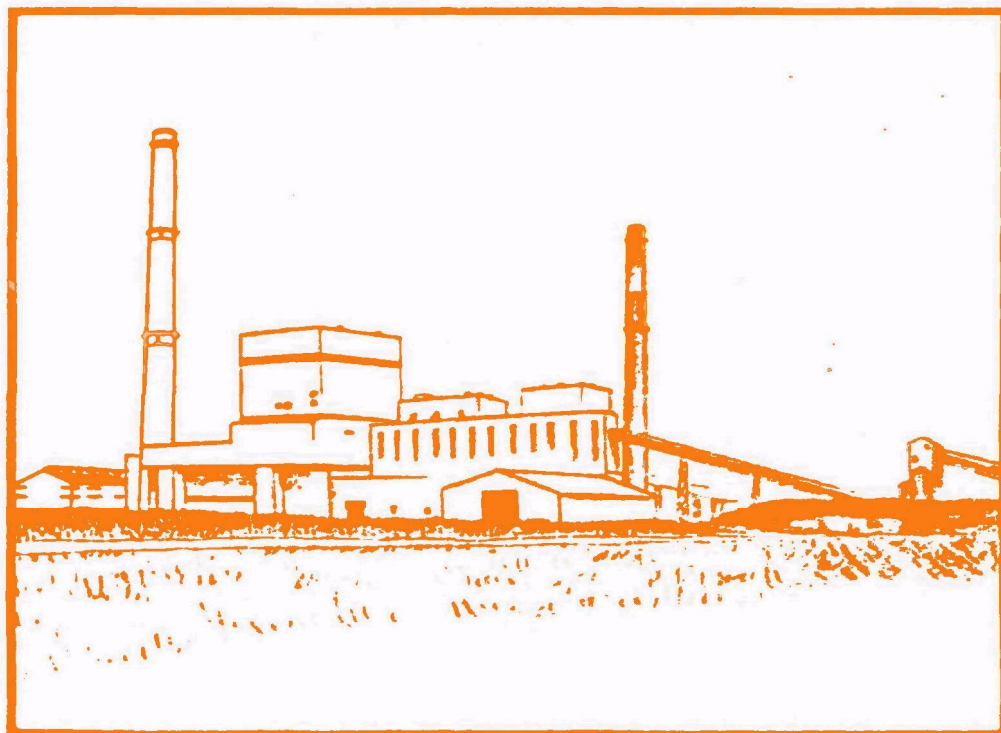




# **Comprehensive Assessment of the Specific Compounds Present in Combustion Processes**

## **Volume 4 National Estimates of Emission of Specific Compounds from Coal Fired Utility Boiler Plants**



COMPREHENSIVE ASSESSMENT OF THE SPECIFIC COMPOUNDS  
PRESENT IN COMBUSTION PROCESSES

VOLUME 4 - NATIONAL ESTIMATES OF EMISSION OF SPECIFIC COMPOUNDS  
FROM COAL FIRED UTILITY BOILER PLANTS

by

Robert M. Lucas  
George W. Kircher  
Research Triangle Institute

SPECIAL REPORT

EPA Prime Contract No. 68-02-3938  
Midwest Research Institute  
MRI Project No. 8501-A(1)

August 8, 1985.

Prepared for

U.S. Environmental Protection Agency  
Office of Pesticides and Toxic Substances  
Field Studies Branch  
401 M Street, S.W.  
Washington, DC 20460

Attn: Dr. Joseph J. Breen, Project Officer  
Mr. Daniel T. Heggem, Work Assignment Manager

#### DISCLAIMER

This document has been reviewed and approved for publication by the Office of Toxic Substances, Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency. The use of trade names or commercial products does not constitute Agency endorsement or recommendation for use.

## PREFACE

The research and preparation of the draft of this report was performed for the U.S. Environmental Protection Agency under Contract No. 68-01-5848, Research Triangle Institute Project No. 1864-25. Mr. Joseph Carra was the Contract Officer and Mr. Jerry Feinstein was the Task Manager. The final revisions and preparations of this final report were completed by Research Triangle Institute under subcontract to Midwest Research Institute under Prime Contract No. 68-02-3938.

MIDWEST RESEARCH INSTITUTE

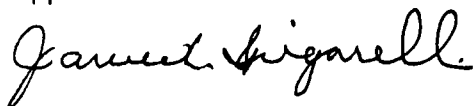


Clarence L. Haile  
Deputy Program Manager



John E. Going  
Program Manager

Approved:



James L. Spigarelli, Director  
Chemical and Biological Sciences  
Department

## CONTENTS

	<u>Page</u>
I. Executive Summary . . . . .	1
II. Introduction . . . . .	1
A. Background. . . . .	1
B. Overview. . . . .	2
III. Survey Design of Coal Combustion Study . . . . .	2
A. Overview. . . . .	2
B. Target Population . . . . .	2
C. Sample Selection and Stratification . . . . .	3
D. Specimen Acquisition (Sampling) Plans . . . . .	6
IV. Overview of Chemical Analysis Results. . . . .	6
A. Target Compounds. . . . .	6
B. Qualitative Summary of the Data . . . . .	6
V. Summary of Emissions Data. . . . .	10
A. Overview. . . . .	10
B. Summary of Flue Gas Emissions . . . . .	10
VI. References . . . . .	18
Appendix A - Statistical Methods . . . . .	19

