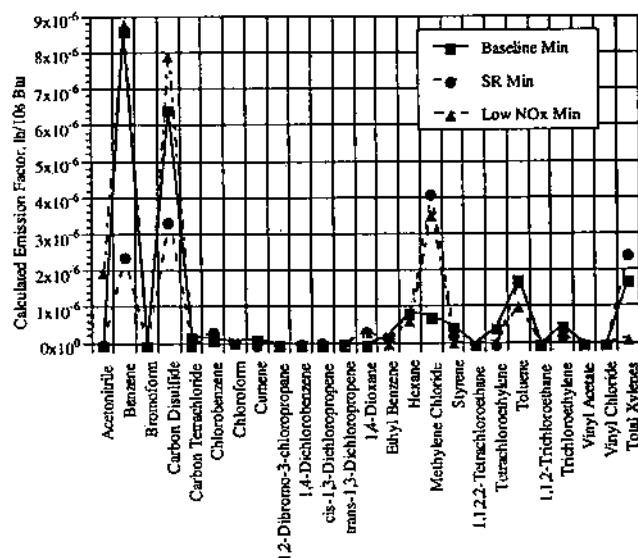

Figure 5. Minimum average emission factors for Title III-listed volatile organic compounds for all three combustion conditions. Minimum averages were calculated assuming all measurements below equipment detection limits are equal to zero. Emission factors are given in lb/10⁶ Btu.

factor of 1.90×10^{-6} g/MJ (4.43×10^{-6} lb/10⁶ Btu) in the low NO$_x$ combustion condition. For all measured non-Title III VOCs, the total maximum emission factor was calculated to be 2.45×10^{-6} g/MJ (5.71×10^{-6} lb/10⁶ Btu) in the baseline condition, 4.43×10^{-6} g/MJ (1.03×10^{-5} lb/10⁶ Btu) for the stoichiometric variation condition, and 4.28×10^{-6} g/MJ (9.96×10^{-6} lb/10⁶ Btu) for the low NO$_x$ condition.

Some caution must be taken when evaluating these results. A set of tubes that were not used to collect flue gases were also put through the analysis procedure. The results from these samples, or field blanks, were compared to the results of actual samples to assess the integrity of the method procedures on the measurements of different compounds. [The field blanks or "trip blanks" were treated the same as the samples, except that no flue gas sample was drawn through them. The blanks were attached to the train, leak checked, stored, and analyzed identically to the samples.] Methylene chloride levels showed higher concentrations in the field blanks than in any of the baseline test samples. When compared to measured values of other Title III compounds, method blanks also showed higher concentrations of total xylenes than the low-NO$_x$ condition average measured for the flue gases. These results indicate that the actual concentrations of these compounds in the flue gases are likely to be considerably less than the values shown in Table 4. In addition, the presence of acetone, acetonitrile, benzene, and styrene in the field blanks means that the tabulated levels of these compounds are likely to be somewhat higher than the actual flue gas concentrations. For these four compounds, however, the levels found in the field blanks were no more than half the average level detected for any of the three test conditions, indicating that the measured compounds were in fact present in the flue gases.

(C) Semivolatile Organic Compounds. The MM5 sampling procedure does not result in multiple sample tubes for each run; thus, the results are for individual runs rather than for individual sample tubes as was the case for the VOST procedure. Collected samples were analyzed using approved analysis procedures for 93 semivolatile organic compounds, 47 of which are listed as hazardous under Title III (18). Of the 47 listed compounds, 19 are polyaromatic hydrocarbons (PAHs). Table 5 lists the semivolatile organic compounds sampled and analyzed. Table 6 shows the calculated emission factors of the semivolatile compounds, including minimum and maximum levels. As was the case for the volatile fraction, the

Table 5. List of Semivolatile Organic Substances for Which Flue Gases Were Analyzed

Non-Title III-Listed Semivolatile Compounds

2-acetylaminofluorene	3,3'-dimethylbenzidene	3-nitroaniline
azobenzene	3,3'-dimethoxylbenzidene	4-nitroaniline
benzyl alcohol	4,6-dinitrol-2-methylphenol	N-nitrosodiethylamine
bis(2-chloroethoxy) ether	2,6-dinitrotoluene	N-nitrosodi-N-butylamine
bis(2-chloroethyl) ether	di-N-octyl phthalate	N-nitrosodiphenylamine
bis(2-chloroisopropyl) ether	diphenylamine	4-nitrosomorpholine
4-bromophenyl phenyl ether	diphenyltriazene	1-nitrosopiperidine
5-chloro-3-methylaniline	hexachloropropene	N-nitrosodi-N-propylamine
4-chlorophenyl phenyl ether	methapyrilene	1-phenylethanone
1,2-dichlorobenzene	methoxymethylbenzenamine	pentachlorobenzene
1,3-dichlorobenzene	2-methylbenzenamine	pentachloronitrobenzene
2,6-dichlorophenol	3-methylcholanthrene	1,2,4,5-tetrachlorobenzene
diethyl phthalate	2-naphthalenamine	2,3,5,6-tetrachlorophenol
2,4-dimethylphenol	N-(4-ethoxyphenyl)acetamine	2,3,4,6-tetrachlorophenol
di-N-butyl phthalate	2-nitroaniline	2,3,4-trichlorophenol
N,N-dimethylaminobenzene		

