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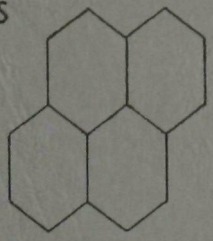
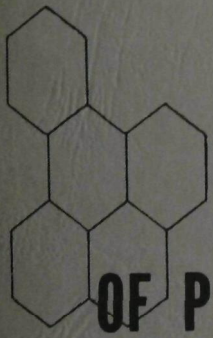
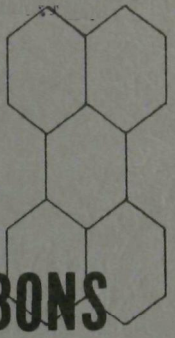
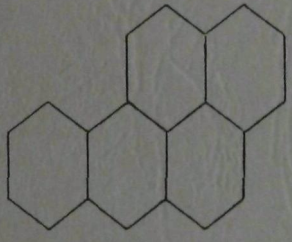
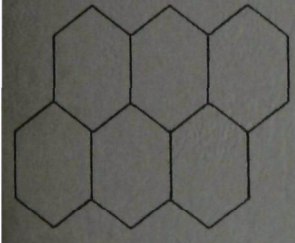


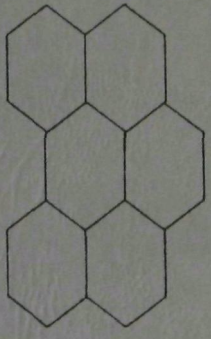


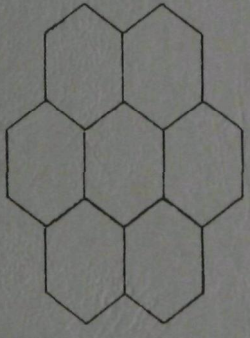


SOURCES OF POLYNUCLEAR HYDROCARBONS IN THE ATMOSPHERE









U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service

SOURCES OF POLYNUCLEAR HYDROCARBONS IN THE ATMOSPHERE

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ABSTRACT

Rates of emissions of polynuclear hydrocarbons were measured at several sources considered likely to produce such emissions. The sources included heat generation by combustion of coal, oil, and gas; refuse burning; industrial processes; and motor vehicles. The annual emissions of benzo(a)pyrene in the United States were estimated for each of the sources surveyed, to provide a rough gauge of the importance of each source. Small, inefficient residential coal-fired furnaces appear to be a prime source of polynuclear hydrocarbons; other sources may be of local importance. Production of polynuclear hydrocarbons was generally associated with conditions of incomplete combustion.

INTRODUCTION

Concern with the health effects of carcinogenic substances dates back at least to 1775, as reflected by the writings of Pott. [1] It was discerned that among persons employed as chimney sweeps in Europe the rate of skin cancer was higher than that of the general population. Since that time, considerable progress has been made in isolating and identifying individual compounds from many suspected cancer-causative agents such as soot and coal tar. The isolation of benzo(a)pyrene (3, 4-benzpyrene) from coal tar in 1933 [2] has particular significance. Although this compound has not been definitely identified as the etiological agent responsible for many of the so-called industrial cancers, laboratory experiments with animals have shown that it is one of the more biologically active organic compounds in the group termed "polynuclear hydrocarbons." The carcinogenic effects of benzo(a)pyrene on animals are well documented in the published literature. [3-5] The biological activities of the other polynuclear hydrocarbons discussed have been reported. Some of these compounds are weakly carcinogenic; some are not carcinogenic; some may inhibit or accelerate the activity of benzo(a)pyrene. [3, 6]

Surveys by the Public Health Service

In the late 1950's, the U.S. Public Health Service, Division of Air Pollution, surveyed concentrations of polynuclear hydrocarbons in the atmosphere of 103 urban and 28 nonurban areas of the United States.[7, 8] The air in all of the 103 urban areas contained benzo(a)pyrene. Concentrations ranged from 0.11 to 61 micrograms per 1000 cubic meters of air, with a geometric mean concentration of 6.6. Concentrations in nonurban areas were much lower, ranging from 0.01 to 1.9 micrograms per 1000 cubic meters, with a geometric mean concentration of 0.4. The relatively large quantities found in the air of urban areas are logically attributed to the higher density of domestic, commercial, and industrial activities.

A very limited amount of published data is available, either on concentrations of polynuclear hydrocarbons in effluent streams from specific air pollution sources or on the atmospheric concentrations to be expected in the vicinity of such sources. Because of the need for information of this type, the U.S. Public Health Service inaugurated a program in 1960 to survey selected processes to evaluate emissions of polynuclear hydrocarbons. The main purpose of the survey was to "screen" processes likely to produce emissions of polynuclear hydrocarbons and thereby to indicate the probable origin of the polynuclear compounds contained in urban air. Individual studies, comprising portions of the over-all survey, have been reported for heat-generation and incineration processes, [9-12] industrial processes, [13] and motor vehicles. [14] This report compiles and summarizes the entire survey and presents some previously unpublished data on residential furnaces and petroleum catalytic-cracking catalyst regenerators.

Significance of the Data

A review of the published literature indicates that no definite atmospheric concentrations of polynuclear hydrocarbons constituting hazards to human health have been established. Therefore, no attempt is made herein to interpret the hygienic significance of the polynuclear hydrocarbon concentrations. The results are presented simply to indicate the relative importance of the processes studied as contributors of polynuclear hydrocarbons to the atmosphere.

SOURCES SURVEYED

The processes to be surveyed were selected from a list of probable potential sources of polynuclear hydrocarbon emissions. The categories of the sources tested are listed in Table 1.

Table 1. SOURCES SURVEYED FOR EMISSIONS OF POLYNUCLEAR HYDROCARBONS

Heat generation: coal, oil, and gas
Refuse burning: municipal and commercial incineration; open burning
Miscellaneous industrial processes:
Petroleum catalytic cracking – catalyst regeneration: FCC, TCC (air lift), TCC (bucket elevator), and Houdriflow
Asphalt air blowing
Asphalt hot-road-mix manufacture
Carbon-black manufacture
Steel and coke manufacture
Chemicals manufacture
Motor vehicle exhaust (gasoline): automobile; trucks

POLYNUCLEAR HYDROCARBON COMPOUNDS DETERMINED

The individual polynuclear hydrocarbons that were quantitatively analyzed are classified in Table 2 in two groups corresponding to the relative reliability of the analytical determinations. Because of interferences that occur during chemical analyses, values for the compounds in Group 2 are of lower quantitative reliability than those for Group 1.

Table 2. **PROPERTIES OF POLYNUCLEAR HYDROCARBONS**[3]

	Compound	Abbreviation	Melting point, °C	Biological activity[a]
Group 1	Pyrene ($C_{16}H_{10}$)	P	150	- -
	Benzo(a)pyrene ($C_{20}H_{12}$)	BaP	178	+++
	Benzo(e)pyrene ($C_{20}H_{12}$)	BeP	178	+
	Perylene ($C_{20}H_{12}$)	Per	275	- -
	Benzo(ghi)perylene ($C_{22}H_{12}$)	B(ghi)P	273	- -
	Anthanthrene ($C_{22}H_{12}$)	Anth	257	- -
	Coronene ($C_{24}H_{12}$)	Cor	435	- -
Group 2	Anthracene ($C_{14}H_{10}$)	A	217	not reported
	Phenanthrene ($C_{14}H_{10}$)	Phen	101	not reported
	Fluoranthene ($C_{16}H_{10}$)	Fluor	110	not reported

[a]Relative activity on mouse epidermis:
+++ active, + weak, - - inactive

SAMPLE COLLECTION AND ANALYTICAL TECHNIQUES

Data were collected in three ways: by direct sampling of stationary sources, by atmospheric sampling near stationary sources for which direct sampling was not practical, and by sampling of exhaust from motor vehicles. The principal items of special equipment were the sample collection trains illustrated in Figures 1 and 2. These sampling trains, designed to minimize loss of condensed polynuclear hydrocarbons from volatilization, have been described in previous publications. 9, 13-15

Stationary Source Testing

In testing of stationary sources (Figure 1) the sample gas stream passes through a series of water bubblers kept at 32°F and then through a series of freeze-out traps immersed in a dry-ice alcohol bath, from which it exits at 0°F. Finally, the sample gas stream passes through a high-efficiency glass-fiber filter. Isokinetic sampling rates ranged from 2.1 to 6.0 standard cubic feet per minute (70°F, 1 atm), and all sources were sampled continuously over periods ranging from 80 minutes to 3 hours.

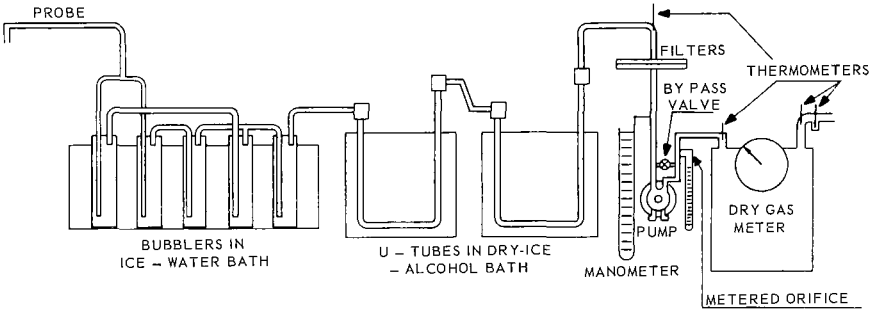

Figure 1 Polynuclear hydrocarbon sample train for stationary source testing.

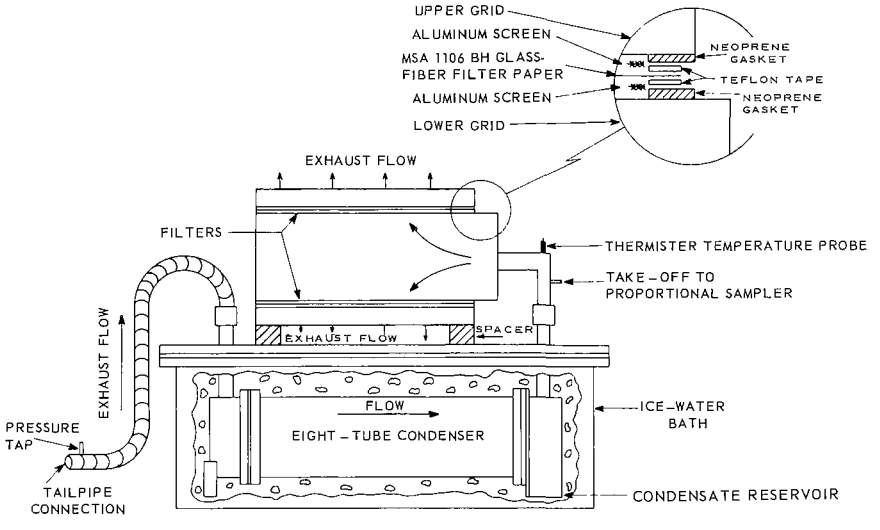

Figure 2. Polynuclear hydrocarbon sample train for motor vehicle testing.

Atmospheric Testing

Some installations were not amenable to direct source testing (e.g., slot-type coke ovens). In addition, some processes are so complex that proper evaluation of emissions of polynuclear hydrocarbons would require the sampling of many related installations (e.g., chemical manufacture). In this survey, such processes were evaluated indirectly by collection of atmospheric samples in urban residential areas near the installations.

Atmopsheric samples were collected with high-volume air samplers.[16] Usually, air samplers were operated simultaneously at

three to five urban residential sites near each installation. All samplers were located at least 15 feet above ground level to minimize the possibility of sampling dust-laden air. Samplers were operated for periods of 1 to 3 days at flow rates ranging from 20 to 65 cubic feet per minute. Tests were conducted over an interval of 2 weeks.

Motor Vehicle Testing

Figure 2 is a diagram of the apparatus used in sampling exhausts from automobiles and trucks. Total exhaust is piped into an ice-chest condenser and then through a filter. Sample volumes ranged from 675 to 1120 standard cubic feet (70°F, 1 atm) of dry exhaust. Maximum instantaneous temperature at the filter ranged from 37° to 80°F for automobiles and from 40° to 60°F for trucks.

Analysis

All of the samples were analyzed by the same technique, which involved benzene extraction of the particulate matter, the condensate, and the rinse liquids. The benzene-soluble fraction of the samples was separated by column chromatography, and the analyses made by ultraviolet-visible spectrophotometry.[17,18]

The analytical scheme is believed to be accurate to within ± 20 percent for benzo(a)pyrene, not including possible variations attributable to sample collection and extraction. This degree of variation is consistent with the complexity of the analysis and the small amounts of material present in samples containing many similar compounds.

