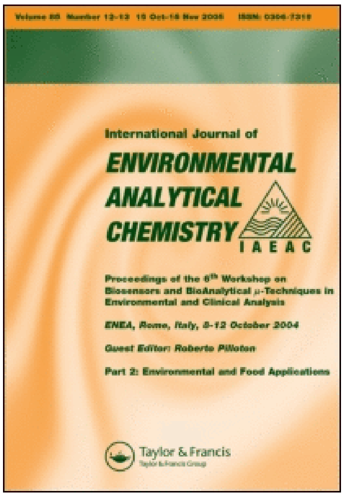

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PRIORITY POLLUTANT PAH ANALYSIS OF INCINERATOR EMISSION PARTICLES USING HPLC AND OPTIMIZED FLUORESCENCE DETECTION

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The U.S. Environmental Protection Agency (EPA) has investigated particle emissions from the incineration of various waste feeds. Emission particles from the incineration of municipal, medical/pathological, plastic and mixed wastes were captured and subsequently tested for biological activity. An ion-exchange fractionation of emission extracts yielded a base/neutral subfraction that contained a large portion of the total biological activity found. This subfraction was known to contain nonpolar neutrals, such as polycyclic aromatic hydrocarbons (PAHs), some of which are known mutagens and carcinogens. A modified version of U.S. EPA Method 610 for PAHs was utilized to quantify 15 of the 16 priority pollutant PAHs found in emission particle extracts. Modification of HPLC Method 610 consisted of time-programmed excitation and emission wavelength selection for fluorescence detection and use of a PAH-specific, reverse-phase C18 LC column. Only the PAH acenaphthylene, which has a low fluorescence intensity, could not be quantified at the desired levels using optimized fluorescence detection. PAH detection limits from 0.001 to 0.07 ng/ml extract were obtained. Emission rates based upon extractable organic matter, stack gas, mass of combusted waste and heating potential were calculated for each PAH and incinerator.

KEY WORDS: Municipal incinerators, polycyclic aromatic hydrocarbons (PAHs), high performance liquid chromatography, fluorescence detection

INTRODUCTION

Incineration technology is currently being used as one of the primary means to dispose of or treat municipal, medical/pathological, hazardous and mixed feed waste[1-4]. The destruction of waste materials by combustion is a complex engineering process requiring controlled high temperatures, thorough mixing/residence times, and sufficient oxygen concentrations to allow stoichometric conversion of the organic constituents to innocuous species[1,2,5,6]. While incineration is often deemed the "best available technology" for waste treatment, little is actually known about the products of incomplete combustion (PICs) formed during the process. This is especially true when "real world" sources such as municipal and medical/pathological wastes are incinerated. These wastes contain a variety of materials (plastics, biomass, metals, fibers, etc.) which when combusted would likely complicate any stack emission analysis due to complexity of the PICs.

The U.S. EPA has conducted a series of studies evaluating the emission products from a number of incinerators[3,4,7–9]. Stack particles were collected from a municipal waste incinerator, an incinerator having a mixture of feeds (municipal-medical/pathological), and a research unit examining sub-optimal combustion of a commercial plastic (polyethylene). Specialized sample collection systems consisting of either a baghouse unit (Baghouse) or a source dilution sampler (SDS) had been previously designed specifically for capture of incineration emissions and were employed in this study. Details concerning the design and use of these capture systems have been reported[7–12].

Preliminary biological analysis of the dichloromethane (DCM) extracts reported here indicated that some were mutagenic in bacterial bioassay systems[3–4]. Bioassay-directed fractionation was then conducted upon these extracts to focus research efforts upon the fractions containing significant biological activity (mutagencity). Fractionation was performed using a previously reported ion-exchange process that yielded base/neutral, polar neutral and acid fractions[4,13]. Bioassay of these fractions indicated significant mass and mutagencity present in the base/neutral fraction[3]. PAH standards such as naphthalene and pyrene analyzed concurrently with the above fractionation were known to elute in the base/neutral subfraction[4,13]. Based upon the known biological activity of some PAHs and their suspected presence in this subfraction, quantitation of 15 priority pollutant PAHs was performed upon the base/neutral subfractions from incinerator sources described above.

A modification of U.S. EPA Method 610[14] was utilized in the analysis of these subfractions. Modification of this high pressure liquid chromatography (HPLC) method consisted of the use of a PAH-specific, reverse-phase C18 LC column, and time-programmed excitation and emission wavelength selection of the fluorescence detector. These modifications allowed for 15 of the 16 PAHs to be satisfactorily resolved at low detection limits with elimination or reduction of chromatographic interferences. Acenaphthylene exhibited extremely low fluorescence intensity and was not able to be quantified at the desired levels using fluorescence methodology. This study reports PAH concentrations in the emission particles and the emission rates for 15 PAHs from three incineration sources.

EXPERIMENTAL

A prototype SDS unit operating at 10 cfm (0.28 m^3/min) was used to collect stack emissions of particles at a municipal waste incinerator (Incinerator A). This sampler brings in a 10-fold ratio of heated (24°C) HEPA (high efficiency particulate free) and charcoal-filtered air to simulate natural flue gas temperature quenching during atmospheric emission. The mixed and diluted stack particles were then collected on a round 66 cm Teflon impregnated glass fiber filter. A 2.5-um cutoff modified SASS (source assessment sampling system) cyclone was used as the sampling inlet. A complete description of this unit has been reported earlier[11]. Two sampling sessions where conducted at Incinerator A during 1988. This was a municipal waste unit, operating 24 h/day, having two identical 100 ton (90 tonne)/day capacity boilers. Each unit had its own ram piston, economizer, and electrostatic precipitator (ESP) with a single common stack.