## TABLES

<u>Number</u>		<u>Page</u>
1	Strata of the Coal Combustion Survey and Sum of Size Measures (in millions of tons). . . . .	6
2	Media Sampled by Plant. . . . .	8
3	Target Polynuclear Aromatic Hydrocarbons and Phthalates . . .	10
4	Detection of PAHs by Facility and Media . . . . .	11
5	Detection of Phthalates by Facility and Media . . . . .	12
6	Method Detection Limits for PCDDs and PCDFs for 5-Day Composite Specimens . . . . .	13
7	Detection of PCBs by Facility and Media . . . . .	15
8	Method Detection Limits for PCB Isomers by Media. . . . .	16
9	Average Emission Rates (g/hr) of Selected Compounds in the Flue Gases by Facility. . . . .	18
10	Estimates of Average National Emission Rates (g/hr) of Selected Target Compounds . . . . .	19
11	Summary of Total National Annual Emission of Selected Target Compounds for Coal-Fired Utility Boilers. . . . .	20

## FIGURES

<u>Number</u>		<u>Page</u>
1	Geographic strata of the coal combustion survey design. . .	5

## I. EXECUTIVE SUMMARY

Specimens were acquired from influents and effluents from seven coal-fired utility boilers. The specimens were chemically analyzed for toxic compounds in the polycyclic organic matter group. The specific target compounds were polychlorinated dibenzo[p]dioxins (PCDDs), dibenzofurans (PCDFs), biphenyls (PCBs), selected polynuclear aromatic hydrocarbons (PAHs) and selected phthalates. Twelve PAH compounds and six phthalate compounds were included among the targetted compounds.

No PCDDs or PCDFs were detected in any of the acquired specimens. PCBs were found in the flue gas emissions from each of the seven plants. The average emission rate for the industry was estimated to be 1.12 g/h for each boiler unit. The total annual national emissions of the industry was estimated to be 7,500 kg. PCBs were only detected in one other media, the influent combustion air.

Naphthalene was the most prevalent PAH compound detected. It was found in the flue gas emissions from all seven facilities. The estimated average emission rate was 1.6 g/h and estimate total national annual emissions was 11,000 kg. Other PAHs were also detected in the coal at all seven facilities but were only rarely detected in the other media.

Bis(2-ethylhexyl)phthalate was the most frequently detected phthalate compound. It was detected in the flue gas emissions from all seven facilities. The estimated average emissions rate was 17.5 g/h and the estimated total annual national emissions was 104,000 kg. Phthalates were sparsely detected in the other media.

## II. INTRODUCTION

### A. Background

The emission of several toxic compounds in the polycyclic organic matter (POM) group, specifically polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and biphenyls (PCBs) have been reported from stationary conventional combustion processes (DC-USA 1978, Olie et al. 1978 and Shin 1979). These compounds are proposed to be ubiquitous in the aqueous environment and it has been claimed that POMs are ubiquitous in air and are being formed from many combustion sources (DC-USA 1978).

A study conducted for the U.S. Environmental Protection Agency (EPA) (Shin 1979) demonstrates that a theoretical potential exists for POMs to be formed during and as a result of conventional combustion processes. These POMs may include PCDDs, PCDFs, and PCBs. The major combustion sources are suspected to involve such fuels as coal-refuse, wood, municipal refuse, waste oil, and coal.

Because the acquisition of field specimens and their chemical determination are very costly, carefully planned studies were needed to ascertain

the level and prevalence of the substances being emitted into the environment. Because inadequate data were available on which to base a statistical design for a national survey, a pilot study was specifically designed and conducted to generate the appropriate data.

A description of the pilot study and its results can be found in a report to the U.S. Environmental Protection Agency (USEPA) Office of Pesticides and Toxic Substances (Haile et al. 1983a) and references therein. A detailed description of the statistical analysis of the data collected in the pilot study and the survey design for part of a nationwide survey of combustion sources is presented in another report to the USEPA Office of Toxic Substances (Lucas and Melroy 1985).

#### B. Overview

This report summarizes estimates of the prevalence and levels of organic emissions from large coal-fired electricity generating facilities as part of a nationwide effort to ascertain organic emissions from major stationary combustion sources. The principal compounds of interest are polynuclear aromatic hydrocarbons, phthalates and chlorinated aromatic compounds, including polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs).

Chapter III reviews the survey design employed to select sample facilities and describes the general sampling plans used to determine sampling points and frequencies. Chapter IV presents the specific compounds targeted for chemical analysis. Chapter V gives the statistical summary of the emissions results. The technical discussion of the statistical analysis of the data is given in Appendix A.

### III. SURVEY DESIGN OF COAL COMBUSTION STUDY

#### A. Overview

The results given in this report are for large (greater than  $10^8$  BTU/h) coal-fired utility boiler facilities. Other types of coal burning facilities and other facilities using different fuels were excluded from this phase of the study. This section summarizes the statistical design used to select facilities in the sample. The survey design was developed under another contract and was originally documented in another report. The final report was prepared under subcontract to Midwest Research Institute (Lucas and Melroy 1985). This section describes aspects of the survey design that directly impact on the statistical analysis of the data.

#### B. Target Population

The target population for this phase of the combustion study is all coal burning utility boiler facilities greater than  $10^8$  BTU/h. To obtain a sample of the target population, a sampling frame (inventory of facilities) was constructed from the National Emissions Data Systems (NEDS) computer file. A listing of the frame can be found in the design report (Lucas and Melroy

1985). For the purposes of this study, each point source of emissions was considered as a sampling unit. Hence, a facility with more than one stack was considered to be more than one sampling unit.