Title III-Listed Semivolatile Compounds

acenaphthene[a]	2-chlorophenol	isophorone
acenaphthylene[a]	chrysene[a]	2-methylnaphthalene[a]
aniline	dibenz[a,b]anthracene[a]	2-methylphenol[b]
anthracene[a]	dibenzofuran	4-methylphenol[c]
benzidine	1,4-dichlorobenzene	naphthalene
benz[a]anthracene[a]	3,3'-dichlorobenzidene	nitrobenzene
benzo[b]fluoranthene[a]	7,12-dimethylbenz[a]anthracene[a]	4-nitrophenol
benzo[k]fluoranthene[a]	dimethyl phthalate	N-nitrosodimethylamine
benzo[ghi]perylene[a]	2,4-dinitrotoluene	pentachlorophenol
benzo[a]pyrene[a]	fluoranthene[a]	phenanthrene[a]
bis(2-ethylhexyl) phthalate	fluorene[a]	phenol
butyl benzyl phthalate	hexachlorobenzene	pyrene[a]
4-chloroaniline	hexachlorobutadiene	1,2,4-trichlorobenzene
4-chloro-3-methylphenol	hexachlorocyclopentadiene	2,4,6-trichlorophenol
1-chloronaphthalene[a]	hexachloroethane	2,4,5-trichlorophenol
2-chloronaphthalene[a]	ideno[1,2,3-cd]pyrene[a]	

[a] Polycyclic aromatic hydrocarbon (PAH). [b] o-Cresol. [c] p-Cresol.

Table 6. Calculated Emission Factors for Three Coal Combustion Conditions for Detected Semivolatile Organic Substances[a]

| compound	baseline averages (lb/10^6 Btu)		SR variation averages (lb/10^6 Btu)		low NO$_x$ averages (lb/10^6 Btu)	
	max	min	max	min	max	min
bis(2-ethylhexyl) phthalate	6.433×10^{-8}	6.433×10^{-8}	1.095×10^{-7}	9.178×10^{-8}	2.386×10^{-8}	6.118×10^{-9}
naphthalene	3.166×10^{-8}	2.371×10^{-8}	2.998×10^{-8}	2.203×10^{-8}	1.364×10^{-7}	1.285×10^{-7}
phenol	2.686×10^{-7}	2.502×10^{-7}	2.325×10^{-7}	2.141×10^{-7}	1.658×10^{-6}	1.640×10^{-6}
total Title III compounds	3.380×10^{-6}	3.383×10^{-7}	4.248×10^{-6}	4.320×10^{-7}	6.490×10^{-6}	2.710×10^{-6}

[a] Maximum values assume compounds not detected in a given run are at the instrument detection level; minimum values assume compounds not detected are at zero concentration. The maximum totals are calculated from all 47 Title III compounds for which samples were analyzed. Emission factors are in lb/10^6 Btu.

minimum emission factors are calculated assuming zero concentrations for those compounds below the instrument detection limits, and the maximum emission factors are calculated assuming that those compounds are at the detection limit. For cases where both runs for a given condition show a detectable amount of a compound, the maximum and minimum will be identical, since no assumptions need be made as to which value to use in calculating the average.

Only three Title III-listed semivolatile compounds were found at levels above equipment detection limits: bis(2-ethylhexyl)phthalate, naphthalene, and phenol. The first compound was detected in the flue gases of four separate runs, and the last two compounds were detected in only three different runs. All three compounds were found in all combustion conditions. Phenol was the compound with the highest concentrations in all three conditions. No semivolatile compounds were detected during analysis of the method blanks, indicating that the presence of the

three semivolatile compounds was not due to analysis procedures, but that they were in fact present in the flue gases. The minimum calculated emission factors for these compounds are shown in Figure 6.