The sampling inlet probe was positioned at the base of the stack just after one of the ESP units so that only the emissions from a single boiler were sampled. Stack gas temperature was 218°C at the probe location. The municipality operating the unit was asked to conduct normal operations, and there were no indications that this was not the case during sampling sessions. Sampling times at this incinerator ranged from 1 to 4.5 h. A complete description of the samples collected has been published[3]. Two of the collected samples are discussed in this study. The first is a composite of 3 filters (Mix1); and the second is a single filter (Filter #2). Data from the collection and DCM extraction of these and all samples reported here are detailed in Table 1.

The second incinerator sampled (Incinerator B) combusted a mixture of municipal and medical/pathological waste. It consisted of two, 50 ton (45 tonne)/day Consumat starved-air boilers having a shared ESP and stack. An estimated 3–5% of the waste combusted daily at the facility was medical/pathological waste. The SDS sampler was operated here as described above. The sampling probe was inserted after the union of the common stack and ESP. Stack gas temperature at the probe location was 251°C. A thorough discussion of Incinerator B has been reported[3]. Two of the collected SDS filters collected at this site (SDS7, SDS23) were analyzed for PAH emissions. Again, sampling, extraction and other data are presented in Table 1.

The last incinerator sampled (Incinerator C) was a pilot scale 73 kW (250,000 Btu/h) rotary kiln simulator operating at the U.S. EPA's Environmental Research Center (RTP,NC). This unit was designed specifically to contain the primary features of operating rotary kilns, yet it allows for operating conditions to be changed as needed to assess combustion factors. This unit has been described, and its operation has been compared to full-scale rotary kilns[8,12].

PAH analyses are reported for particles captured from the combustion of polyethylene (PE) charges placed in the unit. The unit was operated in a "fault" mode. This mode simulates the transient puffs normally encountered when waste charges are introduced into a unit operating under normal conditions. This mode was chosen to investigate a worst-case scenario, and the data collected should not be used to describe emissions from a properly adjusted kiln. PE was chosen as a test sample because it represents 5–10% mass of municipal and medical/pathological wastes[1–2]. PE was combusted under two test conditions. The first (PE Without) represented incineration of ten, 250-g charges batch-fed at 9-minute intervals using only the main combustion chamber of the simulator. A second series of charges were combusted as above, except that the unit's afterburner was employed (PE With). The afterburner was located at the base of the control temperature tower (CTT). Additional auxiliary burners were mounted inside annular regions in the refractory of the CTT. These auxiliary burners served to maintain high temperatures in the CTT without additional flue gas. The afterburner was operated at a firing rate of 125,000 Btu/h in addition to the normal

Table 1 Incinerator sampling conditions and collection summary.

Sample	*Incinerator*	*Waste Combusted*	*Collected (m^3)*	*Sampling Period (min)*	*Sampling Rate (m^3/min)*	*Stack Flow rate (m^3/min)*	*% EOM*	*Particles Collected (g)*	*Probe Temp (C)*	*Combustion Rate (tons/day)*
FILTER #2	A	MWC	57.3	223	0.26	644	0.62	4.0000	218*	100
MIX 1	A	MWC	150.4	652	0.23	644	0.73	6.6000	218*	100
SDS 7	B	MHMWC	68.8	330	0.21	393	0.31	5.4008	251*	2(50)
SDS 23	B	MHMWC	141.6	649	0.22	393	0.46	4.7011	251*	2(50)
PE WITH****	C	PE	253.52	90	2.82	2.68	0.15	8.0000	232**	0.04***
PE W/O ****	C	PE	253.52	90	2.82	1.97	8.42	28.1000	232**	0.04***

MWC=municipal waste combustion

MHMWC=municipal/hospital/medical waste combustion

(*) measured downstream from the electrostatic precipitator outlet (ESP)

(**) measured at the point of dilution

(***) based upon a charge rate of 2.5 kg/90 minutes

(****) small research incinerator operated in a semi-batch mode auxiliary heating at a stoichometric ratio of 1.25. Both conditions called for 200,000 Btu/h to be maintained by methane combustion in the main burner.

Particle sampling for both of the PE combustion conditions was performed using a prototype Baghouse Dilution Sampler (Baghouse). The design and applications of this sampler have been reported previously[3,8,10,11]. This sampler was operated at 2.83 m^3/min and was designed to collect larger quantities of particles as compared to the SDS assembly. All of the stack emissions were captured. Emission temperatures at the stack exit were previously monitored to be 593°C, with temperatures at the point of dilution found to be 232°C. Collected particles were diluted with a 10-fold dilution of HEPA- and charcoal-filtered air. The mixed and diluted stack emissions passed into a baghouse assembly consisting of a GoreTex filter membrane backed with 100% Nomex fiber. Particles trapped on the circular bag filter were periodically dislodged using a reverse stream of purified nitrogen. The dislodged particles fell into a glass collection bulb at the base of the unit. Collection and extraction data for the two PE samples are presented in Table 1.

Sample preparation

Captured particles were extracted with DCM using a sonication procedure described elsewhere[15]. Extracts were filtered through a 0.45-um Teflon filter and concentrated to a known volume using rotary evaporation at 35°C and 440 torr (58.7 kPa) vacuum. Concentrates were quantitatively transferred to volumetric flasks and diluted to 10 ml. Aliquots were removed for gravimetric determination of extractable organic matter (EOM). Known mass aliquots from each incinerator extract concentrate were fractionated into four subfractions using a nonaqueous ion-exchange procedure. Details of this technique are discussed elsewhere[3,4,13]. Ion-exchange fractionation proved useful due to the large percentage of acidic species found in some emission extracts encountered in our study of incineration sources. Acidic components have existed to such an extent that, upon occasion, DCM extracts of incineration particles corroded aluminum weighing pans used in gravimetric determinations. The procedure utilized allowed for extract mass to be fractionated into base/neutral, polar neutral and acid subfractions. Neutral PAHs have been shown to elute completely into the base/neutral subfraction[4,13]. The mass concentration of each subfraction was determined through gravimetric analysis. Dilution of the base/neutral subfraction (in DCM) followed by solvent exchange into acetonitrile was performed for each sample in preparation for HPLC analysis.