Potential for biases result from facilities in the target population that are not included on the frame. Also, inefficiencies could possibly result from ineligible facilities (units not in the target population) being included on the frame. Investigations to assess the magnitude of these potential problems were planned. However, because of funding limitations, the investigation was not performed. Because the NEDS file was updated routinely, particularly for large facilities, the frame is felt to be substantially complete.

### C. Sample Selection and Stratification

Because of the expense of sampling and chemical analysis, the sample was necessarily limited to one point source at each of the seven facilities. The facilities were sampled for five consecutive days. Because of the small sample size, an efficient sampling plan was very important to obtain the most information about total emissions from such plants in the U.S. from the limited data. An accurate size measure is useful in both the allocation of samples and the selection of samples, for improving study efficiency. Because the total emissions was felt to be highly correlated with the amount of coal burned by each plant, the number of tons of coal burned annually was chosen as the measure of size of each point source. In order to disperse the sample geographically, the U.S. was partitioned into seven groups (strata) of contiguous States. The groups were arranged so that the sum of all the size measures (reported or estimated amount of coal burned annually in such facilities in the stratum) were approximately equal. Table 1 lists the States in each stratum and the sum of the size measures for each State and stratum. Figure 1 illustrates the strata.

One point source was selected at random from each stratum. The probability of its selection was proportional to its size measure. This increased the likelihood that the sample would contain a disproportionate number of large emission sources.

Using a random selection technique results in estimates of the emissions that are not subject to biases of the type that typically result from judgement sampling. Also, such samples permits valid estimates of the precision of the survey results, that is, confidence intervals based on the survey data will give ranges for the true emission values. During the planning stages of the study, sampling of facilities in at least two combustion categories, coal-fired boilers and refuse incinerators, was envisioned. Because the number of coal-fired facilities was small (only 7), the precision of estimates for that category was anticipated to be  $\pm 50$  to  $\pm 60$  percent. When other combustion categories are investigated, their results can be combined with the results of the present study to estimate emissions from their union. Precision of these combined estimates is anticipated to be improved.

Table 1. Strata of the Coal Combustion Survey and Sum of Size Measures  
(in millions of tons)

North East	79.5		North Central	75.0
Maine		0.0	Minnesota	12.1
New Hampshire		0.8	Iowa	8.9
Vermont		0.0	Missouri	21.2
Massachusetts		0.0	Illinois	32.8
Rhode Island		0.0		
Connecticut		0.0	South Central	63.6
New York		6.3	Tennessee	22.0
New Jersey		2.4	Mississippi	1.6
Pennsylvania		38.5	Arkansas	7.0
Delaware		0.7	Louisiana	4.5
District of Columbia		0.0	Oklahoma	2.1
Maryland		4.4	Texas	26.1
West Virginia		25.8		
South East	72.5		West	69.9
Virginia		4.8	North Dakota	7.5
North Carolina		20.4	South Dakota	2.4
South Carolina		7.8	Nebraska	1.9
Georgia		17.7	Kansas	7.1
Florida		6.1	Montana	3.2
Alabama		16.7	Wyoming	16.2
			Colorado	8.8
Ohio Valley	74.5		New Mexico	8.0
Ohio		44.9	Idaho	0.0
Kentucky		30.0	Utah	2.5
			Arizona	1.6
Great Lakes	64.2		Washington	4.2
Michigan		21.3	Oregon	0.0
Indiana		31.2	Nevada	4.0
Wisconsin		11.7	California	0.0
			Alaska	0.5
			Hawaii	0.0