HEAT-GENERATION PROCESSES

Combustion units that burn conventional fuels were designated as heat-generation processes. Design and operation data for these units are given in Tables 3, 4, and 5. Data on emissions are summarized in Tables 6, 7, and 8.[9-12]

Coal-Burning Units

The largest units tested were coal-fired boilers with rated capacities ranging from 1, 300, 000 down to 70, 500 pounds of steam per hour (Tables 3 and 4). The larger boilers in this range incorporated pulverized and cyclone firing and were used to generate electric power. The smaller boilers in this size range supplied steam for industrial process heating and electric power generation. Firing was accomplished with pulverized coal, chain grates, or spreader stokers. Smaller coal-burning units tested were rated by Btu input. Units in this group supplied steam for smaller industrial-process heating systems as well as

Table 3. DESIGN AND OPERATIONAL SUMMARY: HEAT GENERATION SOURCES (COAL-FIRED POWER PLANTS)

Sample No.	Test condition	Design data			Fuel and operating data					
					As-received basis			Fuel rate	Gross Btu input	Steam rate
		Type of unit	Rated capacity, 10^3 lb steam per hour	Dust collector	Moisture, %	Volatile, %	Ash, %	per hour		
								tons	million Btu	10^3 lb
ISS-22	100% load	Pulverized coal (vertically-fired, dry-bottom furnace)	1000 (1900 psig, 1000° F)	Multiple cyclone and electrostatic precipitator	1.1	30.8	19.8	64.5	1525	1100
24, 25	100% load				1.1	30.8	19.8	65.2	1541	1100
27	100% load				1.1	30.8	19.8	67.0	1584	1100
28, 29	75% load				1.1	30.8	19.8	48.0	1135	830
30, 31	75% load (slightly higher excess air)				1.1	30.8	19.8	46.2	1092	830
42	100% load	Pulverized coal (front-wall-fired, dry-bottom furnace)	920 (1900 psig, 1000° F)	Electrostatic precipitator	2.3	38.3	9.8	52.0	1315	860
44	100% load				1.2	36.2	8.1	49.5	1340	860
61 + 62	100% load	Pulverized coal (tangentially-fired, dry-bottom furnace)	940 (2565 psig, 1050° F)	Multiple cyclone and electrostatic precipitator	2.8 1.8	37.2 32.9	16.0 11.7	56.6	1365	960
63	100% load (with fly-ash reinjection)	Pulverized coal (opposed-, downward-inclined burners; wet-bottom furnace)	150 (1000 psig, 835° F)	Multiple cyclone	2.0	36.5	7.9	8.8	232	149
64	100% load (without fly-ash reinjection)				2.0	36.5	7.9	10.8	285	152
65	100% load (with fly-ash reinjection)				2.0	36.5	7.9	9.1	240	149
69	100% load	Crushed coal (cyclone-fired, wet-bottom furnace)	1360 (2400 psig, 1050° F)	Electrostatic precipitator	1.1	37.0	7.5	59.0	1647	1320
70	100% load				1.1	37.0	7.5	66.8	1861	1330
71	75% load (normal)	Crushed coal Spreader stoker (traveling grate)	220 (875 psig, 760° F)	Multiple cyclone	4.2	42.3	7.1	9.0	233	160
72	75% load (normal)				4.6	43.7	8.3	9.2	232	160
73	75% load (normal) (slightly higher excess air)				4.9	43.8	8.7	9.3	230	156

Table 4. DESIGN AND OPERATIONAL SUMMARY: HEAT GENERATION SOURCES (INTERMEDIATE-SIZED COAL-FIRED UNITS AND INTERMEDIATE – AND SMALL-SIZED OIL – AND GAS-FIRED UNITS)

Sample No.	Design data							Fuel data			Operating conditions during test				
	Fuel	Firing method	Type of unit	Use	Rated capacity per hr		Dust collector	As-received basis			Fuel rate	Gross Btu input	Steam rate	Steam pressure	Smoke
					10^3 lb steam	million Btu[a]		Moisture, %	Volatile, %	Ash, %	per hr				
											lb	million Btu	10^3 lb	psig	Opacity, %
ISS- 6	COAL	Pulverized (*dry-bottom furnaces*)	Water-tube *boiler*	Process *heating*	200		Multiple *cyclone*	3.2	36	4.3	9,420	130	106	307	60
7		Chain grate stoker	Water-tube boiler	Electric generation	125		None	10.4	44	7.0	12,400	147	111	450	20-40
5		Spreader stoker (with reinjector)		Process heating	70.5		Multiple cyclone	3.0	37	4.7	4,290	59.2	49	160	0-20
4		Underfeed stokers	Fire-tube boiler	Process heating		7.2	None	1.2	36	4.7	317	4.4		110	20-40
14				School heating		3.8		2.0	19	5	214	3.0		37	0-20
8	OIL	Steam-atomized	Water-tube boiler	Process heating	22	23	None	No. 2 fuel oil (28.5° API)			1,110	21	17.9	250	5
12					30	30		No. 6 fuel oil (13.5° API)			769	14.4	10.3	125	5
10		Low-pressure air-atomized	Scotch-marine boiler	Hospital heating		4.2		No. 1 fuel oil (43.5° API)			35	0.70		95	0
17		Pressure-atomized	Cast-iron sectional boiler	Home heating		0.25		No. 2 fuel oil (31.5° API)			8.8	0.17			0
13			Hot-air furnace			0.14		No. 2 fuel oil (31.5° API)			4.4	0.085			0
15		Vaporized	Hot-air furnace	Home heating		0.09		No. 1 fuel oil (43° API)			1.2	0.025			0
11	GAS	Premix burners	Fire-tube boiler	Process heating		7.2	None	*Natural gas* (94.2% methane 3.6% ethane)			402	9.3		108	0
9			Scotch-marine *boiler*	Hospital *heating*		4.2					42	0.98		96	0-20
18			Double-shell boiler	Home heating		0.18					7.9	0.18			0
16			Hot-air furnace			0.21					7.4	0.17			0
21			Wall space heater			0.025					0.51	0.012			0

[a]Gross heat input

for institutional and home heating. Firing was accomplished with underfeed stokers. The smallest units surveyed were domestic underfeed and hand-stoked furnaces used for heating single-family dwellings (Table 5).

Table 5. DESIGN AND OPERATIONAL SUMMARY: HEAT GENERATION SOURCES (COAL-FIRED RESIDENTIAL FURNACES)

Sample No.	Design		Fuel and operating data					
			As-received basis			Fuel rate	Gross Btu input	Smoke
	Firing Method	Type of unit	Moisture, %	Volatile, %	Ash, %	per hr		
						lb	million Btu	Opacity, %
ISS-19	Underfeed Stokers	Cast-iron sectional boiler	3.5	38	3.9	4.8	0.066	0 - 20
34			3.5	38	3.9	4.2	0.058	0 - 15
36			2.0	22	4.0	3.8	0.056	0
59		Hot-air Furnace	2.8	38	2.4	5.0	0.070	0 - 10
60			2.8	38	2.4	4.5	0.063	0 - 10
20	Hand-stoked	Hot-air Furnaces	1.8	38	2.7	8	0.115	40 - 80
57			2.3	38	2.9	6.3	0.089	0 - 70
58			2.3	38	2.9	5.6	0.080	<5 - 70

Rates of emission of polynuclear hydrocarbons from coal-burning units varied widely, depending on the quality of combustion achieved. The highest emission rates were found in small domestic furnaces used to heat single-family homes. For example, tests on hand-fired and underfeed stoker-fired domestic units, with essentially no combustion control, showed emissions ranging from 3800 to 3, 300, 000 micrograms of BaP* per million Btu gross heat input (Table 8). Intermediate-sized and large-sized units incorporating chain-grate stokers, spreader stokers, pulverized feed, and cyclone firing achieved better combustion and produced appreciably lower emissions of polynuclear compounds (17 to 370 micrograms of BaP per million Btu gross heat input) at normal operating conditions (Tables 6 and 7). Among the other large, fully instrumented, coal-fired steam power plants, the cyclone-fired unit, which burns crushed coal, showed the highest emission rate (76 to 370 micrograms of BaP per million Btu gross heat input).

In Figure 3, BaP emission rates are plotted against size of the coal-, oil-, and gas-fired units. Because of the many variables affecting the formation of this compound, a wide range of emissions can be

*Benzo(a)pyrene; abbreviations for other compounds are given in Table 2.

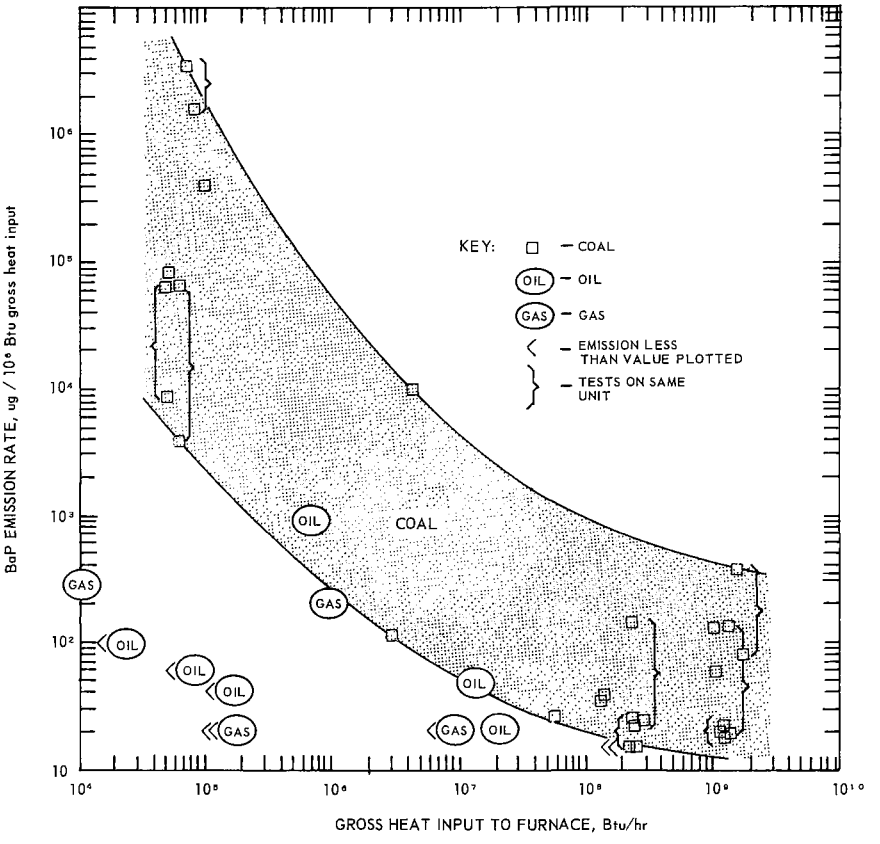

Figure 3. Range of benzo (a) pyrene emissions from coal, oil, and natural gas heat-generation processes.

expected from a given size of unit and the results do not lend themselves to a straight-line relationship. Emissions of BaP from units operating with relatively good combustion conditions would be expected to fall near the lower boundary of the range, whereas emissions from less efficient combustion processes would fall near the upper boundary. Although it is constructed with limited data from oil- and gas-burning sources, the plot in Figure 3 emphasizes that heavier emissions are to be expected from coal-burning units than from gas- or oil-fired units of comparable sizes.

The lower emission rates from the large coal-fired units can be attributed to the more efficient combustion of fuel attainable with closely regulated air-fuel ratios and uniformly high combustion-chamber temperatures.