HPLC analysis

HPLC analysis was performed using a Varian 5560 LC equipped with a Varian 604 Data Station and a Perkin Elmer LS40 fluorescence detector. Modifications of EPA Method 610[14] were made to optimize PAH resolution and enhance detection limits. Method 610 utilizes a non-PAH specific C18 reverse-phase column with ultraviolet (UV 254 nm) or fluorescence detection using only one excitation/emission wavelength pair. Recently, HPLC column manufacturers have prepared C18 bonded silica columns specifically for the resolution of some difficult PAH analyte pairs. Majors has reported on the advantages of these columns over conventional C18 columns[16].

Method 610 utilizes only one wavelength pair for fluorescence detection, thereby enabling quantitation of 10 of the 16 priority PAHs at less than optimum conditions. The remaining PAHs required UV detection with this method. Variable wavelength and time-programmable fluorescence detectors were not available when this method was established; therefore, a single compromise excitation and emission pair was used for the entire HPLC analysis. Because all PAHs have optimum excitation and emission wavelengths that result in lower detection limits and higher specificity (elimination or reduction of fluorescence intensity from interfering analytes), selection of these wavelengths over the course of an HPLC analysis would be advantageous. The use of time-programmable wavelength selection for HPLC analysis of PAHs has been reported by others for environmental analysis[17]. This study used both a PAH specific LC column as well as time-programmed wavelength selection for fluorescence detection. Due to the complexity of incineration emissions, both modifications of Method 610 were necessary for low-level quantitation of the priority PAHs.

Injections of 5 ul from each neutral subfraction, as well as the quantitation standard (National Institute of Standards and Technology—NIST #PAH1647a) were utilized. Injections were made onto a 25 cm × 4.6 mm i.d., 5-um Supelcosil LC-PAH column (#5–8229). A Supelco C18 guard column (5–9554, 2 cm × 4.6 mm) was used in line with the analytical column. All HPLC solvents (acetonitrile, water) were from Burdick and Jackson and were HPLC grade, with only one lot of each used throughout the analysis. Solvents were degassed using helium sparging to eliminate possible oxygen quenching during fluorescence. A solvent mixture with a 25 minute gradient elution program consisting of an initial 65% water/35% acetonitrile mixture which was maintained for two minutes followed by a 14 minute linear gradient to 100% acetonitrile, which was followed by a 9 minute plateau at 100% acetonitrile allowed for adequate PAH resolution before the end of the program.

Solvent blanks were analyzed prior to incineration samples as part of quality assurance. Linear response curves were performed for each of the 15 PAHs using a minimum of three concentrations. These standards ranged up to 0.7 ng/ml over three orders of magnitude. PAH results were corrected for blank interferences and quantitated using a single-point calibration standard. Excitation and emission wavelengths were selected that offered the best compromise between compound specificity and fluorescence intensity, allowed for use of longer excitation wavelengths to reduce or eliminate detection of nonaromatic analytes, and allowed for compromise wavelength and attenuation factors when adjacent peaks lacked 1.0 resolution factors and wavelengths could not be changed.

RESULTS

Data concerning calibration results, limits of detection, wavelength and attenuation selection, and retention times of each PAH are presented in Table 2. Calibration coefficients (r^2) were found to exceed 0.990 for the 15 quantified PAHs and in most cases exceeded 0.999. Specific wavelengths were utilized when possible. Analyte pairs failing to completely

Table 2 HPLC analysis parameters.

PAH	*EX*	*EM*	*Calibration Coefficient*	*Limits of Detection (ug/l)*	*Retention Time (min)*
Naphthalene	276	323	0.9952	0.030	10.83
Acenaphthylene	290	337	ND	>1.0x10^6	11.80
Acenaphthene	290	337	0.9904	0.005	12.59
Fluorene	290	337	0.9902	0.013	12.76
Phenanthrene	297	367	0.9949	0.015	13.42
Anthracene	255	380	0.9992	0.001	13.97
Fluoranthene	290	447	0.9991	0.009	14.70
Pyrene	276	391	0.9999	0.004	15.18
Benzo(a)anthracene	265	380	0.9996	0.009	16.61
Chrysene	265	380	0.9997	0.003	16.89
Benzo(b)fluoranthene	290	430	0.9999	0.005	18.21
Benzo(k)fluoranthene	290	430	0.9998	0.001	18.70
Benzo(a)pyrene	298	407	0.9999	0.001	19.25
Dibenzo(a, h)anthracene	298	398	0.9994	0.002	20.01
Benzo(ghi)perylene	302	500	0.9970	0.072	20.92
Indeno(1, 2, 3-cd)pyrene	302	500	0.9999	0.022	21.29

Detection using the LS40 detector and a standard injection volume of 5ul
Limits of detection are based upon an unattenuated detector signal to the data station (attenuation factor of 1)
ND = not determined
EX=excitation wavelength
EM=emission wavelength

resolve included acenaphthene and fluorene, benzo(a)anthracene and chrysene, benzo(b)fluoranthene and benzo(k)fluoranthene, and benzo(ghi)perylene and indeno(1,2,3-cd)pyrene. Acenaphthylene exhibited extremely low fluorescent intensity during detector response evaluations and was not evaluated further. Limits of detection for this compound exceeded 1.0X10^6 ug/l. Acenaphthylene can be detected using UV (322 nm max), but no attempt was made to quantify this component due to the high concentrations needed in extracts for UV detection.