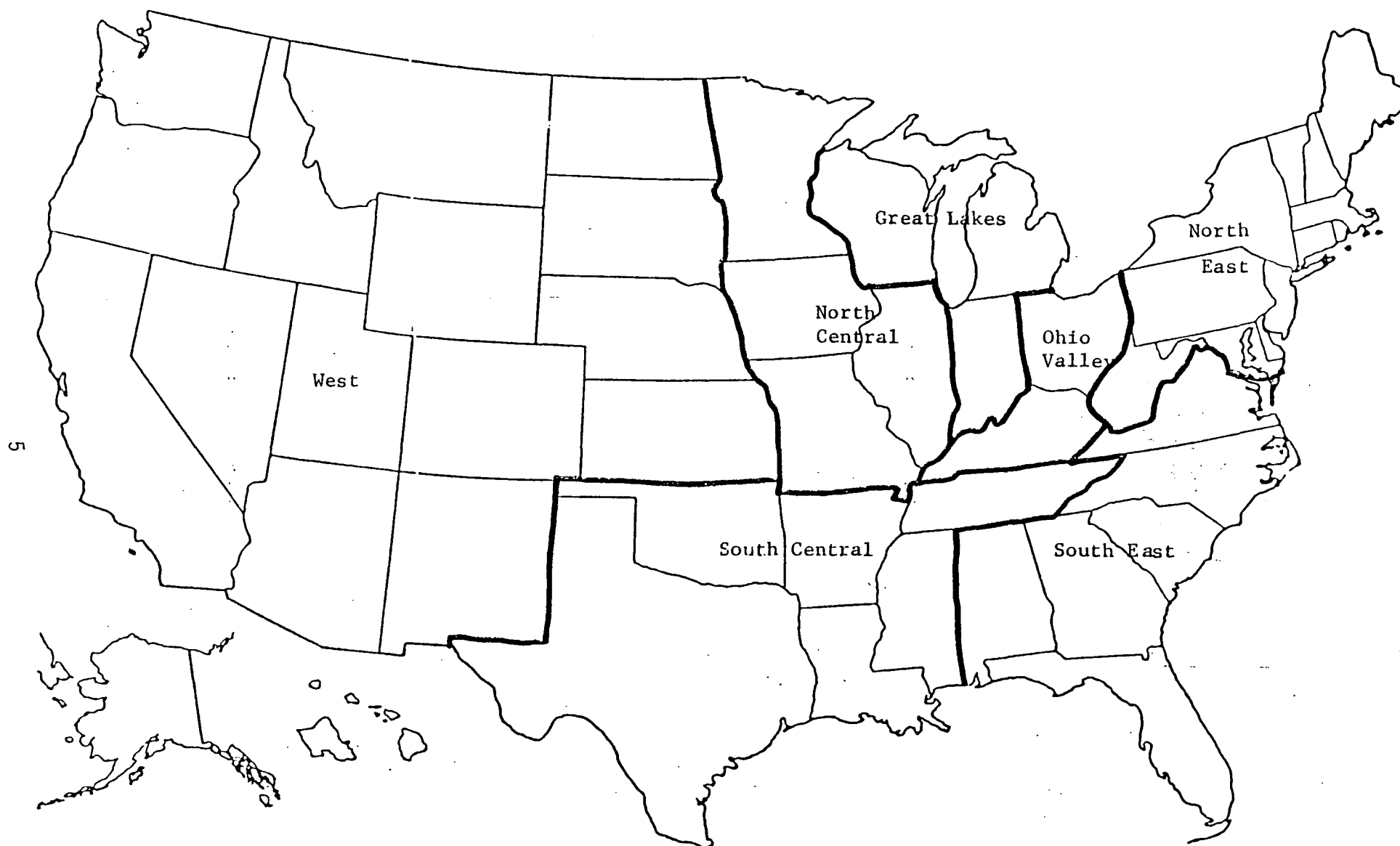


Figure 1. Geographic strata of the coal combustion survey design.

#### D. Specimen Acquisition (Sampling) Plans

Specimens were acquired for 5 days from each point source selected in the sample. The specimen acquisition plans were based on the pilot study that is described in detail in the design report (Lucas and Melroy 1985). In general, the plan involved a complex multimedia design to collect specimens of solid, liquid, and gaseous influents and effluents. Measurements of process parameters were also recorded during the sampling periods.

All point sources had similar process flows of influents and effluents. However, each source was sufficiently unique to require site specific adaptations of the general plan. The details of the site specific plans for facilities are given in a report to the USEPA Office of Pesticides and Toxic Substances (prepared by MRI (Haile et al. 1983b)). Table 2 presents a concise summary of the media from which specimens were acquired by facility.

### IV. OVERVIEW OF CHEMICAL ANALYSIS RESULTS

#### A. Target Compounds

The study objective was to estimate the total emissions of organic compounds from major stationary combustion sources. The specific compounds of interest belong to three general categories, polynuclear aromatic hydrocarbons (PAHs) phthalates and chlorinated aromatic compounds (CACs). The specific PAHs and phthalates targeted in the chemical analysis are given in Table 3. The specific CACs are PCBs, PCDPs, and PCDFs.

The reader interested in a detailed presentation of the chemical analysis results is referred to the MRI reports (Haile et al. 1983b) previously mentioned. In the sections below, only a qualitative summary of the data is presented to give a feel for the frequencies of which classes of compounds were detected. Chapter V presents the summary of the estimated emissions of the target compounds of the study for which a consequential amount of data was collected.

#### B. Qualitative Summary of the Data

##### 1. Polynuclear Aromatic Hydrocarbons

At least one of the PAH target compounds was found in flue gas specimens collected at all seven facilities. They were found much less frequently in the other effluent media. Table 4 presents the facilities and media at which PAHs were detected. Naphthalene was the only PAH detected at all seven facilities. Phenanthrene was found at all facilities except No. 5. Four compounds, acenaphthene, benzo[k]fluoranthene, dibenz[a,h]anthrene and benzo[g,h,i]perylene were not detected in the flue gas at any of the seven facilities. The other compounds were detected in from two to five facilities.

Table 2. Media Sampled by Plant

		Facility Number						
		1	2	3	4	5	6	7
Influents	Air	S	S	S	S	S	S	S
	Water	S <sup>a</sup>	S <sup>b</sup>	S	S	S	S	S <sup>e</sup>
	Coal	S	S	S	S	S	S	S
Effluents	Flue gas	S	S	S	S	S	S	
	Water	S <sup>c</sup>	S <sup>c</sup>	NS	S <sup>d</sup>	S <sup>d</sup>	S <sup>d</sup>	S <sup>d</sup>
	Fly ash	S	S	S	S	S	S	S
	Bottom ash	S	S	S	S	S	S	S
	Economizer ash	NS	NS	NS	NS	NS	NS	S

Note: S denotes media from which samples were acquired; NS denotes media for which no samples were acquired.

<sup>a</sup>Make-up water and influent water to bottom ash hopper.

<sup>b</sup>Influent river water and boiler seal water.

<sup>c</sup>Overflow water.

<sup>d</sup>Sluice water collected simultaneously with bottom ash.

<sup>e</sup>Quench water from cooling tower.