Emission factors for the non-Title III semivolatile compounds are not tabulated here. The only non-Title III compounds detected were di-N-butyl phthalate, di-N-octyl phthalate, and 1-phenylethanone. The last two compounds were detected only in a single run under low NO$_x$ conditions. Emission factors for these two compounds were calculated to be 2.68×10^{-8} g/MJ (6.24×10^{-8} lb/10^6 Btu) for the di-N-octyl phthalate and 4.72×10^{-7} g/MJ (1.10×10^{-6} lb/10^6 Btu) for the 1-phenylethanone. Di-N-butyl phthalate was detected in all three combustion conditions. Calculated emission factors for this compound ranged from 4.02×10^{-7} g/MJ (9.36×10^{-7} lb/10^6 Btu) under low NO$_x$ conditions to 6.01×10^{-8} g/MJ (1.40×10^{-7} lb/10^6 Btu) under the stoichiometric ratio variation condition.
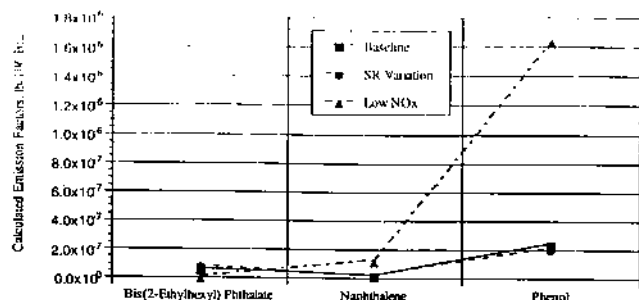
Figure 6. Minimum average emission factors for Title III-listed semivolatile organic compounds for all three combustion conditions. Minimum averages were calculated assuming that all measurements below equipment detection limits are equal to zero. Emission factors are given in lb/10^6 Btu.

(D) Total Emissions of Organic HAPs. A value for the total emission of organic HAPs can be found by simply summing the volatile and semivolatile fractions. If the minimum VOC and semivolatile levels for a given condition are summed, the minimum total emission is found; the maximum total can be found in a similar manner. As the most conservative estimate, consider the maximum total emission of organic HAPs. The maximum total baseline emission factor for organic HAPs is found to be 1.44 × 10^{-5} g/MJ (3.35 × 10^{-5} lb/10^6 Btu), while the maximum total for the stoichiometric ratio variation condition is 1.21 × 10^{-5} g/MJ (2.82 × 10^{-5} lb/10^6 Btu), and the low NO$_x$ maximum total is 1.70 × 10^{-5} g/MJ (3.94 × 10^{-5} lb/10^6 Btu).

It is important to place these values in proper perspective. As noted previously, a 9091 kg/year emission limit is placed on any single pollutant listed as hazardous under Title III of the CAAA, or a 22 727 kg/year limit for any combination of listed pollutants. As a comparison, consider the 22 727 kg annual limit for a large coal-fired electricity generating unit. Assuming a 1000 MW(e) unit with a 34% thermal efficiency (10 000 Btu kW^{-1} h^{-1} heat rate), 50% capacity factor, [Capacity factor is calculated by dividing the plant output in kilowatt hours by (plant capacity in kilowatts times 8760 h/year).] and using the same coal with a heat content of 30 896 kJ/kg (13 295 Btu/lb), an annual emission of 22 727 kg/year would be reached with an average emission rate of 9.83 × 10^{-4} g/MJ (2.29 × 10^{-3} lb/10^6 Btu). This is almost 2 orders of magnitude greater than the maximum total measured average organic HAP emission level (measured for the low NO$_x$ combustion condition). In addition, altering combustion conditions has a relatively small effect on total organic emissions. Although the increase in maximum total emissions is approximately 40% from SR variation condition to low NO$_x$, the absolute increase is only 4.84 × 10^{-6} g/MJ (1.13 × 10^{-5} lb/10^6 Btu). This translates to an increase of less than 1100 kg (500 lb)/year in total organic HAP emissions from the model plant described above, compared with an annual decrease of approximately 4.5 × 10^6 kg (9.9 × 10^6 lb) of NO. It must be emphasized that this comparison assumes that flue gas HAP concentrations from the model full-scale unit would be the same as in the small-scale tests. It should also be noted that for a given emission factor, the annual total mass emissions may vary significantly with size, thermal efficiency, or utilization levels of different sources.

The maximum total organic HAP emission rate of 1.70 × 10^{-5} g/MJ (3.94 × 10^{-5} lb/10^6 Btu) compares to an estimated maximum emission rate of metal HAPs of 2.99 × 10^{-3} g/MJ (6.93 × 10^{-3} lb/10^6 Btu). This figure is calculated by summing the measured trace metal concentrations and the detection limits of trace metals shown in Table 2. If only detectable metals are included in the calculation, the maximum metal HAP emission would be 1.70 × 10^{-3} g/MJ (3.93 × 10^{-3} lb/10^6 Btu). This figure includes chromium, lead, manganese, and nickel (all listed as HAPs under Title III). These values assume that all metals in the coal will be contained in the flue gases exiting the unit, and that these emissions are uncontrolled. The calculated emission level of detectable metal HAPs would then be above the 22 727 kg (25 t)/year rate for the model plant described above and would be roughly 100 times that of the maximum emission rate of organic HAPs. Note that these calculations show the relative levels of emissions and are not predictions of actual full-scale emission rates.