Retention times were found to average 0.09% RSD as evidenced by the retentions obtained from triplicate analyses of the NIST standard. Careful selection of attenuation factors for the LS40 fluorescence detector had to be performed. This instrument is configured so that only an attenuated detector response can be acquired by a data station (integrator). Attenuation factors at each wavelength change were determined through experimentation so that acceptable noise and sensitivity levels were achieved. Limits of detection were calculated based upon an injection volume of 5 ul of an NIST standard stock solution and using a 5 X S/N ratio with an attenuation signal of 1 to the data station. Benzo(ghi)perylene was found to have the highest detection limit (0.07 ug/l) under the test conditions.

Chromatograms of the NIST standard, PE With, and PE Without neutral fraction extracts are shown in Figure 1 and are representative of those obtained for the other incineration extracts reported here. Extra peaks not labeled in the NIST standard chromatogram are additional PAHs included by NIST in their mixture. The NIST standard chromatographed satisfactorily as indicated by the peak shape as well as the resolution seen between near

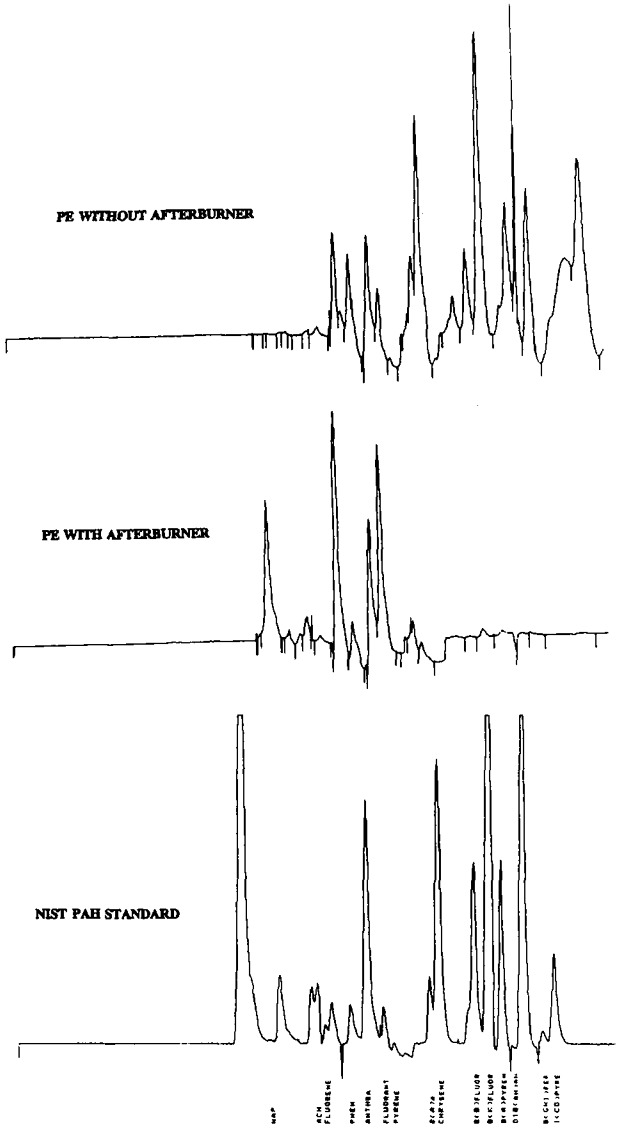

Figure 1 HPLC chromatograms of NIST standard and polyethylene combustion in Incinerator C. HPLC conditions are listed in the text. Notice the subsequent loss of high molecular weight PAHs when the afterburner (middle trace) was employed during incineration. Legends are as follows:
NAP=Naphthalene, ACN=Acenaphthene, FLUORENE=Fluorene, PHEN=Phenanthrene,
ANTHRA=Anthracene, FLUORANT=Fluoranthene, PYRENE=Pyrene,
B (A) A=Benz (a) anthracene, CHRYSENE=Chrysene, B(B)FLUOR=Benz(b)fluoranthene,
B(K)FLUOR=Benz(k)fluoranthene, B(A)PYREN=Benz(a)pyrene, DIB(AH)AN=Dibenzo(a, h)anthracene,
B(GHI)PER=Benzo(g, h, i)perylene, I(CD)PYRE=Indeno(c, d)pyrene.

eluting peaks. As depicted on the upper two chromatograms, peak shapes in the incineration extracts were sometimes affected by interfering species. Capillary gas chromatography (not depicted) of the incineration extracts reported here revealed a myriad of components present in addition to the PAHs of interest. Gas chromatography was not utilized in quantitation efforts due to limits of detection far higher than those established for the fluorescence technique. The effect of incineration using an afterburner is revealed in review of the two PE extracts in the figure. There is noticeable loss of PAHs in the PE With (afterburner) sample as compared to the PE Without. The higher weight PAHs were reduced one to three orders of magnitude (PAH/mg EOM); whereas, the lower weight PAHs, such as naphthalene, were increased by similar magnitudes.

Particle concentrations of the PAHs found in the neutral fractions of the incineration emission particle extracts as well as various emission rates are detailed in Tables 3–8. Comparison of the calculated particle concentration of each PAH (ng PAH/g particle) reveals differences between the various incinerators. Benzo(a)pyrene, for example, was found to range from 0.004 to 875 ng/mg particle. Further comparison reveals that emissions

Table 3 PAH emission rates (calculated for individual PAHs) MIX 1 (filters 2, 3, & 4) (Site A).