Among the seven polynuclear hydrocarbons for which the analytical technique was most reliable, pyrene, BaP, and benzo(e)pyrene were detected in all coal-fired units tested (see Tables 6 through 8). In all

Table 6. POLYNUCLEAR HYDROCARBON EMISSION SUMMARY: HEAT GENERATION SOURCES (COAL-FIRED POWER PLANTS)

Sample No.[a]	Type of unit	Sampling Point[b]	Benzene-soluble Organics	Group 1											Group 2		
				BaP[c]			BaP	P	BeP	Per	BghiP	Anth	Cor	A	Phen	Fluor
			g per 10^6 Btu	µg/g φsoluble[d]	µg per 1000 m³[e]	µg per lb fuel	Micrograms per million Btu heat input									
ISS-22		B	3.0	16	110	0.58	49	150			45	16				370
24	Pulverized coal (vertically-fired, dry-bottom furnace)	B	0.99	22	50	0.26	22	130								190
25		A	1.7	11	42	0.23	19	190								210
27		A	2.0	9.3	42	0.22	19	120								190
28		B	1.4	39	130	0.66	56	180	33		19					320
29		A	1.4	38	120	0.63	55	230	41							410
30		B	1.3	330	930	5.3	440	840	250	66	160	35	4.7	110	820	1700
31		A	1.2	110	270	1.5	130	74	79	23	83					84
42	Pulverized coal (front-wall-fired, dry-bottom furnace)	A	0.34	48	39	0.21	17	200	55		14				200	160
44			0.62	33	48	0.28	21	160								13
61+62	Pulverized coal (tangentially-fired, dry-bottom furnace)	A	0.65	220	320	1.7	140	140	84	71	150	4.9	7.1		32	390
63	Pulverized coal (opposed-, downward-inclined burners; wet-bottom furnace)	A	1.3	110	330	1.9	140	130	420		1100		93			210
64			1.1	21	57	0.29	22	51	110		190		19			65
65			1.0	21	46	0.28	21	39	72		150		8.1			55
69	Crushed coal (cyclone-fired, wet-bottom furnace)	A	2.1	175	730	5.2	370	1800	680	34	360					110
70			0.92	83	170	1.1	76	250	110		36		11			44
71	Spreader stoker (traveling grate)	A	1.1	22	58	0.31	24	59	61				9.5			59
72			1.8	<8.5	< 36	<0.19	< 15	32								32
73			1.4	<11	< 33	<0.19	< 15	21								21

[a]Additional filter used before the bubblers in the sampling train as shown in Figure 1

[b]B: sampling point before fly ash collector; A: after fly ash collector.

[c]"Less than" values for benzo (a) pyrene were calculated for those samples having concentrations below the limit of quantitative determination (approximately 0.6 microgram per sample). Similar calculations were not included for the other polynuclear hydrocarbons (indicated by blanks in the table).

[d]Micrograms per gram of benzene soluble organics.

[e]Micrograms per 1000 cubic meters of flue gas at standard conditions (70°F, 1 atmosphere).

Table 7. POLYNUCLEAR HYDROCARBON EMISSION SUMMARY: HEAT GENERATION SOURCES (INTERMEDIATE-SIZED COAL-FIRED UNITS AND INTERMEDIATE- AND SMALL-SIZED OIL-AND GAS-FIRED UNITS)

				Group 1										Group 2		
Sample No.	Fuel	Firing method	Benzene-soluble organics	BaP	BaP[a]		P	BeP	Per	B(ghi)P	Anth	Cor	A	Phen	Fluor
			μg per 10^6 Btu	μg/g Ø sol.[b]	μg per 1000 m^3[c]	μg per lb fuel	Micrograms per million Btu heat input								
ISS- 6	COAL	Pulverized	2.9	11	75	0.43	32	240	92				370		550
7		Chain grate stoker	1.9	19	71	0.44	37	390	130						680
5		Spreader stoker	5.4	4.7	49	0.35	26	590	350			26			360
4		Underfeed stokers	3.0	3,400	7,900	140	10,000	16,000	7,900	1,600	4,500	290	330	850	10,000	38,000
14			4.0	29	61	1.6	120	1,700	230						1,000	3,200
8	OIL	Steam-atomized	1.4	<11	<38	<0.3	<20	49								56
12			3.3	15	40	0.89	47	300							1,800	270
10		Low-pressure air-atomized	14	65	1,900	18	900	6,100			300		2,100	3,900	3,500	1,900
17		Pressure atomized	8.1	<4.6	<26	<0.9	<40	1,800							8,900	5,000
13			3.6	<17	<27	<1	<60	15								76
15		Vaporized	3.5	<33	<34	<2	<100	1,200								15,000
11	GAS	Premix burners	1.1	<17	<29	<0.4	<20	160				14				100
9			1.2	170	350	4.6	200	18,000	490		1,800	200	5,300			2,900
18			0.95	<21	<23	<0.5	<20	170								320
16			0.65	<35	<30	<0.6	<20	120	18						77	110
47			5.2	51	71	6.1	270	16,000	1,500		2,300	73	830			8,000

[a]"Less than" values for benzo(a)pyrene were calculated for those samples having concentrations below the limit of quantitative determination (approximately 0.6 microgram per sample). Similar calculations were not included for the other polynuclear hydrocarbons (indicated by blanks in the table).
[b]Micrograms per gram of benzene-soluble organics.
[c]Micrograms per 1000 cubic meters of flue gas at standard conditions (70°F, 1 atmosphere).

Table 8. POLYNUCLEAR HYDROCARBON EMISSION SUMMARY: HEAT GENERATION SOURCES (COAL-FIRED RESIDENTIAL FURNACES)[a]

Sample No.	Firing method	Benzene-soluble organics	Group 1										Group 2		
			BaP			BaP	P	BeP	Per	BghiP	Anth	Cor	A	Phen	Fluor
		g per 10^6 Btu	μg/g ø sol.[b]	μg per 1000 m^3[c]	μg per lb fuel	Micrograms per million Btu heat input									
ISS-19	Underfeed Stokers	2.4	1,600	3,400	52	3,800	7,700	5,400		580		1,200		29,000	47,000
34		47	1,400	40,000	900	65,000	300,000	39,000	7,900	61,000	6,100	4,100	70,000	610,000	330,000
36		73	1,100	44,000	1,200	81,000	190,000	59,000	4,800	58,000	3,000		48,000	350,000	150,000
59		20	3,400	18,000	930	67,000	160,000	55,000	5,500	59,000	1,300	3,400	14,000	170,000	320,000
60		8.7	990	2,200	120	8,600	45,000	7,700	430	6,300			1,300	51,000	76,000
20	Hand-stoked	91	3,900	340,000	6,000	400,000	600,000	100,000	60,000	300,000	90,000	30,000	400,000	1,000,000	1,000,000
57		170	10,400	690,000	25,000	1,700,000	2,700,000	870,000	220,000	1,400,000	270,000	49,000	1,100,000	2,300,000	4,300,000
58		350	9,400	1,500,000	46,000	3,300,000	9,100,000	1,500,000	350,000	2,200,000	490,000	97,000	2,900,000	7,500,000	11,000,000

[a]A blank indicates that the compound was not detected in the sample.

[b]Micrograms per grams of benzene-soluble organics.

[c]Micrograms per 1000 cubic meters of flue gas at standard conditions (70°F, 1 atmosphere).

but two tests, the ratio of pyrene to BaP was greater than 1, varying from 0.6 to 23. Ratios of BaP to benzo(ghi)perylene ranged from 0.9 to 6.6 except for one power plant for which the ratio was 0.13. Ratios of BaP to coronene ranged from 1.0 to 94. Average ratios for the residential coal-fired furnaces are as follows: P/BaP, 2.6; BaP/BghiP, 1.7; BaP/Cor, 19. These results tend to confirm the data reported by Sawicki[19] regarding the ratios of these compounds in particulate samples collected from the atmosphere. Sawicki states that particulate pollution from coal-burning sources (as opposed to auto exhaust) might be characterized by ratios of BaP to benzo(ghi)perylene greater than 0.6 and ratios of BaP to coronene greater than 1. He further suggests that the ratio of pyrene to BaP might indicate the "age" of the particulate pollution, since pyrene is less stable in the atmosphere than is BaP and tends more to be lost by volatilization. This interpretation is substantiated by the finding that ratios of pyrene to BaP in particulate matter collected from the atmosphere in cities throughout the United States were less than 1 in most cases reported.[8]

Comparison of polynuclear hydrocarbon emissions with other products of incomplete combustion indicates that polynuclear emission rates are generally high when carbon monoxide and total gaseous hydrocarbons are high.[9]

Oil-Burning Units

The capacities of the oil-burning units tested ranged from 0.09 to 30 million Btu per hour gross heat input (Table 4). The largest of these boilers produced steam for process heating and was fired by steam-atomizing burners. The smaller units (up to 4.2 million Btu/hr, heat input) produced hot water and hot air for institutional and home-heating uses; most of these units were fired by air-atomizing and pressure-atomizing burners.

Polynuclear hydrocarbon emissions from oil-burning sources were generally much lower than from coal-burning sources of equivalent size (Table 7). Detectable BaP concentrations were found in only two of the six oil-burning units tested, but pyrene was present in all sources. Ratios of pyrene to BaP for the two BaP-emitting units averaged 6.6. Ratios of BaP to benzo(ghi)perylene were >2 and 3.0, and ratios of BaP to coronene were 0.4 and >5. The highest BaP emission rate from oil-burning occurred in a unit with an air-atomizing burner.

Low BaP emissions from liquid-petroleum-fired units have also been reported by Howe.[20] In a study of household-sized units (12,000 to 250,000 Btu per hour) and small industrial-sized units (6,000 pounds of steam per hour), no BaP was detected in the samples collected. Two of the small household-size units produced smoke during testing.

Gas-Burning Units

The gas-burning units tested ranged in capacity from 0.025 to 7.2 million Btu per hour gross heat input (Table 4). The larger units provided steam for process and institutional heating; the smaller units (0.21 million Btu per hour gross heat input and below) provided hot water and hot air for single-family home heating.

Polynuclear hydrocarbon emissions from gas-fired units were generally lower than from coal-fired units and were about the same as emissions from oil-fired units (Table 7). For three of the five gas-fired sources the only compound of consequence was pyrene. Two gas-fired sources (Samples ISS-9 and ISS-47) produced more polynuclear hydrocarbons than the others, apparently because of improper adjustment of the air-fuel ratio as evidenced by high concentrations of CO and total gaseous hydrocarbons. The ratio of pyrene to BaP for these sources averaged 75. The ratios of BaP to benzo(ghi)perylene and BaP to coronene averaged 0.1 and 0.2, respectively; these values contrast with the higher ratios obtained in tests of coal-fired units and are more similar to the lower ratios for auto exhaust. [19]

REFUSE BURNING

Incinerators

Waste materials burned during the incinerator tests were typical of present-day municipal and commercial wastes collected from households, grocery stores, and restaurants. Municipal units included a continuous-feed 250-ton-per-day furnace and a batch-charged 50-ton-per-day furnace equipped with water spray scrubbers. Commercial incinerators included a 5.3-ton-per-day unit and a 3-ton-per-day unit equipped with an auxiliary gas burner. (See Table 9).

Polynuclear hydrocarbon emissions produced by municipal and commercial incinerators are summarized in Tables 10 and 11. BaP and benzo(e)pyrene, both of which have demonstrated carcinogenic qualities, were detected in the flue gases from every incinerator tested. The concentrations of pyrene from each unit were higher than those of any of the other polynuclear hydrocarbon compounds detected, and ratios of pyrene to BaP ranged from 6.0 to 120. Ratios of BaP to benzo(ghi)perylene ranged from 0.3 to more than 2, and ratios of BaP to coronene ranged from 0.3 to 2.5. Following the pattern of the coal-fired sources, the small-sized commercial incinerators with relatively poor combustion emitted more polynuclear hydrocarbons than the intermediate- and large-sized municipal units. The largest municipal unit, operating at relatively constant temperatures above 1600°F and with longer gas retention times in the high-temperature zone, produced the least of these compounds in terms of emissions per pound of refuse charged. In additional tests run with less underfire air (50 and 20 percent versus 80 percent) this low emission rate was reduced only slightly.

Table 9. DESIGN AND OPERATIONAL SUMMARY: INCINERATION AND OPEN-BURNING SOURCES

Sample No.	Design data					Fuel data		Operating data				
	Type of unit		Rated capacity	Grate area	Dust collector	Type	Moisture content,%	Charging rate	Underfire air	Excess air	Gas temp.	Smoke
			tons/day	ft^2				tons/day	%	%	°F	Opacity,%
INC-19+20	Municipal Incinerators	Multiple chamber, traveling grate (continuous feed)	250	288	Settling Chamber	Residential refuse (14 to 20% non-combustible/	35	260	80	185[a]	1940[b]	20
11+17 12+18	Municipal Incinerators	Multiple chamber batch charged, reciprocating stoker grates	50	85.5	Water spray scrubber	Residential and commercial refuse (14 to 20% noncombustible)	25	49	50-60	108[a]	1470[a]	0
38+39	Commercial Incinerators	Single chamber	5.3	13	None	Cardboard, Packing crates	20	4.7	0	465[c]	1300[b]	0-20
35+37	Commercial Incinerators	Multiple chamber with auxiliary gas burner in primary chamber	3	19.7	None	60% paper 40% wet garbage	50	2.3			1850[b]	0-50
24+25	Open Burning	On-site air samples				Municipal refuse	20					20-100
27	Open Burning	On-site air samples				Automobile tires						20-100
29+30	Open Burning	On-site air samples				Grass clippings, leaves, tree branches						20-100
31+32 33+34	Open Burning	On-site air samples				Automobile bodies						20-100
40+41	Open Burning	Facility for research on open burning fires				Municipal refuse						
42+43	Open Burning	Facility for research on open burning fires				Grass clippings, leaves, tree branches	25					
44	Open Burning	Facility for research on open burning fires				Automobile components						

[a]In breeching.
[b]In furnace.
[c]In stack.