Table 3. Target Polynuclear Aromatic Hydrocarbons and Phthalates

Category	Compounds
Polynuclear aromatic hydrocarbons	Naphthalene Acenaphthylene Acenaphthene Fluorene Phenanthrene Fluorathene Pyrene Chrysene Benzo[k]fluoranthene Benzo[a]pyrene Dibenz[a,h]anthracene Benzo[g,h,i]perylene
Phthalates	Dimethyl phthalate Diethyl phthalate Di-n-butyl phthalate Butylbenzyl phthalate Bis(2-ethylhexyl) phthalate Di-n-octyl phthalate

Table 4. Detection of PAHs by Facility and Media

Media	Facility number						
	1	2	3	4	5	6	7
Influents							
Air	ND	ND	ND	ND	ND	D	ND
Water	ND	ND	ND	ND	D	D	D
Coal	D	D	D	D	D	D	D
Efluents							
Flue gas	D	D	D	D	D	D	D
Water	ND	ND	-	ND	D	D	ND
Fly ash	ND	ND	ND	ND	ND	ND	ND
Bottom ash	ND	ND	ND	ND	D	ND	D
Economizer ash	-	-	-	-	-	-	D

Legend: D denotes detection of one or more of PAH target compounds.

ND denotes no PAH target compound detected.

- indicates media for which no specimens were acquired.

Source: Compiled by the Research Triangle Institute from information supplied by the Midwest Research Institute.

## 2. Phthalates

At least one of the phthalate target compounds was detected in the flue gas from each of the seven facilities. Bis(2-ethylhexyl) phthalate was detected at all seven facilities. Dimethyl phthalate (the least frequently detected) was detected at the plants 1, 6, and 7. The other phthalate compounds were detected at four of the seven facilities. Table 5 summarizes the detection of phthalates by facility and media.

## 3. Chlorinated Aromatic Hydrocarbons

No PCDDs or PCDFs were detected in any of the media sampled from any plant. Table 6 gives the method detection limits for these compounds by media. PCBs were detected in the flue gas specimens collected from each of the seven facilities. PCBs were detected in the influent air (combustion) at six of the seven facilities. Facility number 3 was the only one for which no PCBs were detected in the influent air. PCBs were not detected in any of the other media from which specimens were acquired. Table 7 presents the detection of PCBs by facility and media. Table 8 presents the method detection limits for PCBs by media.

# V. SUMMARY OF EMISSIONS DATA

## A. Overview

This chapter summarizes emission results of selected target PAHs, phthalate compounds and PCBs. PAH or phthalate compounds that were rarely detected are excluded from the summaries. Also, because of the small sample size, estimates for even the frequently detected compounds are less precise than is usually desirable. The emissions are summarized by calculating several intervals for estimates of the true emission rates. These intervals will have different confidence levels (probability of coverage) ranging from 50 to 95 percent.

## B. Summary of Flue Gas Emissions

Table 9 summarizes the average emission rates of PCBs and PAHs, and phthalates detected during the study by facility. Table 10 summarizes the data of selected compounds given in Table 9. Only compounds detected at four or more facilities are included. Table 11 summarizes the estimated total annual emissions of selected target compounds. The statistical methods used to calculate the estimates are based on theory presented in Hansen et al. (1953) and described in Appendix A.

Table 5. Detection of Phthalates by Facility and Media

Media	Facility number						
	1	2	3	4	5	6	7
Influents							
Air	ND	ND	ND	ND	ND	D	ND
Water	ND	ND	ND	ND	D	D	ND
Coal	ND	ND	ND	ND	D	D	ND
Efluents							
Flue Gas	D	D	D	D	D	D	D
Water	ND	ND	-	ND	D	D	D
Fly ash	ND	ND	ND	ND	D	D	D
Bottom ash	ND	ND	ND	ND	ND	D	ND
Economizer ash	-	-	-	-	-	-	D

Legend: D denotes detection of one or more of phthalate target compounds.  
 ND denotes no phthalate target compound detected.  
 - indicates media for which no specimens were acquired.

Source: Compiled by the Research Triangle Institute from information supplied by the Midwest Research Institute.

Table 6. Method Detection Limits for PCDDs and PCDFs for  
5-Day Composite Specimens

Sample Type	Units	Dioxin and furan isomers			
		Cl <sub>1</sub> -Cl <sub>3</sub>	Cl <sub>4</sub>	Cl <sub>5</sub> , Cl <sub>6</sub>	Cl <sub>7</sub> , Cl <sub>8</sub>
Flue gas <sup>a</sup>	pg/dscm	250	100	500	700
Bottom ash <sup>b</sup>	pg/g	25	10	50	70
Fly ash <sup>b</sup>	pg/g	25	10	50	70
Economizer ash <sup>b</sup>	pg/g	25	10	50	70
Plant background air <sup>c</sup>	pg/dscm	50	20	100	140
Aqueous samples <sup>d</sup>	pg/ℓ	500	200	1,000	1,400

Source: Reproduced from a report to the U.S. EPA Office of Pesticides and Toxic Substances prepared by the Midwest Research Institute (Haile et al. 1983b).

<sup>a</sup>All flue gas specimen diluted 1:10 for HRGC/MS-SIM analysis. The 5-day composite was calculated as equivalent to 10 dscm.

<sup>b</sup>The 5-day composite is equivalent to a 100-g specimen.

<sup>c</sup>The 5-day composite is equivalent to a 50-dscm specimen.

<sup>d</sup>The 5-day composite is equivalent to a 5-ℓ specimen.