PAHs	*Total Particles ng/mg (ppm)*	*PAHng/ mgEOM*	*PAHng/ m^3stack gas*	*PAHng/min*	*PAHng/ kgfuel*	*PAHng/MJ*
1 Naphthalene	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*
2 Acenaphthylene	ND	ND	ND	ND	ND	ND
3 Acenaphthene	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*
4 Fluorene	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*
5 Phenanthrene	0.11	15.00	4.81	3096.03	49.14	4.23
6 Anthracene	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*
7 Fluoranthene	2.33	319.00	102.24	65842.24	1045.11	89.99
8 Pyrene	0.38	51.50	16.51	10629.70	168.73	14.53
9 Benzo(a)anthracene	0.73	100.50	32.21	20743.40	329.26	28.35
10 Chrysene	1.61	221.10	70.86	45635.48	724.37	62.37
11 Benzo(b)fluoranthene	3.97	544.00	174.35	112282.69	1782.26	153.46
12 Benzo(k)fluoranthene	1.32	181.30	58.11	37420.68	593.98	51.14
13 Benzo(a)pyrene	0.34	46.30	14.84	9556.41	151.69	13.06
14 Dibenzo(a, h)anthracene	0.84	114.80	36.79	23694.95	376.11	32.38
15 Benzo(g, h, i)perylene	3.36	460.50	147.59	95048.12	1508.70	129.90
16 Indeno(1, 2, 3-cd)pyrene	3.11	425.30	136.31	87782.77	1393.38	119.97
Totals	18.10	2479.30	794.62	511732.48	8122.74	699.39

EQUATIONS UTILIZED:
PAHng/mgEOM × 0.3205 mgEOM/m^3 stack gas = PAHng/m^3 stack gas
PAHng/m^3 stack gas × 644 std. m^3/min = PAHng/min
PAHng/min × 1min/63kg = PAHng/kg fuel
PAHng/kg fuel × 1kg msw/11.614MJ = PAHng/MJ

EOM for stack gas = 0.3205 mg/m^3 (for mix neutral fraction)
Site A total stack flow = 644 std. m^3/min
Site A fuel burn rate = 63 kg/min
11.614 MJ/kg = literature value of municipal solid waste
(*) not detected above detection limits
ND = not determined

Table 4 PAH emission rates (calculated for individual PAHs) Filter #2 (Site A).

PAHs	*Total Particles ng/mg (ppm)*	*PAHng/ mgEOM*	*PAHng/ m^3stack gas*	*PAHng/min*	*PAHng/ kgfuel*	*PAHng/MJ*
1 Naphthalene	0.11	26.16	5.76	3706.35	58.83	5.07
2 Acenaphthylene	ND	ND	ND	ND	ND	ND
3 Acenaphthene	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*
4 Fluorene	0.10	23.19	5.10	3285.56	52.15	4.49
5 Phenanthrene	1.08	257.43	56.63	36472.68	578.93	49.85
6 Anthracene	0.01	1.19	0.26	168.60	2.68	0.23
7 Fluoranthene	0.25	58.86	12.95	8339.28	132.37	11.40
8 Pyrene	0.17	41.02	9.02	5811.71	92.25	7.94
9 Benzo(a)anthracene	0.48	113.00	24.86	16009.84	254.12	21.88
10 Chrysene	1.10	260.40	57.29	36893.47	585.61	50.42
11 Benzo(b)fluoranthene	0.01	2.38	0.52	337.20	5.35	0.46
12 Benzo(k)fluoranthene	0.08	18.43	4.05	2611.16	41.45	3.57
13 Benzo(a)pyrene	0.04	8.32	1.83	1178.78	18.71	1.61
14 Dibenzo(a,h)anthracene	0.02	4.76	1.05	674.40	10.70	0.92
15 Benzo(g, h, i)perylene	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*
16 Indeno(1, 2, 3 -cd)pyrene	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*
Totals	3.45	815.14	179.33	115489.04	1833.16	157.84

EQUATIONS UTILIZED:
PAHng/mgEOM × 0.22mg EOM/m^3Stack gas = PAHng/m^3 stack gas
PAHng/m^3 stack gas × 644 std. m^3/min = PAHng/min
PAHng/min × 1min/63kg = PAHng/kg fuel
PAHng/kg fuel × 1kg msw/11.614MJ = PAHng/MJ

EOM for stack gas = 0.22 mg/m^3
site A total stack flow = 644 std. m^3/min
site A fuel burn rate = 63 kg/min
11.614 MJ/kg = literature value of municipal solid waste
(*) not detected above detection limits
ND = not determined

from Incinerator B, a unit combusting mixed municipal and medical/pathological waste, had the lowest overall particle concentrations of PAHs. Particle concentrations from SDS samples 7 and 23 at this incinerator ranged from below detectable quantities to only 0.2 ng/mg (benzo[a]anthracene—SDS 23) for example. Even though different "loads" of waste were combusted at this incinerator during capture of the two samples, the PAH concentrations were similar.

Whole particle concentrations found in samples from Incinerator A were found to be slightly higher than those from Incinerator B and also more variable. Filter #2 had concentrations ranging 0.005 to 1.1 ng/mg. The Mix 1 filter sample had nondetectable levels of the early eluting (low molecular weight) PAHs, with compounds phenanthrene through indeno(1,2,3-cd)pyrene present in a tight range of 0.1–4.0 ng/mg. Differences between the two samples at this site may well have been due to composition of the waste feeds, but rainy weather may have played a part. Wet waste, due to a rain storm, was fed into the incinerator prior to capture of the Filter #2 sample. Water vapor exiting the stack was so prevalent that

Table 5 PAH emission rates (calculated for individual PAHs) SDS 7 (SITE B).