Table 10. POLYNUCLEAR HYDROCARBON EMISSION SUMMARY: INCINERATION AND OPEN BURNING SOURCES[a]

Sample No.	Type of unit		Sampling point	Benzene-soluble organics	Group 1								Group 2		
					BaP		BaP	P	BeP	Per	BghiP	Anth	Cor	A	Phen	Fluor
				g/lb of refuse	μg/g ∅ sol[b]	μg per 1000 m³[c]	Micrograms per pound of refuse charged									
INC-19+20	Municipal	250-ton/day Multiple chamber	Breeching (before settling chamber	0.018	4.2	19	0.075	8.0	0.34				0.24			9.8
11+17		50-ton/day Multiple chamber	Breeching (before scrubber)	0.0031	2000	2700	6.1	52	12		34		15		18	4.6
12+18			Stack (after scrubber)	0.0060	15	17	0.089	2.1	0.58		0.63		0.63			3.3
38+39	Commercial	5.3-ton/day Single chamber	Stack	0.012	4500.0	11,000	53	320	45	3.1	90	6.6	21	47	140	220
35+37		3-ton/day Multiple chamber	Stack	0.065	5900	52,000	260	4200	260	60	870	79	210	86	59	3900
40+41	Open burning	Municipal refuse	Stack (facility for research on open-burning fires)	3.37	45	2800	153	800	105		70					730
42+43		Grass clippings, leaves, branches		3.48	45	4200	157	780	70	17	73	12				505
44		Automobile components		3.03	4300	173,000	13,000	34,300	6570	1180	8900	1000	1090	1420	9690	24,400

[a]A blank indicates that the compound was not detected in the sample.

[b]Micrograms BaP per gram benzene-soluble organics.

[c]Micrograms per 1000 cubic meters of flue gas at standard conditions (70° F., 1 atmosphere).

Table 11. POLYNUCLEAR HYDROCARBON CONTENT OF PARTICULATE MATTER EMITTED: INCINERATION AND OPEN BURNING SOURCES[a]

Sample No.[b]	Type of unit		Sampling point	Group 1							Group 2		
				BaP	P	BeP	Per	BghiP	Anth	Cor	A	Phen	Fluor
				Micrograms per gram of particulate									
INC-19+20	Municipal incinerators	250-ton/day Multiple chamber	Breeching (before settling chamber)	0.016	1.9	0.08				0.06			2.2
11+17	Municipal incinerators	50-ton/day Multiple chamber	Breeching (before scrubber)	3.3	28	6.5		19		8.2		9.8	2.5
12+18	Municipal incinerators	50-ton/day Multiple chamber	Stack (after scrubber)	0.15	3.6	0.97		1.1		1.1			5.5
38+39	Commercial incinerators	5.3-ton/day Single chamber	Stack	58	350	49	3.3	98	7.1	23	51	150	240
35+37	Commercial incinerators	3-ton/day Multiple chamber	Stack	180	2600	180	36	540	45	130	53	62	2400
24+25	Open Burning	Municipal refuse	In smoke plume (on-site air samples)	11	29	4.5					4.7		13
27	Open Burning	Automobile tires	In smoke plume (on-site air samples)	1100	1300	450	72	660	53	81	110	450	470
29+30	Open Burning	Grass clippings, leaves, branches	In smoke plume (on-site air samples)	35	120	21		5.4			4.7		110
31+32 33+34	Open Burning	Automobile bodies	In smoke plume (on-site air samples)	270	670	120	33	150	12	15	220	160	450
40+41	Open Burning	Municipal refuse	Stack (facility for research on open-burning fires)	28	146	19		12					133
42+43	Open Burning	Grass clippings, leaves, branches	Stack (facility for research on open-burning fires)	29	152	14	2.8	12	1.8				100
44	Open Burning	Automobile components	Stack (facility for research on open-burning fires)	380	1000	190	35	260	29	32	43	280	710

[a]A blank indicates that the compound was not detected in the sample.

[b]Additional filter used before the bubblers in the sampling train as shown in Figure 1 for tests 40 through 44).

A water-spray scrubber used to control fly ash from the smaller municipal unit proved highly effective in reducing the level of polynuclear hydrocarbons emitted to the atmosphere. Emissions of BaP, for example, were reduced 98 percent by use of the scrubber. Additional tests with a combination of lower-than-normal underfire air (19 percent versus 50 to 60 percent) and higher excess air (220 percent versus 108 percent) also reduced emissions at a rate equivalent to that obtained with the scrubber.

Open-Burning Sources

Emissions from open fires were evaluated by two different methods: on-site sampling and sampling at a special test facility. In on-site sampling a high-volume air sampler attached to the end of an 8-by-10-inch duct collected particulate samples on MSA 1106-BH glass-fiber filters. The open end of the duct was positioned in the smoke plume. Separate samples were taken from the open burning of municipal refuse, automobile tires, grass and tree branches, and automobile bodies. Refuse burning rates and combustion gas flow rates were not obtained during these tests because of the difficulty of making such measurements in the field. Hence, results can be compared only on the basis of the amounts of polynuclear hydrocarbons in the particulate matter collected. Table 11 summarizes the results.

The facility designed specifically for research on open fires was made available by the Air Pollution Research Center of the University of California at Riverside. This facility consists of a "burning table" with an inverted conical hood suspended above it to collect and funnel the combustion products into a stack. Instrumentation allowed the measurement of flue-gas flow, weight of fuel remaining, and temperature, and the analysis of gases. Quantitative emissions were determined for the open burning of municipal refuse, grass and tree branches, and automobile components. Results are given in Tables 10 and 11.

The comparatively high emissions of polynuclear hydrocarbons from open burning, especially of automobile components, is consistent with the general pattern that has developed for other combustion processes; i.e., the inadequate combustion conditions typical of uncontrolled burning processes consistently produce the highest levels of these compounds. Ratios of pyrene to BaP ranged from 1.2 to 2.6, BaP to benzo(ghi)perylene from 1.7 to >20, and BaP to coronene from 6.6 to >60. These ratios are similar to those for residential coal furnaces.

INDUSTRIAL PROCESSES: DIRECT SAMPLING

Petroleum Catalytic Cracking -- Catalyst Regeneration

Concentrations of polynuclear hydrocarbons in the waste gases of catalyst regenerators were measured for each of the major types of petroleum catalytic cracking units: Fluid catalytic crackers (FCC);

Thermofor catalytic crackers (TCC), both air lift and bucket elevator catalyst carriers; and a Houdriflow catalytic cracker (HCC).

The objective of catalytic cracking is to upgrade heavier petroleum fractions by breaking up long-chain hydrocarbons to obtain high-octane gasoline and distillate fuels. The most common feed-stock is the gas-oil fraction obtained from the crude distillate unit.

Although the catalytic cracking units surveyed may differ somewhat in equipment, geometry, and actual operation, the cracked products and basic chronology of the process are the same. Preheated gas-oil and silica-alumina type catalyst are charged into a reactor maintained at about 900°F and 15 psig. The cracked products are separated by fractionation and further processed. The spent catalyst, laden with coke, is rejuvenated in a catalyst regenerator kiln. Here the coke is burned off the catalyst at temperatures near 1000°F and pressures ranging from 2 to 20 psig, depending on the type of unit; the catalyst is recycled to the reactor. The regenerator flue gases, high in carbon monoxide and unburned hydrocarbons, are then exited directly to the atmosphere or to a carbon monoxide waste heat boiler. Typical flow diagrams of the units tested are given in Figures 4, 5, and 6. Table 12 summarizes the operational data.

The emission rates measured are presented in Table 13. High concentrations were present in the regenerator waste gases from the HCC and TCC air-lift units. Emissions of BaP, pyrene, benzo(e)pyrene, and benzo(ghi)perylene were especially high. The average BaP emission rates for the HCC and TCC air-lift units were 218, 000 and 90, 000 micrograms per barrel of oil charged. By comparison, the highest BaP emission rates from TCC bucket elevator and FCC units were 31 and 460 micrograms per barrel of oil charged. These large variations in emission rates cannot be explained by analysis of data from the small number of tests performed in this screening program.

Concentration ratios for the high-emission units are as follows:

Unit	P/BaP	BaP/BghiP	BaP/Cor
HCC	0.58	0.65	15
TCC, air lift	1.1-4.3	1.7-1.2	

The HCC and FCC units incorporated CO waste heat boilers to effect complete combustion of the regenerator flue gases. The CO boilers, providing combustion with auxiliary fuels or a catalyst, greatly reduced emissions of carbon monoxide and total gaseous hydrocarbons. In addition, all the polynuclear hydrocarbons detected in the HCC regenerator waste gases, including BaP, underwent more than 99 percent reduction upon passage through the CO boiler. BaP emissions were reduced from 218, 000 to 45 micrograms per barrel of oil charged. The CO boilers on the FCC units further reduced the low emissions.

The TCC air-lift units were equipped with plume burners. The plume burner is a secondary stage of combustion built into the regenerator kiln. This type of burner has successfully increased the clarity of plumes from regenerator waste gases; however, compared to a CO waste heat boiler, the plume burner is ineffective as a control device for reducing emissions of polynuclear hydrocarbons, total gaseous hydrocarbons, and carbon monoxide.

In 1964, CO boilers in the United States burned regenerator gases from 65 percent of the total HCC capacity and 31 percent of the total

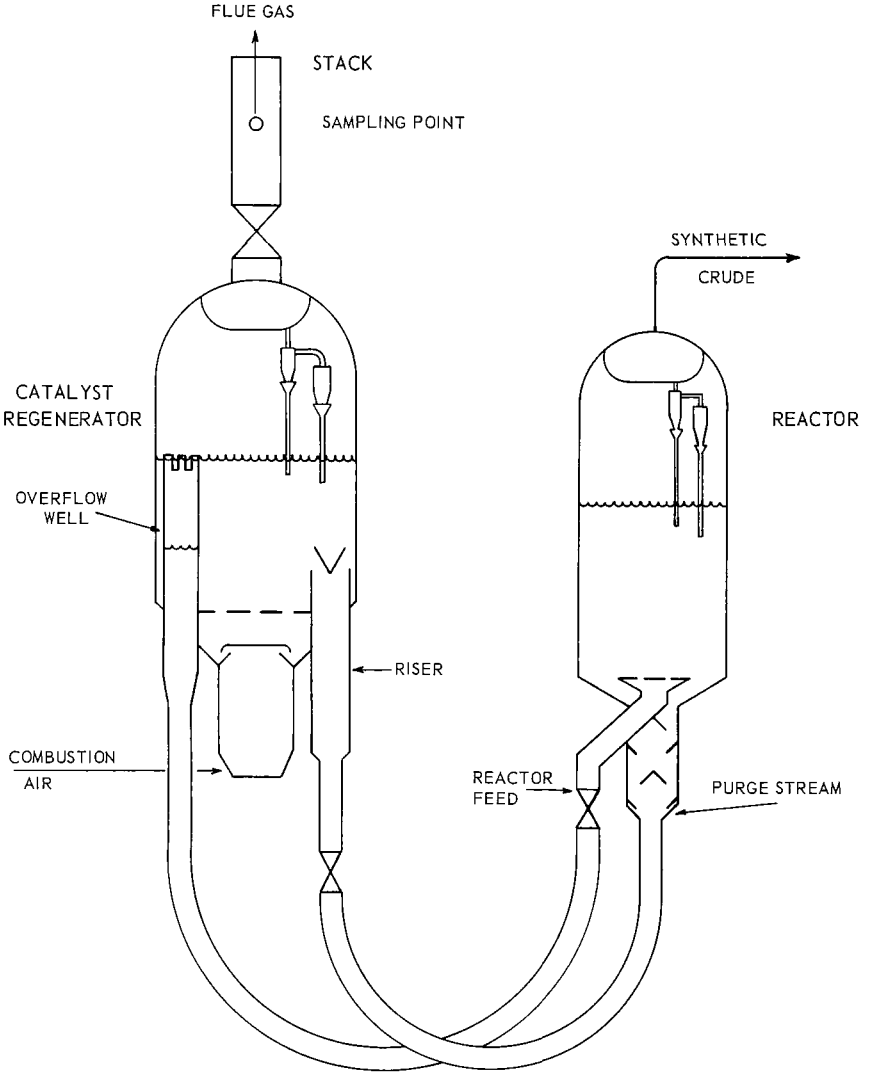

Figure 4. Fluid catalytic cracking unit, Model IV.