Table 7. Detection of PCBs by Facility and Media

Media	Facility number						
	1	2	3	4	5	6	7
Influents							
Air	D	D	ND	D	D	D	D
Water	ND	ND	ND	ND	ND	ND	ND
Coal	ND	ND	ND	ND	ND	ND	ND
Efluents							
Flue gas	D	D	D	D	D	D	D
Water	ND	ND	-	ND	ND	ND	ND
Fly ash	ND	ND	ND	ND	ND	ND	ND
Bottom ash	ND	ND	ND	ND	ND	ND	ND
Economizer ash	-	-	-	-	-	-	ND

Legend: D denotes PCBs detected.

ND denotes PCBs not detected.

- indicates media for which no specimens were acquired.

Source: Compiled by the Research Triangle Institute from information supplied by the Midwest Research Institute.

Table 8. Method Detection Limits for PCB Isomers by Media

Sample type	Detection limit
Bottom ash <sup>a</sup>	1 ng/g
Fly ash <sup>a</sup>	1 ng/g
Economizer ash <sup>a</sup>	1 ng/g
Aqueous samples <sup>b</sup>	20 ng/l
Plant background air <sup>c</sup>	2 ng/dscm

Source: Reproduced from a report to the U.S. EPA Office of Pesticides and Toxic Substances prepared by the Midwest Research Institute (Haile et al. 1983b).

<sup>a</sup>Five-day composite equivalent to a 100-g specimen.

<sup>b</sup>Five-day composite equivalent to a 5-L specimen.

<sup>c</sup>Five-day composite equivalent to 50 dscm.

Table 9. Average Emission Rates (g/hr) of Selected Compounds  
in the Flue Gases by Facility

	Facility number						
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7
PCBs	8.5	0.40	≤ 0.005	3.1	0.048	0.32	0.031
Napthalene	1.4	1.5	0.470	1.7	5.0	2.7	0.58
Acenaphthylene	0.038	0.072					
Fluorene	0.036	0.12		0.035			0.003
Phenanthrene	0.81	1.8	0.045	0.25		0.20	0.061
Fluoranthene	0.19	0.21		0.047			
Pyrene	0.088	0.058					
Chrysene	0.034	0.16		0.11	0.005	0.033	
Benzo[a]pyrene	0.007						
Dimethylphthalate	0.039					0.16	0.017
Diethylphthalate	25	4.6	0.62	9.6			
Di[n]butyl- phthalate	23	13	0.019	0.60			
Butylbenzyl- phthalate	3.4	0.92	0.21	0.55			
Bis(2-ethylhexyl)- phthalate	41	0.86	11	16	57	15	6.7
Di[n]octyl- phthalate	10				2.2		

Source: Report to the U.S. EPA Office of Pesticides and Toxic Substances by  
the Midwest Research Institute (Haile et al. 1983b).

Table 10. Estimates of Average National Emission Rates per Plant (g/h) of Selected Target Compounds

Compound	Mean	Standard deviation	Median	Confidence intervals			
				50%	75%	90%	95%
PCBs	1.12	0.66	0.32	( 0.63 , 1.62 )	( 0.23 , 2.02 )	*	*
Naphthalene	1.76	0.32	1.5	( 1.52 , 1.99 )	( 1.33 , 2.18 )	(1.08, 2.43)	(0.88, 2.64)
Fluorene	0.021	.012	0.0	( 0.012, 0.030)	( .005, .037)	*	*
Phenanthrene	0.35	0.15	0.20	( 0.23 , 0.46 )	( 0.14 , 0.55 )	(0.02, 0.67)	*
Chrysene	0.046	0.022	0.033	( 0.029, 0.062)	( 0.016, 0.075)	*	*
Diethylphthalate	3.72	1.94	0.62	( 2.28 , 5.16)	( 1.12 , 6.32 )	*	*
Di[n]butyl phthalate	2.91	0.12	0.019	( 2.82 , 3.00)	( 2.75 , 3.07 )	(2.66, 3.16)	(2.58, 3.24)
Butylbenzyl phthalate	0.45	0.13	0.21	( 0.35 , 0.55)	( 0.27 , 0.63 )	(0.16, 0.74)	(0.08, 0.82)
Bis(2-ethylhexyl) phthalate	17.5	4.41	15	(14.3 , 20.8 )	(11.6 , 23.4 )	(8.1 , 26.9 )	(5.3 , 29.8 )

\* These entries were excluded where the calculation would result in inadmissible results. For example, the normal 90% confidence interval for PCBs is (-0.29, 2.53). The lower bound being less than zero implies that the data is too variable to accept the validity of the 90 percent confidence statement.

Table 11. Summary of Total National Annual Emission of Selected Target Compounds for Coal-Fired Utility Boilers

Compound	Mean (kg)	Standard deviation (kg)	Confidence interval			
			50%	75%	90%	95%
PCBs	7,500	4,400	( 4,200, 10,000)	( 1,500, 13,400)	*	*
Naphthalene	11,000	2,000	( 9,200, 12,000)	( 8,000, 13,000)	( 6,700, 15,000)	( 5,100, 16,000)
Fluorene	140	51	( 100, 180)	( 72, 210)	( 32, 250)	*
Phenanthrene	2,200	980	( 1,500, 2,900)	( 900, 3,500)	( 100, 4,300)	*
Chrysene	300	150	( 190, 410)	( 100, 500)	*	*
Diethylphthalate	25,000	18,000	(12,000, 38,000)	(10,000, 49,000)	*	*
Di[n]butyl phthalate	19,000	670	(18,500, 19,500)	(18,000, 20,000)	(17,500, 20,500)	(17,000, 21,000)
Butylbenzyl phthalate	2,900	790	( 2,300, 3,500)	( 1,800, 4,000)	( 1,200, 4,600)	( 700, 5,100)
Bis(2-ethylhexyl) phthalate	104,000	31,000	(81,000, 127,000)	(63,000, 145,000)	(38,000, 170,000)	(19,000, 189,000)

\*These entries were excluded where the calculations would result in inadmissible results. For example, the nominal 90% confidence interval for PCBs is (-1,900, 16,900). The lower bound being less than zero implies that the data are too variable to accept the validity of the 90% confidence statement.