PAHs	*Total Particles ng/g (ppb)*	*PAHng/ mgEOM*	*PAHng/ m^3stack gas*	*PAHng/min*	*PAHng/ kgfuel*	*PAHng/MJ*
1 Naphthalene	25.20	8.10	1.94	763.99	12.13	1.04
2 Acenaphthylene	ND	ND	ND	ND	ND	ND
3 Acenaphthene	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*
4 Fluorene	28.50	9.20	2.21	867.74	13.77	1.19
5 Phenanthrene	42.00	13.60	3.26	1282.75	20.36	1.75
6 Anthracene	1.20	0.40	0.10	37.73	0.60	0.05
7 Fluoranthene	20.70	6.70	1.61	631.94	10.03	0.86
8 Pyrene	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*
9 Benzo(a)anthracene	7.40	2.40	0.58	226.37	3.59	0.31
10 Chrysene	3.60	1.20	0.29	113.18	1.80	0.15
11 Benzo(b)fluoranthene	31.10	10.10	2.42	952.63	15.12	1.30
12 Benzo(k)fluoranthene	7.80	2.60	0.62	245.23	3.89	0.34
13 Benzo(a)pyrene	3.60	1.20	0.29	113.18	1.80	0.15
14 Dibenzo(a, h)anthracene	1.00	0.30	0.07	28.30	0.45	0.04
15 Benzo(g, h, i)perylene	92.30	29.90	7.18	2820.17	44.76	3.85
16 Indeno(1, 2, 3-cd)pyrene	30.10	9.80	2.35	924.34	14.67	1.26
Totals	294.50	95.50	22.92	9007.56	142.98	12.31

EQUATIONS UTILIZED:
PAHng/mgEOM × 0.24mgEOM/m^3stack gas = PAHng/m^3 stack gas
PAHng/m^3 stack gas × 393 std. m^3/min = PAHng/min
PAHng/min × 1min/63kg = PAHng/kg fuel
PAHng/kg fuel × 1kg msw/11.614MJ = PAHng/MJ

EOM for stack gas = 0.24 mg/m^3
site B= 393 std. m^3/min total stack flow
site B fuel burn rate = 63 kg/min
11.614 MJ/kg = literature value of municipal solid waste
(*) not detected above detection limits
ND = not determined

the Baghouse sampler, attached to the unit to capture emissions simultaneously with the SDS unit, had to be turned off due to large intakes of condensing water. The temperature quenching effect of high moisture content may very well have reduced conditions necessary for PAHs to be formed or had a scrubbing effect upon the stack emissions.

Particle stack emissions from the incineration of PE (Incinerator C) were found to have the highest levels of all PAHs. This is not unexpected, since the tests on Incinerator C were run deliberately under sub-optimal combustion conditions. Concentrations found in the PE Without sample were found to range up to 4000 ng/mg particle (pyrene). As mentioned earlier, afterburning reduced the levels one to four orders of magnitude. Incinerators A and B did not have afterburners, so no comparison could made on PAH reductions from these units. PAH formation from combustion of PE should be more favored to that formed from municipal wastes containing a variety of fuel materials due to the higher amount of organic carbon available in the PE emissions for production of ringed aromatic compounds. Further evidence of this fact is seen in comparing emission factors. The high concentrations of PAHs

Table 6 PAH emission rates (calculated for individual PAHs) SDS 23 (SITE B).

PAHs	*Total Particles ng/g (ppb)*	*PAHng/ mgEOM*	*PAHng/ m^{3}stack gas*	*PAHng/min*	*PAHng/ kgfuel*	*PAHng/MJ*
1 Naphthalene	60.10	13.10	1.96	772.24	12.26	1.06
2 Acenaphthylene	ND	ND	ND	ND	ND	ND
3 Acenaphthene	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*
4 Fluorene	13.70	3.00	0.45	176.85	2.81	0.24
5 Phenanthrene	50.60	11.10	1.66	654.34	10.39	0.89
6 Anthracene	11.60	2.50	0.38	147.38	2.34	0.20
7 Fluoranthene	84.40	18.40	2.76	1084.68	17.22	1.48
8 Pyrene	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*
9 Benzo(a)anthracene	203.50	44.40	6.66	2617.38	41.55	3.58
10 Chrysene	110.70	24.20	3.63	1426.59	22.64	1.95
11 Benzo(b)fluoranthene	90.70	19.80	2.97	1167.21	18.53	1.60
12 Benzo(k)fluoranthene	38.00	8.30	1.25	489.29	7.77	0.67
13 Benzo(a)pyrene	14.80	3.20	0.48	188.64	2.99	0.26
14 Dibenzo(a, h)anthracene	13.70	3.00	0.45	176.85	2.81	0.24
15 Benzo(g, h, i)perylene	15.80	3.50	0.53	206.33	3.28	0.28
16 Indeno(1, 2, 3-cd)pyrene	60.10	13.10	1.96	772.24	12.26	1.06
Totals	767.70	167.60	25.14	9880.02	156.83	13.50

EQUATIONS UTILIZED:
PAHng/mgEOM × 0.15mgEOM/m^{3}stack gas = PAHng/m^3 stack gas
PAHng/m^3 stack gas × 393 std. m^3/min = PAHng/min
PAHng/min × 1min/63kg = PAHng/kg fuel
PAHng/kg fuel × 1kg msw/11.614MJ = PAHng/MJ

EOM for stack gas = 0.15 mg/m^3
site B total stack flow = 393 std. m^3/min
site B fuel burn rate = 63 kg/min
11.614 MJ/kg = literature value of municipal solid waste
(*) not detected above detection limits
ND = not determined

produced with PE combustion may indicate that plastics may be responsible for a significant portion of municipal waste PAH emissions.