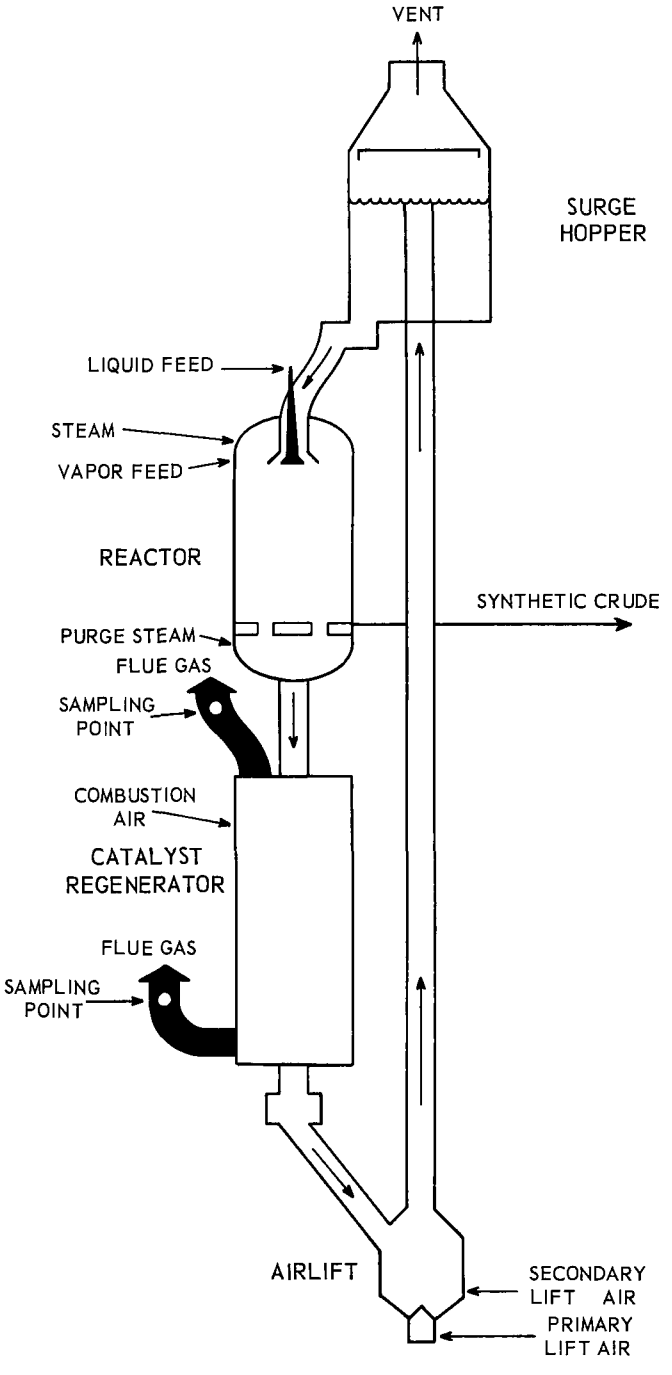

Figure 5. Airlift TCC catalytic cracking unit.

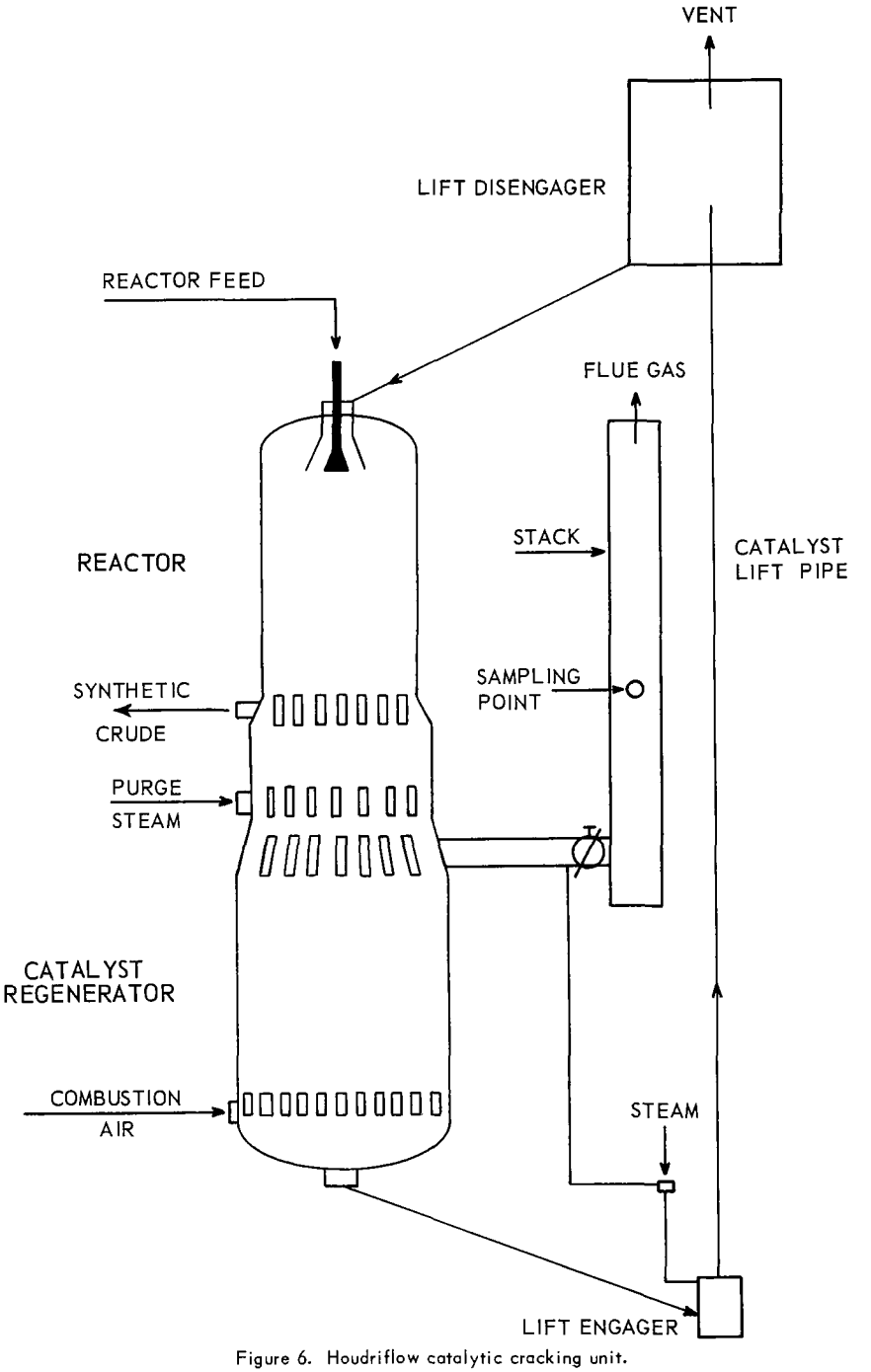

Figure 6. Houdriflow catalytic cracking unit.

Table 12. OPERATIONAL SUMMARY: PETROLEUM CATALYTIC CRACKING, CATALYST REGENERATION

Sample No.	Catalytic reactor				Catalyst regenerator			
	Type of unit	Process rate (fresh feed and recycle)		Charge stock	Waste gas		Catalyst	
		bpsd[a]	Recycle, %	°A.P.I.	CO, %	Combustion equipment	Geometry	Circulation rate, tons/hr
ISS-49,50	FCC	20,200	46	31	6.5	Waste Heat Boiler	Powder	
51,52		23,000	41		9.1			
78	FCC	46,250	44	30.5	10.0	Waste Heat Boiler	Powder	2,500
80,81		46,600	44		9.8			2,500
53,54	HCC	37,200	30	30	4.2	Catalytic Waste Heat Boiler	Bead	890
55,56		34,400	27		5.1			920
66	TCC (Air lift)	19,600	15	25	6.3[b]	Plume Burner	Bead	550
74+75	TCC (Air lift)	22,800	42	35	4.1[b]	Plume Burner	Bead	440
76+77		23,800	45		3.3[b]			440
67	TCC (Bucket lift)	13,200	31	29	4.2	None	Bead	148
68		10,000	33	30	4.7			148

[a]Barrels per stream day.

[b]Average composition from two stacks.

Table 13. POLYNUCLEAR HYDROCARBON EMISSION SUMMARY: PETROLEUM CATALYTIC CRACKING, CATALYST REGENERATION[a]

Sample No.	Type of Unit	Sampling point	Benzene-soluble organics	Group 1									Group 2		
				BaP		BaP	P	BeP	Per	BghiP	Anth	Cor	A	Phen	Fluor
			grams per barrel oil charged	μ g per gm ϕsol.[b]	μ g per 1000 m3c	Micrograms per barrel oil charged (fresh feed plus recycle)									
ISS-49[d]	FCC	Regenerator outlet	0.69	63	400	44	167	53		15					160
50[d]		CO boiler outlet	0.95	12	46	11	87	21							72
51[d]		Regenerator outlet	0.21	20	46	4.3	40	11							44
52[d]		CO boiler outlet	0.84	< 7.5			25								20
78+80	FCC	Regenerator outlet	1.82	253	6,400	460	28,000	3,600		424			2,070	400.000	20,000
81		CO boiler outlet	0.22	97	212	21.5	165	18		55					85
53[d]	HCC	Regenerator outlet	9.0	22,700	2,800,000	205,000	131,000	310,000	34,000	300,000	15,000	11,200	920	21,000	8,300
55[d]			14	17,000	2,700,000	231,000	130,000	380,000	34,000	380,000	18,000	26,000	2,000	29,000	11,400
54+56[d]		CO boiler outlet	0.09	502	610	45	39	97	4.8	125	3.2	8.0	7.9	83	23
66[d]	TCC[e] (Air lift)	Regenerator outlets	36	3,280	1,200,000	120,000	132,000	120,000	10,000	72,000	4,400		24,000	78,000	
74+75	TCC (Air lift)	Regenerator outlets	12.2	4,560	680,000	56,000	250,000	56,000	8,800	44,000	1,300		10,300	352,000	29,000
76+77			13.5	4,590	780,000	62,000	260.000	75,000	5,500	54,000	1,750	360	10,600	330,000	10,600
67[d]	TCC (Bucket lift)	Regenerator outlet	0.26	120	320	31	280	82							59
68[d]			0.38	< 24			360								106

[a] A blank indicates that the compound was not detected in the sample.
[b] Micrograms per gram of benzene-soluble organics.
[c] Micrograms per 1000 cubic meters flue gas at standard conditions (70°F, 1 atmosphere).
[d] Additional filter used before the bubblers in the sampling train as shown in Figure 1.
[e] Emmission rates for this unit are only approximate.

air-lift TCC capacity. Fifty-one of a total of approximately 113 FCC units are equipped with CO boilers. The use of plume burners on air-lift TCC units amounted to 45 percent of total capacity.

Asphalt Air-Blowing Process

The asphalt plant surveyed processed about 140,000 gallons of asphalt per day (24 tons per hour). The air-blowing operation involved charging 10 enclosed reactors of 5,000- and 10,000-gallon capacity each with petroleum-base asphalt; the material was then heated externally by gas burners and maintained at temperatures ranging from 430 to 500°F. Air then was bubbled through the hot asphalt continuously for periods ranging from 8 to 16 hours. The partially oxidized end products, more viscous and less resilient than ordinary asphalt, are termed either flexible coating, linoleum saturate, or shingle material. A summary of the polynuclear hydrocarbon emissions and a flow sheet of the asphalt-blowing process are given in Figure 7.

The gaseous emissions from the 10 reactors in operation were vented to the atmosphere through a system consisting of a common duct, oil knock-out tanks, and a stack. The individual reactors are charged on a rotating schedule; hence, the gases vented to atmosphere at any given time represent materials emitted at different stages of the air-blowing process.

The lower section of the stack was equipped with a steam spray-baffle arrangement. Pyrene was detected in large quantities in samples collected at the inlet and outlet sides of this baffle arrangement. The pyrene emission rate at the inlet was 3.5 grams per ton of material processed. Anthracene was present in smaller quantities. Phenanthrene and fluoranthene were detected in trace amounts. BaP, if present, was not detected because of interferences from unknown compounds. On the basis of the threshold concentration for this analysis, the BaP concentration in the gases would be at most 10 milligrams per ton of processed material. At this concentration, the daily contribution of BaP from this asphalt-blowing source would be less than that from two hand-stoked residential coal furnaces. By comparison, an equivalent emission of pyrene would require 250 hand-stoked furnaces (see Table 8).

Simultaneous with collection of the source samples, atmospheric concentrations of polynuclear hydrocarbons were measured in the immediate plant vicinity. For this purpose, high-volume air samplers were situated 1/4 to 1/2 mile from the plant in five residential areas of the city. Benzene extracts from the collected atmospheric samples (July 1962) were composited for a single analysis. BaP from this analysis measured 0.42 microgram per 1000 cubic meters air. This concentration is considerably lower than the 3.9 micrograms per 1000 cubic meters (July 1958) reported previously[7] for the downtown area of the same city.