## VI. REFERENCES

DC-USA. 1978. Dow Chemical U.S.A. The trace chemistries of fire - A source of and routes for the entry of chlorinated dioxins into the environment. The Chlorinated Dioxin Task Force, the Michigan Division.

Haile CL, Stanley JS, Lucas RM, Melroy DK, Nulton CP, Yauger WL, Jr. 1983a. Comprehensive assessment of the specific compounds present in combustion processes: Vol. 1. Pilot study of combustion emission variability. Final report. Environmental Protection Agency. Contract 68-01-5915. EPA 560/5-83-004, NTIS PB-84-140-870.

Haile CL, Stanley JS, Walker T, Cobb GR, Boomer BA. 1983b. Comprehensive assessment of the specific compounds present in combustion processes. Volume 3. National survey of organic emissions from coal-fired utility plants. EPA Publication EPA-560/5-83-006.

Hansen MH, Hurwitz WN, Madow WG. 1953. Sample survey methods and theory. Vol. I. John Wiley and Sons.

Lucas RM, Melroy DK. 1985. A survey design for refuse and coal combustion processes. Research Triangle Institute, Research Triangle Park, NC. RTI/1864/11-01F. Prepared under subcontract PO No. 71180 for Midwest Research Institute, Kansas City, MO.

Olie K, Vermeulen PL, Hutzinger O. Chlorodibenzo-p-dioxins and chlorodibenzofurans are trace components of fly ash and flue gas of some municipal incinerators in The Netherlands. Chemosphere. 2. p. 105-172.

Shin C, Ackerman D, Scinto L, Moon E, and Fishman. 1979. POM emissions from stationary conventional combustion processes with emphasis on polychlorinated compounds of dibenzo-p-dioxin (PCDD's), biphenyl (PCB's) and dibenzofuran (PCDF's). Draft report prepared by TRW, Inc. for the U.S. Environmental Protection Agency.

APPENDIX A  
STATISTICAL METHODS

## OVERVIEW

The purpose of this appendix is to supplement the materials presented in Chapter V of the text.

### A. Estimation of Means and Totals

Because the facilities in the study were selected with probability proportional to their size, the calculation of statistical estimates must incorporate this probability. Let  $Z(i)$  denote an observation from plant  $i$ ,  $i = 1, \dots, 7$ . Then the estimated total of the  $Z$ 's is calculated using the formula:

$$\hat{Z} = \sum_{i=1}^7 W(i)Z(i) \quad (A.1)$$

where  $W(i)$  is the sampling weight, the inverse of the probability that facility  $i$  was selected in the sample. The probability that unit  $i$  was selected in the sample was calculated using the expression

$$S(i)/S^+(i) \quad i = 1, 2, 3, \dots, 7$$

where  $S(i)$  denotes the size measure for the facility selected in stratum  $i$  and  $S^+(i)$  denotes the sum of all the size measures for facilities in stratum  $i$ . The sampling weights are given in Table A.1. To estimate the total annual emission, the average hourly emission rate for plant  $i$  (say  $X(i)$ ) is multiplied by  $H(i)$  (the total annual operating hours given in Table A.1) and substituted into equation A.1 for  $Z(i)$ . This was done for the targeted compounds with sufficient information to produce reliable information. The summary of the total annual emissions is given in Table 11 in the text.

To estimate the average hourly emission rate,  $X(i)$  is directly substituted for  $Z(i)$  in equation A.1 and the result divided by the sum of the weights, giving the equation

$$\bar{Z} = \left( \sum_{i=1}^7 W(i)Z(i) \right) / \left( \sum_{i=1}^7 W(i) \right) \quad (A.2).$$

To estimate the proportion of the plants emitting detectable levels, an indicator (define 0 for not detect or 1 for detected) random variable can be substituted for  $Z(i)$ .

Table A.1 Sampling Weights and Operating Hours Per Year  
for the Seven Study Facilities

Facility number	Sampling <sup>a</sup> weight	Operating <sup>b</sup> hours/year
(i)	(W(i))	(H(i))
1	45.93	8,400
2	87.10	8,400
3	226.46	7,200
4	125.42	8,736
5	68.11	6,552
6	175.16	8,064
7	50.61	8,736

<sup>a</sup>Calculated by the Research Triangle Institute from the probability mechanism used to select the sample.

<sup>b</sup>Obtained from the National Emission Data System (NEDS) computerized data file.