Tables 3–8 also present emission rates expressed in terms of fuel sources and combustion data. Emission rates from Incinerators A and B were based upon an estimated fuel combustion rate of 100 ton/day (63 kg/min) and a heating value of 11.6 MJ/kg. The incinerator operators do not weigh charges prior to loading them into the units, and the above heat value is one that has been reported for municipal waste[3]. Emission rates were calculated likewise for the two PE samples based upon a known combustion rate of 0.070 kg/min and a PE fuel value of 46.5 MJ/kg. Incinerators A and B were self firing; whereas, the simulator (Incinerator C) used methane to promote combustion. Any PAH contributions from the methane have not been accounted for in the calculations. Previous testing of this simulator indicated little if any contributions from the combustion of methane[8].

Calculation of emission rate data from the combustion of mixed municipal and medical/pathological waste at Incinerator B reveals that samples SDS 7 and 23 were comparable.

Table 7 PAH emission rates (calculated for individual PAHs) PE With Afterburner (Site C).

PAHs	*Total Particles ng/mg (ppm)*	*PAHng/ mgEOM*	*PAHng/ m^3stack gas*	*PAHng/min*	*PAHng/ kgfuel*	*PAHng/MJ*
1 Naphthalene	5.80	3931.20	516.99	1385.52	19708.70	423.74
2 Acenaphthylene	ND	ND	ND	ND	ND	ND
3 Acenaphthene	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*
4 Fluorene	0.70	458.80	60.34	161.70	2300.15	49.45
5 Phenanthrene	18.70	12679.90	1667.51	4468.93	63569.48	1366.74
6 Anthracene	0.50	344.10	45.25	121.28	1725.11	37.09
7 Fluoranthene	11.30	7643.40	1005.17	2693.86	38319.46	823.87
8 Pyrene	29.60	20104.30	2643.88	7085.61	100791.01	2167.01
9 Benzo(a)anthracene	0.80	573.50	75.42	202.13	2875.19	61.82
10 Chrysene	0.10	62.60	8.23	22.06	313.84	6.75
11 Benzo(b)fluoranthene	0.10	62.60	8.23	22.06	313.84	6.75
12 Benzo(k)fluoranthene	0.03	20.90	2.75	7.37	104.78	2.25
13 Benzo(a)pyrene	0.20	146.00	19.20	51.46	731.96	15.74
14 Dibenzo(a, h)anthracene	0.01	3.10	0.41	1.09	15.54	0.33
15 Benzo(g, h, i)perylene	0.70	458.80	60.34	161.70	2300.15	49.45
16 Indeno(1, 2, 3-cd)pyrene	0.10	73.00	9.60	25.73	365.98	7.87
Totals	68.64	46562.20	6123.32	16410.49	233435.19	5018.86

EQUATIONS UTILIZED:
PAHng/mgEOM × (33.34mgEOM/253.52m^3stack gas) = PAHng/m^3 stack gas
PAHng/m^3stack gas × 2.68 std. m^3/min =PAHng/min
PAHng/min × 1min/0.0703kg = PAHng/kg fuel
PAHng/kg fuel × 0.0215kg/MJ = PAHng/MJ

EOM for stack gas = 33.34 mgEOM/253.52 m^3 =0.13 mg/m^3
Total stack flow = 2.68 std. m^3/min
Fuel burn rate = 0.0703 kg/min
0.0215 kg/MJ = total kg of polyethyene burned per total MJ of heat released for PE
(*) not detected above detection limits
ND = not determined

Individual PAHs were found to be as high as 44.40 ng/mg EOM (benzo[a]anthracene—SDS 23). PAH's mass/volume of stack gas were determined to be from nondetectable levels to 7 ng/m^3 (benzo[g, h, i]perylene—SDS 7). As much as 2820 ng/min of this analyte was calculated to be emitted from Incinerator B based upon sample SDS 7. Using an estimated combustion rate of 100 tons refuse/day, PAHs/mass of fuel varied between nondetectable to >40 ng/kg fuel (benzo[g, h, i]perylene, benzo[a]anthracene). Analyte emissions relating to heating values were generally on the order of 1 ng/MJ. An estimated heating value of 11.614 MJ/kg of urban waste[3] was utilized in this calculation.

Emission rates from Incinerator A were found to vary more between collection periods and individual PAHs compared to Incinerator B. Six- and five-ring compounds like benzo(g, h, i)perylene and pyrene were found at concentrations near 400–500 ng/mg EOM in the Mix 1 extract, with nondetectable levels of two- and three-ring compounds (naphthalene/anthracene/etc.). The Filter #2 extract had just the opposite findings with low to nondetectable quantities of PAH/mass EOM observed for the larger ringed compounds with two- and

Table 8 PAH emission rates (calculated for individual PAHs) PE Without Afterburner (Site C).