SAMPLING LOCATION	GAS FLOW	BENZENE-SOLUBLE ORGANICS	POLYNUCLEAR HYDROCARBONS[a]			
			PYRENE		BaP	ANTHRACENE
	scfm	grams per ton processed	micrograms per 1000 cubic meters (70° F, 1 atm)			
Inlet	8,400	1,800	3.5	5,800,000	<20,000	310,000
Outlet	18,600	4,400	4.1	3,100,000	< 4,000	220,000

[a]Detected: phenanthrene (outlet), fluoranthene (inlet)
Not Detected: Benzo(e)pyrene, perylene, benzo(ghi)-perylene, anthanthrene and coronene

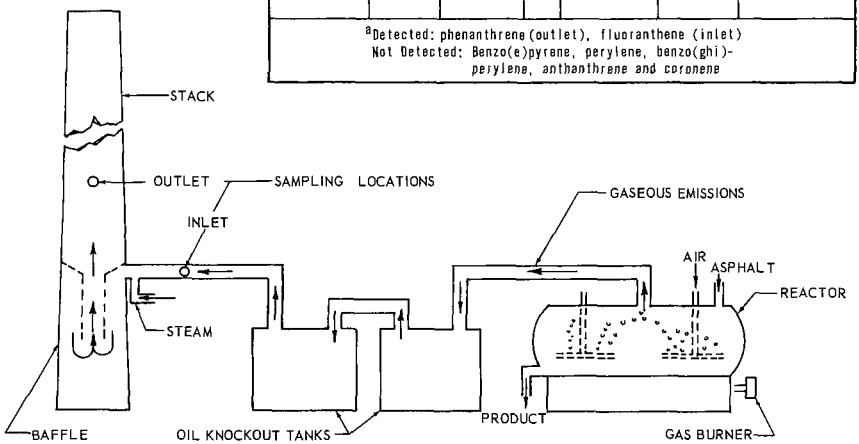

Figure 7. Flow sheet of effluent gases from asphalt air-blowing process-batch operation.

Thus, both the source samples and the air samples indicate that polynuclear hydrocarbons larger than pyrene are not volatilized to any significant extent by the air-blowing process. This process does not appear to emit significant amounts of BaP or other polynuclear hydrocarbons of equal or greater molecular weight. One other point of significance is that Sawicki[22] has found that the samples contain large quantities of alkyl-type polynuclear hydrocarbons (the analytical technique did not permit the determination of specific compounds of this type). Alkyl polynuclear hydrocarbons such as 9, 10-dimethyl anthracene and 1, 2, 4-trimethyl phenanthrene have been shown to be carcinogenic in studies with animals.[4, 5] Because of the nature of the asphalt air-blowing process, one would also expect the presence of oxygenated hydrocarbons. Epstein[23] has shown that the oxygenated fraction of the benzene extract from atmospheric particulate samples produces skin cancers on mice.

In summary, asphalt air blowing does not appear to be an important source of BaP. The source surveyed did emit large quantities of unidentified alkyl polynuclear hydrocarbons. Future identification of these alkyl compounds, and determination of oxygenated polynuclear hydrocarbons or the absence thereof, should define more precisely the importance of asphalt air blowing as a source of carcinogenic compounds.

Asphalt Hot-Road-Mix Plant

An asphalt hot-road-mix plant with a capacity of 3 tons per batch was tested for polynuclear hydrocarbon emissions by direct measurements. The plant was operating at a rate of 133 tons of finished mix per hour. A typical weighed 3-ton batch consisted of 6 percent asphalt and 94 percent sand and crushed stone. The mixture of sand and crushed stone was dried and charged to a mixer at 400°F. Asphalt at 250°F was then added to the mixer, and the materials were blended for 1 minute or less before being discharged to waiting trucks. A flow sheet of the process and a summary of emissions during the test are given in Figure 8.

Effluent gases from both the mixer and the rotary drier (45,000,000 Btu per hour) were passed in sequence through a cyclone and a water spray tower to remove process contaminants. Samples were collected simultaneously before and after passage through the spray tower. Duplicate samples were taken at each sampling location and combined for one analysis at each location.

SAMPLING LOCATION	GAS FLOW	BENZENE-SOLUBLE ORGANICS	POLYNUCLEAR HYDROCARBONS[a]					
			Pyrene	BaP	BeP	BghiP	A	Fluor
	scfm	grams per ton processed	micrograms per 1000 cubic meters (70° F, 1 atm)					
Inlet	37,000	18	0.0041	6,900	1,350	740	1,300	3,800	2,700
Outlet	41,000	9.8	0.0016	3,000	<100			1,400	2,500

[a]Detected: phenanthrene (outlet)
Not detected: perylene, anthanthrene, coronene

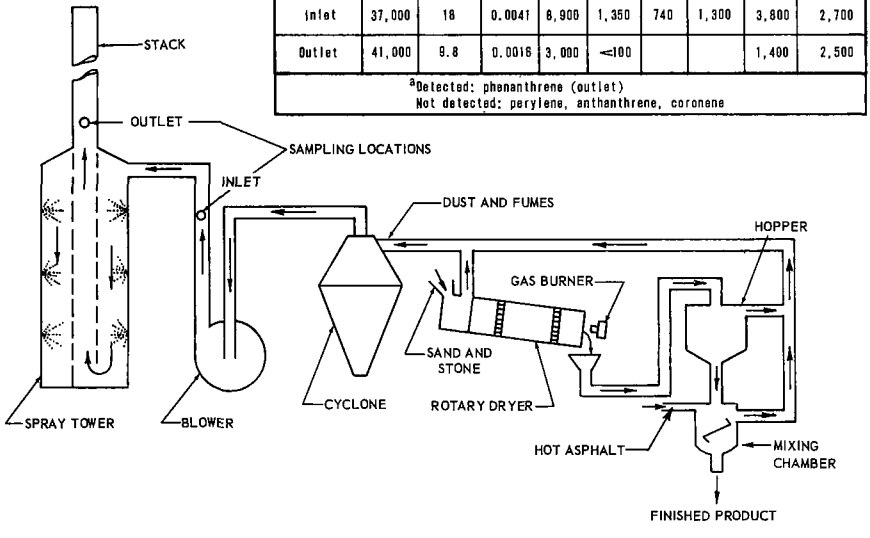

Figure 8. Flow sheet of effluent gases from asphalt hot-road mix process—batch operation.

Nearly all the emissions reported from this hot-road-mix plant are attributed to combustion gases emitted from the rotary dryer and not to effluent gases from the mixing chamber. This is evidenced by the results for a sample of the suspended particulates collected

directly from the mixing chamber. Of the 10 polynuclear hydrocarbons under consideration only anthracene was qualitatively identified. In the sample collected from the gas stream prior to the spray tower, however, six polynuclear hydrocarbons, including BaP, were detected. At this sampling location, the gas stream consisted of flue gases from the dryer and effluent gases from the mixing chamber.

Concentrations of the Group 1 polynuclear hydrocarbons are reduced considerably by the scrubbing effect in the spray tower. For example, the BaP concentration was reduced from 630 micrograms per ton of processed material to less than 50 micrograms per ton.

Because of the low inlet concentrations and the ease with which pollutants are removed, the asphalt hot-road-mix process does not appear to be a potentially important contributor of polynuclear hydrocarbon emissions to the atmosphere.

INDUSTRIAL PROCESSES: ATMOSPHERIC SAMPLING

The remaining industrial processes were evaluated by collection of atmospheric samples in urban residential areas in the vicinity of the installation. General atmospheric samples do not, of course, indicate anything about the relative distribution in the atmosphere, e.g., high concentrations that may exist only a few feet from a source having relatively small total emissions. For example, in one case reported by Sawicki, et al., [24] BaP concentrations as high as 78,000 micrograms per 1000 cubic meters of air were found a few feet downwind from a sidewalk tarring operation in which coal tar pitch was being used.

Carbon-Black Manufacturing

Samples of suspended particulates were collected at several urban residential sites in the vicinity of carbon-black manufacturing plants. The sites were located 1 to 3 miles from two adjacent carbon-black plants. Figure 9 (City A) shows the general location of sampling sites.

Carbon black was manufactured primarily from incomplete combustion of natural gas by both the furnace and channel processes. Some residual oil was burned intermittently with natural gas in the furnace process. One plant used both the furnace and channel methods whereas the other used only the furnace method. At the time of testing, one plant operated 360 burner houses for channel black and 2 production-size units for furnace black. The other plant operated five production-size furnace units.

The degree of carbon-black buildup on the filters varied from heavy loadings when the sampling sites were fumigated by the carbon-

black plume to light loadings at other times. All samples showed the presence of carbon black.

Concentrations of polynuclear hydrocarbons in atmospheric particulate samples collected in winter and summer are summarized in Tables 14 and 15. In Figure 10 the BaP concentrations near the three processes investigated indirectly are compared with the average winter and the average summer concentrations for a number of cities. These comparisons can be used very generally to determine the BaP emission potential of the three processes surveyed.

The winter BaP concentration in City A was well below the arithmetic mean winter concentration calculated from previously reported

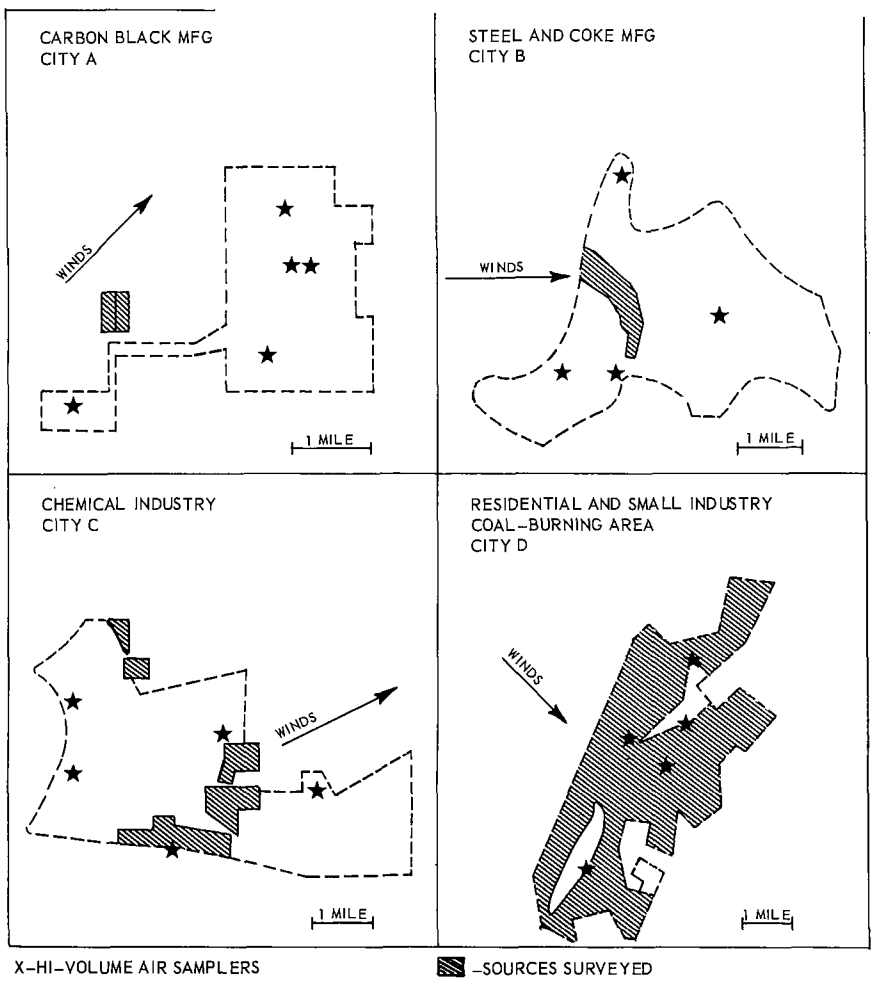

Figure 9. Maps of cities and sources included in the atmospheric survey.

data[7] for 102 United States cities (Figure 9). In fact, the BaP concentration of 0.58 microgram per 1000 cubic meters air in City A would be the fourth lowest concentration if it were included in this 102-city survey. On the basis of micrograms of BaP per gram suspended particulate, the concentrations in City A would rank eighth lowest.