### B. Variance Estimation

Because of the small sample size of one facility per stratum, a variance approximation suggested by Hansen et al. (1953) was used to estimate the variance of the total annual emissions and average emission rate. The equation is

$$V^2(\hat{Z}) = \sum_{g=1}^3 (L(g)/(L(g)-1)) \sum_{h=1}^{L(g)} (Y(g,h) - A(g,h) Y(g,+)/A(g,+))^2. \quad (A.3)$$

The terms in the expression are defined and their values given in Table A.2. This essentially involves collapsing the seven strata into three groups of 2, 2, and 3 facilities. To estimate the variance of  $\bar{Z}$ , equation A.3 is used with  $Z(i) = H(i)X(i)$ . To estimate the variance of  $\bar{Z}$ , the equation

$$V^2(\bar{Z}) = V^2(\hat{Z}) / \left( \sum_{i=1}^7 W(i) \right)^2$$

is used where  $Z(i) = X(i)$ .

### C. Interval Estimator

Confidence intervals are estimated using the expression:

$$(\hat{Z} - V(\hat{Z})t(\alpha,4) \quad , \quad \hat{Z} + V(\hat{Z})t(\alpha,4))$$

or

$$(\bar{Z} - V(\bar{Z})t(\alpha,4) \quad , \quad \bar{Z} + V(\bar{Z})t(\alpha,4))$$

where  $\hat{Z}$ ,  $\bar{Z}$ ,  $V(\hat{Z})$ , and  $V(\bar{Z})$  are given above. The  $t(\alpha,4)$  denotes the table value of students t distribution with 4 degrees of freedom. The degrees of freedom are calculated by taking the number of strata (7) minus the number of groups (3).

Table A.2 Definition and Values of Terms for Equation A.3

Facility Number	$g^a$	$h^b$	$L(g)^c$	$Y(g,h)^d$	$A(g,h)^e$
1	2	1	2	Z(1)	69.9
2	2	2	2	Z(2)	72.5
3	3	1	2	Z(3)	64.2
4	1	1	3	Z(4)	74.5
5	1	2	3	Z(5)	79.5
6	1	3	3	Z(6)	75.0
7	3	2	2	Z(7)	63.6

<sup>a</sup> $g$  denotes the group number

<sup>b</sup> $h$  denotes the unit number within group  $g$

<sup>c</sup> $L(g)$  denotes the number of units in group  $g$

<sup>d</sup> $Y(g,h)$  denotes the values of the  $Z$  renumbered by group and unit within group.

$Y(g,+)$  denotes the sum of the  $Y(g,h)$  over the levels of  $h$  in group  $g$ .

<sup>e</sup> $A(g,h)$  is the size measure of the stratum renumbered by group and unit within group.  $A(g,+)$  denotes the sum of the  $Y(g,h)$  over the levels of  $h$  in group  $g$ .

<b>REPORT DOCUMENTATION PAGE</b>	<b>1. REPORT NO.</b> 560/5-83-007	<b>2.</b>	<b>3. Recipient's Accession No.</b>
<b>4. Title and Subtitle</b> Comprehensive Assessment of the Specific Compounds Present in Combustion Processes, Volume 4. National Estimates of Emission of Specific Compounds from Coal Fired Utility Boiler Plants			<b>5. Report Date</b> August 1985
<b>7. Author(s)</b> Robert M. Lucas and Denise K. Melroy			<b>6.</b>
<b>9. Performing Organization Name and Address</b> Midwest Research Institute with subcontract to Research Triangle Institute P.O. Box 12194 Research Triangle Park, NC 27709			<b>8. Performing Organization Rept. No.</b>
<b>12. Sponsoring Organization Name and Address</b> Field Studies Branch USEPA 401 M Street, S.W. Washington, DC 20460			<b>10. Project/Task/Work Unit No.</b> 1A
			<b>11. Contract(C) or Grant(G) No.</b> (C) 68-02-3938 (G)
<b>15. Supplementary Notes</b> J. J. Breen, Project Officer D. T. Heggem, Work Assignment Manager			<b>13. Type of Report &amp; Period Covered</b> Final
			<b>14.</b>
<b>16. Abstract (Limit: 200 words)</b> <p>Specimens were acquired from influents and effluents from seven coal-fired utility boilers. The specimens were chemically analyzed for toxic compounds in the polycyclic organic matter group. The specific target compounds were polychlorinated dibenzo[p]-dioxins (PCDDs), dibenzofurans (PCDFs), biphenyls (PCBs), selected polynuclear aromatic hydrocarbons (PAHs) and selected phthalates. Twelve PAH compounds and six phthalate compounds were included among the targetted compounds.</p> <p>Naphthalene was the most prevalent PAH compound detected. It was found in the flue gas emissions from all seven facilities. The estimated average emission rate was 1.6 g/h and estimate total national annual emissions was 11,000 kg. Other PAHs were also detected in the coal at all seven facilities but were only rarely detected in the other media.</p> <p>No PCDDs or PCDFs were detected in any of the acquired specimens. PCBs were found in the flue gas emissions from each of the seven plans. The average emission rate for the industry was estimated to be 1.12 g/h for each boiler unit. The total annual national emissions of the industry was estimated to be 7,500 kg. PCBs were only detected in one other media, the influent combustion air.</p>			
<b>17. Document Analysis a. Descriptors</b> <p>Combustion, Emission estimates, PAH, PCB, PCDD, PCDF</p> <p><b>b. Identifiers/Open-Ended Terms</b></p> <p><b>c. COSATI Field/Group</b></p>			
<b>18. Availability Statement</b> Release to Public		<b>19. Security Class (This Report)</b> Unclassified	<b>21. No. of Pages</b> 28
		<b>20. Security Class (This Page)</b> Unclassified	<b>22. Price</b>