Discussion and Conclusions

The results of the combustion tests indicate that the combustion of coal does result in the emission of Title III listed organic HAPs and that the use of low-NO$_x$ combustion modifications causes increased emissions of such compounds. The total emission rate of these compounds is likely to be very low and is likely to be significantly less than the rate of metal HAP emissions. However, these conclusions must be made with some important caveats.

First, the experimental conditions and the scale of the equipment do not exactly mimic full-scale units. The high CO levels of the baseline test condition initially were of concern, since CO is typically a good indicator of incomplete combustion. In addition, the low feed rates of coal used in the experiments were also an area of concern, since it was questioned whether combustion zone temperatures would be as high as those seen in a full-scale unit. Second, the emission factor values presented in Tables 4 and 6 must not be considered "actual" and should not be used to determine emissions from full-scale units. Differences in scale, combustion conditions, and coals may lead to significantly different emissions from individual plants; such differences may be either higher or lower than the tabulated values. Additionally, the relatively small volumes of flue gas collected make the precise quantification of individual compounds more difficult. The "minimum–maximum" approach provides the most accurate information on the levels of organic HAP emissions for these small-scale results. It should also be noted that the "total" organic levels reported here are not all the organic emissions, but rather the total sum of the target analytes. The actual total organic emissions may include compounds which are not extractable and which may represent a significant fraction of the total organic mass, but which cannot be identified using standard GC methods. However, the targeted compounds are an excellent indicator of the level of emissions of compounds listed as hazardous under Title III.

Further, the total organic HAP emission rate is very low when compared with the calculated maximum possible rate of metal HAP emissions, indicating that the major concern in the area of HAP emissions control is likely to be toxic metal emissions. Since the initial Title III requirements are based on total mass emissions, a comparison between the organic and metal HAP emission levels can be based only on mass. Studies have shown that metals

often form small particles which are likely to exit the furnace in the form of submicron fly ash; however, significant amounts of many metals are also captured in either bottom ash or slag and are not emitted even in systems lacking in particulate removal equipment (19–22). This behavior will reduce the ratio of metal to organic HAPs, although in an uncontrolled system, the metal HAPs will most likely still remain the largest fraction of total air toxic emissions for pulverized coals. Finally, these tests did not evaluate the effects of different coals. Changes in volatile versus fixed carbon content as well as other factors such as chlorine, nitrogen, or sulfur content may play a significant role in the types and amounts of organic compounds that are likely to be present in the combustion flue gases. However, it was beyond the scope of this project to include these effects.

When comparing these results to full-scale systems, the values presented above must account for the presence of pollution control equipment. Efficient particulate control equipment can reduce the emissions of metal HAPs by over 90%. Although some portion of the organic HAPs may adsorb to the particulate matter and be collected in an electrostatic precipitator (ESP) or other particulate control device, a significant fraction of these compounds will pass through uncollected due to the volatility of most organic species. The presence of a wet acid gas scrubbing system will probably provide additional control of organic compounds through absorption into the scrubber liquor. However, the organic compound measurements were taken at the exit of the primary combustion zone, and the analyses do not consider low-temperature downstream recombination of lower mass compounds into larger and often more hazardous materials. This phenomenon has been observed in municipal waste combustion systems, particularly for chlorinated dioxins and furans (23–25). It is quite possible that the presence of metals such as copper found in ESPs may well enhance the reformation of cyclic organics, leading to higher emissions than would be seen at the exit of the combustion section of the boiler.

While the findings of these experiments are not directly applicable to full-scale units, they do provide significant information as to the likelihood of organic HAP emissions from the combustion of pulverized coal. The trends in emissions from the small-scale combustor should hold for larger scale systems, making several conclusions possible. To the degree that the experiment's combustion environment adequately simulates that of a full-scale unit, it can be concluded that (1) organic HAP emissions from the combustion of pulverized coal are not likely to be excessive relative to Title III requirements, provided good furnace combustion conditions are maintained; (2) several HAPs not previously considered in most pulverized coal emission tests are likely to be present in pulverized coal flue gas streams, and a complete characterization of air toxic compounds should include many more compounds than are now typically considered; and (3) the inherent presence of chlorine in coal can result in emissions of chlorinated organic compounds from the combustion of pulverized coal, some of which have been shown to be participants in low-temperature formation of chlorinated dioxins and furans downstream of the combustion zone in municipal solid waste incinerators. These conclusions should be used as guidance in evaluating full-scale data and in planning future test programs at both full and pilot scales.

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