Table 14. SUMMARY OF CONCENTRATIONS (BY VOLUME) OBTAINED IN ATMOSPHERIC SAMPLING NEAR AIR POLLUTION SOURCES

(micrograms per 1000 cubic meters of air)[a]

Air pollution source		Carbon black		Steel and coke	Chemical
City		A		B	C
Time of year		Summer	Winter	Summer	Winter
Benzene-soluble organics		1260	3800	6700	4600
Suspended atmospheric particulates		60,000	65,000	100,000	169,000
GROUP 1	Benzo (a) pyrene	0.035	0.58	8.6	6.9
	Pyrene	0.15	0.33	6.6	0.37
	Benzo (e) pyrene	0.18	0.76	4.1	0.57
	Perylene		0.03	1.0	
	Benzo (ghi) perylene	0.37	1.6	7.1	1.5
	Anthanthrene			0.83	
	Coronene	0.16	0.59	0.44	0.78
GROUP 2	Anthracene			2.4	
	Phenanthrene				
	Fluoranthene	0.43	0.07	3.2	0.30

[a]A blank indicates that the compound was not detected in the sample.

Carbon-black manufacture does not appear to be an important source of polynuclear hydrocarbon emissions for the following reasons: (1) the industry is relatively small; (2) although 87 percent of the carbon black in 1961 was manufactured by the furnace process, only 20 percent of the furnace black was classified as either "semi-reinforcing" or "high modulus" furnace black, the classes shown by Falk, et al, [26, 27] to contain the most polynuclear hydrocarbons; (3) low BaP concentrations were detected in the vicinity of the furnace-black plant tested. These results might be expected since published data by Lindsey, et al, [28] show no detectable BaP in a carbon-black sample of American origin manufactured for industrial use. Other data reported by Lindsey, et al, [29] show BaP concentrations as high as 1 percent by weight in two carbon-black samples of European origin.

Other previously reported studies also appear to support the conclusion that carbon-black manufacture is not an important source. Nau,

et al, [30, 33] showed that whole carbon black manufactured by the channel and furnace processes in the United states produces no appreciable carcinogenic effect on animals. Ingalls [34] concluded from a statistical study that the carbon-black worker faces no more than the ordinary risks of cancer encountered by other groups of the male working population.

Table 15. SUMMARY OF CONCENTRATIONS (BY WEIGHT) OBTAINED IN ATMOSPHERIC SAMPLING NEAR AIR POLLUTION SOURCES

(micrograms per gram suspended particulate)[a]

Air pollution source		Carbon black		Steel and coke	Chemical
City		A		B	C
Time of year		Summer	Winter	Spring	Summer
GROUP 1	Benzo (a) pyrene	0.58	8.8	89	41
	Pyrene	2.4	5.0	75	12
	Benzo (e) pyrene	3.0	11	43	89
	Perylene		0.4	10	
	Benzo (ghi) perylene	6.1	24	77	43
	Anthanthrene			9.1	
	Coronene	2.7	8.9	4.1	6.1
GROUP 2	Anthracene			29	
	Phenanthrene				
	Fluoranthene	7.2	1.1	33	12

[a]A blank indicates that the compound was not detected in the sample.

Steel and Coke Manufacturing

Samples of atmospheric suspended particulate were collected at four urban residential sampling sites in the vicinity of an integrated steel and coke manufacturing plant. Sampling sites were located 1/4 to 1-1/2 miles from the source in City B. Figure 9 shows the general location of the sampling sites.

Air pollutants from the steel and coke processes come primarily from two sources: (1) slot-type coke ovens and (2) oxygen-lanced open-hearth furnaces. During the test period the coke ovens, with an average capacity of 18 tons per charge, were operated at the rate of 383 oven charges per day. Meanwhile 11 of the 14 oxygen-lanced open-hearth furnaces (420 ton average size) were in operation. The open-hearth furnaces did not utilize control equipment to reduce dust emissions.

The BaP concentration during the spring test period in City B approximates the average winter concentration of 102 United States cities (Figure 10). Since samples were collected during the spring

season, the contribution from the periodic use of residential coal furnaces would be included in the measured result. Residential-size coal furnaces, as previously mentioned, are important sources of BaP emissions.

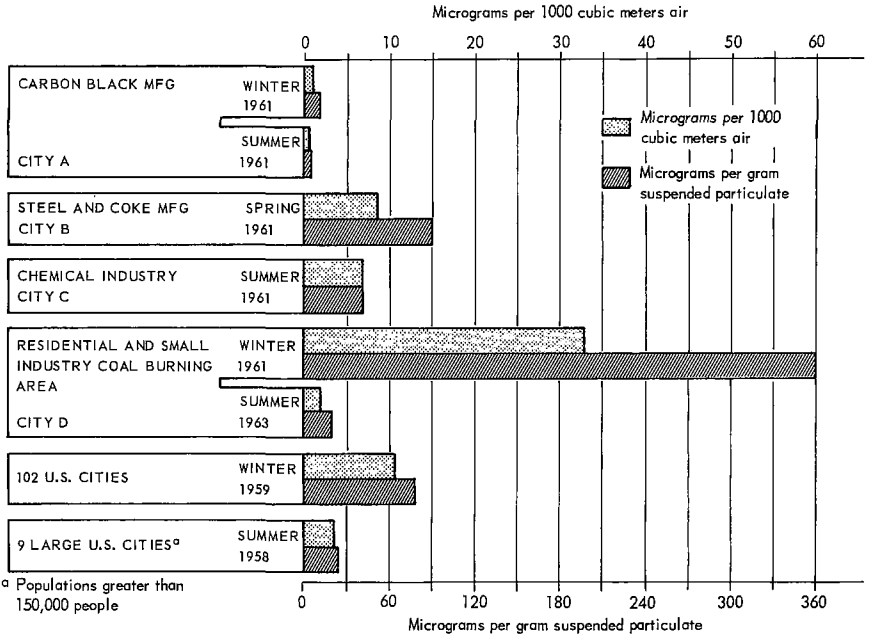

Figure 10. Comparison of atmospheric benzo (a) pyrene concentration in the United States.

The relative contribution of polynuclear hydrocarbons from the coking operations and the steel operations in City B cannot be ascertained by atmospheric sampling. No data were found in the published literature on polynuclear hydrocarbon emissions from steel manufacturing, but BaP concentrations ranging from 120 to 1700 micrograms per gram particulate have been reported by Yanysheva [35] in discharge gases from coke ovens in the U.S.S.R. These samples were aspirated from the upper areas of the coke oven.

Slot-type coke ovens are normally equipped with a chemical recovery system, and polynuclear hydrocarbon emissions result mainly from gas leakage. Therefore, even though high BaP concentrations have been reported in the particulates from coke ovens, the use of chemical recovery systems on the coke ovens operating in City B unquestionably restricted emissions of BaP to the atmosphere.

Higher polynuclear hydrocarbon emissions would be expected from the now-obsolete beehive coke ovens. Since production by this method amounted to only 6 percent of the total United States coke production in 1960, [36] no attempt was made to sample a beehive oven.

Chemical Manufacturing Complex

Atmospheric suspended particulate samples were collected at five urban residential sampling sites within a chemical industry complex in City C (Figure 9). This chemical complex produces graphite products, metallurgical products, inorganic acids and alkalies, and many organic compounds including organic polymers.

Concentrations of polynuclear hydrocarbons in the atmospheric particulate samples, which were taken during the summer, are summarized in Tables 14 and 15. The BaP concentrations on a volume basis and on a weight basis are only 80 percent and 70 percent higher, respectively, than the average summer concentrations[7] for nine larger United States cities (population greater than 150,000). On this basis, benzo(a)pyrene emissions to the atmosphere from such a chemical industry complex do not appear to be unusually high.

MOTOR VEHICLES

Eight automobiles and four trucks, representing two popular vehicle makes, were tested. To avoid obscuration of any relationship between emissions and the combined effects of age and mileage, automobiles of a given make were selected with the same type of engine: vehicles of Make A were powered by in-line 6-cylinder engines; those of Make B, by V-8 engines. All trucks tested were powered by in-line 6-cylinder engines. All automobiles were equipped with automatic transmissions and all trucks with standard transmissions. This choice was a compromise in the attempt both to represent typical usage and to exclude the influence of transmission type in comparisons of emissions from individual passenger cars and individual trucks. Each vehicle was carefully checked to ascertain that the mileage on the odometer was correct and that no major engine work had been done. Vehicle statistics and operating data are given in Table 16.

After a brief warmup to give a "hot start," all vehicles traversed the same 11.8-mile route, which consists of a realistic composite of business, arterial, and rapid-transit driving. Average run times were 31.9 and 34.4 minutes for the automobiles and trucks, respectively, at average speeds of 22.2 and 20.6 mph. Trucks were loaded with barrels of water to a weight representing 50 percent of rated payload capacity. All vehicles burned the same regular-grade fuel having medium aromatic content of 25 percent.

Emission data for polynuclear hydrocarbons are given in Table 17. The average BaP emission for the eight automobiles tested equals 11 micrograms per vehicle mile traveled. The average emission rate for Make-B automobiles (V-8 engines) was 14 micrograms per mile; the average rate for Make-A automobiles (6-cylinder engines) was 8.6 (see Table 17). The higher total emissions for Make B are expected in view of the larger engine displacements, but the average emission rate is also higher on the basis of micrograms of BaP per gallon of fuel. In

Table 16. VEHICLE STATISTICS AND OPERATION DATA

Sample No.	Vehicle		Year	Mileage	Engine Type	Displacement, cu in	Weight-to-power ratio[a] lb/hp	Fuel rate gph	Average speed mph	Exhaust flow (dry) scfh
AE-52	Automobiles	Make A	1962	19,000	Inline 6-cyl.	235.5	29.4	1.45	23.5	1410
46			1962	26,000		235.5	29.4	1.37	23.6	
47								1.43	21.3	1320
54			1959	49,000		235.5	30.4	1.33	20.8	1190
49			1956	58,000		235.5	26.4	1.46	25.6	1380
			4-car average					1.41	23.1	1320
60		Make B	1964[b]	14,000	V-8	289	18.2	1.60	21.6	1470
61								1.42	20.9	1420
57			1962	19,000		352	19.2	1.59	20.6	1460
58								1.57	23.9	1620
59								1.69	22.1	1580
50			1959	53,000		292	19.9	1.35	20.9	1490
56			1957	67,000		292	19.1	1.65	22.9	1350
			4-car average					1.53	21.8	1460
67	Trucks	Make A	1963[b]	17,000	Inline 6-cyl.	230	39.2	1.46	24.0	1340
65			1956	50,000		235.5	28.6	1.87	21.0	1380
			2-truck average					1.66	22.5	1360
68		Make B	1964[b]	6,000	Inline 6-cyl.	223	51.8	1.91	21.5	2320[c]
62			1963[b]	17,000		223	50.4	1.78	21.0	1980
63								1.57	16.9	1550
			2-truck average					1.79	20.2	2040

[a]Automobiles: shipping weight plus 500 pounds for passengers, oil, coolant, and fuel. Trucks: shipping weight plus 50 percent of rated payload capacity.

[b]Vehicles equipped with blowby devices; unit on 1964 Make-B automobile was plugged.

[c]Exhaust flow rate for first 10.5 miles of route.

view of the limited quantity of data and the possibility of a strongly skewed distribution of emission rates with mileage, the nonparametric outside-count and sign tests were applied to the data to determine whether the BaP emissions from Make A were statistically different from those from Make B. [37] These tests indicate no difference at the 10 percent level of significance.

A large jump in BaP emission rates at about 50,000 miles (1957 model or older) was observed for both makes of automobiles. Emissions averaged 28 micrograms per mile, whereas the average for the newer, lower-mileage automobiles was 5.5. A clear trend is not discernible at lower mileages. These values may indicate that at some stage in engine life changes occur that cause higher emissions. The character of the emissions for the two high-mileage automobiles is anomolous in one respect. For Make A, both the BaP and total benzene-soluble organic emissions were high (Table 17); but for Make B, the BaP emission was high although the benzene-soluble organic emission was not high.

BaP emissions from trucks averaged more than 40 micrograms per mile. The average rate for the Make-B trucks is probably low because total mileages were relatively low on both trucks.

Table 17. POLYNUCLEAR HYDROCARBON EMISSION SUMMARY: MOTOR VEHICLES

Sample No.	Vehicle				Group 2											Group 2		
					Benzene-soluble organics	BaP			BaP	P	BeP	Per	B(ghi)P	Anth	Cor	A	Phen	Fluor
			Year	Mileage	gm/mile	$\mu g/gm_{\phi so}$[a]	$\mu g/gal$[b]	$\mu g/10^3 m^3$[c]	micrograms per vehicle mile									
AE-52	AUTOMOBILES	Make A	1962	19,000	0.175	32	91	3,300	5.6	81	9.5	0.28	26	2.30	9.6	5.8		39
46			1962	26,000	0.120	35	72		4.2	70	8.1	0.78	35	0.64	10.7	3.6	27	39
47					0.108	27	43	1,660	2.9	12.9	4.7	0.34	34	0.33	17.2	3.9	46	6.7
54			1959	49,000	0.072	55	62	2,400	3.9	27	8.6	0.57	14.3	0.30	4.1	d	4.4	39
49			1956	58,000	0.511	42	380	14,100	21.5	119	23.5	1.38	77	3.17	32.2	d	d	102
			4-car average		0.218	40	147	5,400	8.6	67	12.0	0.70	38	1.56	15.0	2.4	10.3	51
60		Make B	1964	14,000	0.0956	e	60[f]	e	4[f]	76	e	d	6.7	d	7.2	1.34	53	42
61					0.1098	e	60[f]	e	4[f]	67	e	d	9.4	d	7.7	1.04	36	32
57			1962	19,000	0.0662	160	137	5,300	10.6	142	13.9	1.72	65	0.36	19.9	7.6	92	67
58					0.0597	88	80	2,700	5.3	125	9.6	0.78	49	0.37	18.5	5.7	32	65
59					0.0566	66	49	1,800	3.7	58	6.3	0.54	28	d	8.5	3.6	8.5	32
50			1959	53,000	0.1112	94	162	5,200	10.5	103	17.8	1.89	41	0.68	11.1	11.1	49	76
56			1957	67,000	0.0633	530	470	20,100	33.5	341	31.6	3.54	144	4.56	63.9	12.7	75	223
			4-car average		0.0703		190		14	156		1.7	60	1.37	25	7.7	53	98
67	TRUCKS	Make A	1963	17,000	0.077	>32	> 40	>1560	> 2.5	410	>3.5	0.84	94	d	61	10.0	260	220
65			1956	50,000	0.618	210	1450	70,000	130	1500	105	20	480	118	240	270	1030	980
			2-truck average		0.348	>120	>750	>36,000	>66	960	>54	10	290	59	150	140	650	600
68		Make B	1964	6,000	0.159	120	216		19.2	440	39	2.55	92	d	38	23.0	340	310
62			1963	17,000	0.243	52	149	4,700	12.6	640	48	1.02	153	d	102	13.6	290	440
63					0.233	27	68	2,400	6.3	600	42	1.12	94	d	61	7.0	290	330
			2-truck average		0.199	80	160		14.4	530	42	1.81	108	d	60	16.7	320	350

[a]Micrograms per gram of benzene-soluble organics.

[b]Micrograms per gallon of fuel input.

[c]Micrograms per 1000 cubic meters of dry exhaust at 68°F and 1 atmosphere.

[d]Compound not detected in sample.

[e]Interference prevented determination.

[f]Estimate based on average of pyrene to BaP ratios for tests 57, 58, and 59.

Nearly every sample contained all of the polynuclear hydrocarbons for which analyses are reported, and the emission trends in general followed those reported for BaP. In addition, the compounds benz(a)-anthracene and chrysene were detected. Pyrene was present in the greatest quantities; the average ratios of pyrene to BaP were 9.4 and 12.5 for the Make-A and Make-B automobiles and more than 90 and 48 for Make-A and Make-B trucks, respectively. Ratios of BaP to benzo-(ghi)perylene and BaP to coronene averaged approximately 0.2 and 0.6 for both makes of automobiles. These values are consistent with ratios reported earlier by Sawicki:[8] BaP to benzo(ghi)perylene, less than 0.6; and BaP to coronene, less than 1.0.

Two sets of preliminary tests yielded less substantial, but still comparable data. The first series of measurements was designed to determine which modes of operation of an automobile produced the greatest quantities of polynuclear hydrocarbons. A portion of the exhaust gas was sampled from an automobile having a 6-cylinder engine, mounted on a chassis dynamometer. Tests were made at constant-speed conditions of 20-mph cruise, 40-mph cruise, 20-mph deceleration, 40-mph deceleration, idle, and 20-mph acceleration. On the basis of micrograms per vehicle-mile, the 20-mph acceleration produced the highest BaP emission rate, 14 micrograms per mile.

The second series of preliminary measurements consisted of road tests similar to those described earlier. Total exhaust flow was sampled from three automobiles: two with V-8 engines (283 cubic inches, 5600 miles and 292 cubic inches, 32,000 miles). Emissions of BaP ranged from an average of 5.3 micrograms per mile for the V-8 engines to 77 micrograms per mile for the 6-cylinder engine.

Larsen[38] reports an estimated BaP emission rate of 49 micrograms per mile* determined by simultaneous particulate sampling and measurements of ventilation air flow and traffic flow in the Sumner Tunnel in Boston.

Begeman[39] reports a BaP emission rate of 9.6 micrograms per minute from a dynamometer-mounted V-8, 364-cubic-inch gasoline engine operated on a simulated city-driving cycle. At the average cycle speed of 23 miles per hour,[39] the reported emission rate equals 25 micrograms per mile. Samples taken over successive mileage intervals showed the possibility of increasing BaP emissions.[39, 40, 41]

Mileage Interval		BaP Emission Rate,	
		µg/min	µg/mile[a]
8,000	12,000	9.6	25[b]
19,300	25,500	6.2	16
25,500	29,000	9.0	24
29,000	33,000	27[c]	74[c]

[a] Calculation based on 23-mph average cycle speed.
[b] Takes into account high BaP content of condenser collected tar.
[c] Malfunction of engine reported reference 40.

*Corrected value; emission rates for polynuclear hydrocarbons as given in this reference are in error by a factor of 10.

The higher aromatic content of the gasoline used in Begeman's tests (36 percent versus 25 percent aromatic by fluorescence indicator analysis) may have contributed to the slightly higher emission rates.

More recently, Hoffman [6] reported BaP emission rates at two levels of oil consumption for the same dynamometer-mounted V-8 engine. BaP emission rates equivalent to 19 and 250 micrograms per mile were determined for oil consumptions of 1 quart per 1600 miles and 1 quart per 200 miles, respectively. The 13 times greater emission for the high-oil-consumption test suggests a partial explanation of the high BaP emission rates for the older, higher-mileage vehicles.

SUMMARY AND CONCLUSIONS

A screening survey of likely sources of emissions of BaP and other polynuclear hydrocarbons has produced some semi-quantitative data on possible major contributors of these compounds to the atmosphere. The sources were evaluated either by direct sampling of the effluent gases from the process or by atmospheric samples taken in residential areas in the vicinity of the process. The survey was not intended to establish statistically sound average emissions for every source category; such a study would have required many times the effort and funds expended. Enough emission data are available, however, to reveal the probable major sources, when annual consumption or production figures are considered. Table 18 is presented for this purpose. In interpreting the significance of this information, one should keep in mind that the calculation of total emissions involved considerable estimating and a number of assumptions, with respect to both emission rates and annual consumption or production figures. Also, the aggregate emissions from a number of small sources not considered in this study, although probably small, cannot be calculated.

The sources were classified in four major categories: heat generation, refuse burning, industrial processes, motor vehicles. This study has revealed that each category must be considered a factor affecting the atmospheric loading of BaP. Generally, the importance of a particular category or source has been evaluated in terms of the United States as a whole, but the importance of a particular source relative to concentrations found in the atmosphere undoubtedly varies considerably with locality; e.g., no coal is burned in Los Angeles County, but that city has areas of exceptionally high traffic density. Other factors may also influence the concentrations of BaP and other polynuclear hydrocarbons found in the atmosphere, e.g., decomposition or reaction with smog constituents in the atmosphere.

Heat Generation

Although each process surveyed undoubtedly contributes to the atmospheric loading of BaP, the most important source of BaP is the inefficient combustion of coal, typified by residential and small indus-

Table 18. ESTIMATED ANNUAL BaP EMISSIONS FOR THE UNITED STATES

Source	Estimated BaP emission rate	Estimated ann. consumption or production	Estimated ann. BaP emission, tons
Heat generation	(μg/10^6Btu)	(10^{15}Btu)	
Coal			
Residential			
i hand-stoked	1,400,000	0.26	400
ii underfeed	44,000	0.20	9.7
Commercial	5,000	0.51	2.8
Industrial	2,700	1.95	5.8
Electric generation	90	6.19	0.6
Oil	200	6.79	1.5
Gas	100	10.57	1.2
Total			421.6
Refuse burning	(μg/ton)	(10^6 tons)	
Incineration			
Municipal	5,300	18	0.1
Commercial	310,000	14	4.8
Open Burning			
Municipal refuse	310,000	14	4.8
Grass, leaves	310,000	14	4.8
Auto components	26,000,000	0.20	5.7
Total			20.2
Industries	(μg/bbl)	(10^6 bbl)	
Petroleum Catalytic Cracking (catalyst regeneration)			
FCC			
i no CO boiler	240	790	0.21
ii with CO boiler	14	790	0.012
HCC			
i no CO boiler	218,000	23.3	5.6
ii with CO boiler	45	43.3	0.0024
TCC (Air lift)			
i no CO boiler	90,000	131	13.0
ii with CO boiler	<45	59	<0.0029
TCC (Bucket lift)			
i no CO boiler	31	119	0.0041
ii with CO boiler	<31	0	0
Asphalt road mix	50μg/ton	187,000 tons	0.000010
Asphalt air blowing	<10,000μ g/ton	4,400 tons	<0.000048
Carbon-black manufacture	Atmospheric samples indicate that BaP emissions from these processes are not extremely high		
Steel and coke manufacture			
Chemical complex			
Total			18.8
Motor vehicles	(μg/gal)	(10^{10} gal)	
Gasoline			
Automobiles	170	4.61	8.6
Trucks	>460	2.01	>10
Diesel	690	0.257	2.0
Total			>20.6
Total (all sources tested)			481

trial coal-fired furnaces. BaP concentrations were determined during the winter and summer in a city in which the number of residential and small-industry coal-burning units was unusually high (Figure 9, City D). In Figure 10 these concentrations are compared with averages for United States cities and with the concentrations measured in the vicinity of processes surveyed by atmospheric sampling. This figure shows that

the atmospheric concentration during the winter for City D is considerably higher than the other concentrations shown.

The efficient combustion of coal in modern industrial process heating boilers and power plants and the combustion of fuel oil and natural gas do not appear to be significant contributors.

Replacement of inefficient coal-fired furnaces would greatly reduce emissions attributable to heat-generation.

Refuse Burning

In refuse burning, as in coal burning, efficiency of combustion governs the emission of polynuclear compounds. Inefficient combustion in small incinerators and open burning results in considerable formation of BaP and other polynuclear hydrocarbons, whereas good combustion in municipal incinerators leads to very little BaP formation.

The burning of all refuse, especially that which has a high ratio of hydrogen to carbon, in modern municipal incinerators or disposal by noncombustion methods would almost eliminate emissions attributable to refuse burning.

Industrial Processes

Results from direct and indirect sampling of industrial sources, although not conclusive, indicate that the following are not major sources of BaP: (1) an asphalt air-blowing process (pyrene emissions were high), (2) an asphalt hot-road-mix plant, (3) a carbon-black manufacturing area, (4) a steel and coke manufacturing area, and (5) a chemical industry complex.

Direct samples of the effluent from the catalyst regenerators of petroleum catalytic cracking units indicate that Houdriflow and Thermofor (air-lift) units can be significant sources of BaP and other polynuclear hydrocarbons among industrial sources. Emissions of these compounds can be and frequently are reduced to negligible amounts through the use of CO-waste heat boilers on individual "cat-cracker" catalyst regenerators. Thermofor (bucket lift) and Fluid units incorporate catalyst regenerator designs that result in only minor emissions. Considerable additional testing would be necessary to report contributions from catalyst regenerators with statistical assurance, as is the case for all of the sources tested.

Motor Vehicles

Consideration of the emission rates determined for gasoline-powered automobiles and trucks and the annual fuel usage leads one to

believe that motor vehicles are a major contributor of BaP to the atmosphere. This is confirmed by Colucci, [42] who reports automotive BaP contributions of 5 to 42 percent based on ratios of lead to BaP in exhaust and in the atmosphere. Evidence indicates that the older, higher-mileage vehicles and those with poorly adjusted engines yield the highest emission rates.

Limited data indicate higher emission rates for gasoline-powered trucks. Diesel-powered trucks may also yield higher rates; [43, 44] however, diesel fuel usage by trucks and buses accounts for only about 4 percent of the total petroleum consumption for motor vehicles. The over-all contribution from trucks and buses possibly exceeds that from automobiles, even though the total fuel usage for this category is about half that for automobiles.

Control systems applied to automobiles and trucks for the purpose of reducing emissions of total gaseous hydrocarbons should reduce emissions of BaP and other polynuclear hydrocarbons, but no data are available to confirm this.

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KEY WORDS:

Air Pollution

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Emissions

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