PAHs	*Total Particles ng/mg (ppm)*	*PAHng/ mgEOM*	*PAHng/ m^3stack gas*	*PAHng/min*	*PAHng/ kgfuel*	*PAHng/MJ*
1 Naphthalene	15.20	180.30	1682.67	3314.85	47152.98	1013.79
2 Acenaphthylene	ND	ND	ND	ND	ND	ND
3 Acenaphthene	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*
4 Fluorene	108.00	1282.10	11965.32	23571.69	335301.36	7208.98
5 Phenanthrene	2037.50	24199.10	225840.45	444905.68	6328672.61	136066.46
6 Anthracene	231.10	2744.40	25612.38	50456.39	717729.55	15431.19
7 Fluoranthene	2193.60	26052.10	243133.75	478973.49	6813278.66	146485.49
8 Pyrene	4006.80	47586.80	444108.43	874893.60	12445143.73	267570.59
9 Benzo(a)anthracene	349.20	4146.70	38699.48	76237.98	1084466.23	23316.02
10 Chrysene	301.10	3575.80	33371.50	65741.86	935161.54	20105.97
11 Benzo(b)fluoranthene	350.00	4156.70	38792.81	76421.83	1087081.48	23372.25
12 Benzo(k)fluoranthene	230.20	2734.40	25519.05	50272.54	715114.30	15374.96
13 Benzo(a)pyrene	874.60	10386.80	96935.82	190963.56	2716409.15	58402.80
14 Dibenzo(a, h)anthracene	12.70	150.24	1402.13	2762.19	39291.53	844.77
15 Benzo(g, h, i)perylene	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*
16 Indeno(1, 2, 3-cd)pyrene	797.00	9465.30	88335.83	174021.59	2475413.75	53221.40
Totals	11507.00	136660.74	1275399.62	2512537.25	35740216.86	768414.66

EQUATIONS UTILIZED:
PAHng/mgEOM × (2366 mgEOM/253.52 m^3 stack gas) = PAHng/m^3 stack gas
PAHng/m^3stack gas × 1.97 m^3/min = PAHng/min
PAHng/min × 1min/0.0703kg = PAHng/kg fuel
PAHng/kg fuel × 0.0215kg/MJ = PAHng/MJ

EOM for stack gas = 2366 mgEOM/253.52 m^3 =9.33 mg/m^3
Total stack flow = 1.97 std. m^3/min
Fuel burn rate = 0.0703 kg/min
0.0215kg/MJ = total kg of polyethylene burned per total MJ of heat released for PE
(*) not detected above detection limits
ND = not determined

three-ring compounds present near 250 ng/mg EOM. These findings may be due to differences in fuel composition, combustion parameters, or maybe the effect of high moisture content of Filter #2 sampling discussed earlier. Other emission rates for Incinerator A were one to two orders of magnitude greater as compared to those obtained for Incinerator B. Noteworthy is the calculated release of many PAHs exceeding 20 ug/min. Based upon fuel combustion, Incinerator A had rates 100- fold higher than those found for Incinerator B in some cases.

Emission rates calculated for the combustion of PE by Incinerator C without an afterburner were found to be two to three orders of magnitude greater compared to the other two incinerators. This incinerator was operated under fault conditions, and higher emissions values were expected. Benzo(a)pyrene was estimated to be emitted at 10 ug/mg EOM. Pyrene had an emission rate of 0.44 mg/m^3. Indeno(1,2,3-cd)pyrene was found to have rates exceeding 0.17 mg/min. Because of the organic-rich nature of PE as compared to municipal waste, it was not surprising to find extreme differences in the production of PAHs/mass fuel.

Most PAHs were produced at levels at or above 1 mg/kg fuel. This was five to six orders higher in production as compared to the municipal waste incinerators. Emission rates based upon fuel value ranged from nondetectable levels to 0.26 mg/MJ. Combustion with an afterburner resulted in levels higher than those seen in the other incinerators but markedly lower than when PE was combusted without one. As noted in Tables 7–8, most PAHs were emitted at 2 to 100 times less using an afterburner. Data with and without secondary combustion were not available from municipal waste incinerators, so no comparisons could be made with results from Incinerator A or B.

DISCUSSION

Although a large volume of information on PAH levels in fly ash exists, there are relatively few reported studies on PAH emission levels from aerosol particles from incinerators[18–19]. This is probably due to the technical difficulties involved in stack sampling as well as getting permission to sample directly from commercial/public incineration units. Difficulties also abound in direct comparisons due to differences encountered in combustion unit and sampling designs, incinerator operating conditions and waste feed streams. Kamiya and Ose[19] reported the capture of both vapor-phase and particle PAHs from a batch-fed incinerator having emission control systems similar to those described in this study for Incinerators A and B. They discovered PAH concentrations from stack emissions ranging from 2.13 (phenanthrene), 1.19 (benzo[a]pyrene), and 0.52 ug/m^3 (benzo[ghi]perylene) using a combination filter/impinger sampling train. The above concentrations are approximately 100 times greater than those found in Incinerator A or B. The difference probably relates in part to our capture of only particle-phase PAHs.

Davies *et al.*[18] collected stack emissions from a modern continuous-feed combustion unit under operating and sampling conditions that more closely paralleled those utilized here for incinerators A and B. They found concentrations of fluoranthene (580 ng/m^3), benzo(ghi)perylene (420 ng/m^3), and indeno(1,2,3-cd)pyrene (180 ng/m^3) among other PAHs. Their results compare favorably with ours to within one order of magnitude for Incinerators A and B.

This study demonstrates that measurable quantities of condensable PAHs can be emitted from certain incinerators and quantified. HPLC with programmed wavelength fluorescence was capable of low limits of detection with high specificity during quantitation. Emission rates based upon particle mass, extractable organics, volume of stack gas, fuel heating value, etc., were able to be determined. Variations were shown to exist between two incinerators (A and B), where over 95% of the refuse combusted was municipal waste. Differences were expected due to differences in operating conditions and variability of waste feed streams.

Results from the sub-optimal incineration of PE indicated that this type of plastic (and presumably others) when combusted in this manner may result in a high emission rate of PAHs. This also reveals that an afterburner may be a critical component even of a well-operated incinerator, especially if a significant portion of its feed is introduced in batches of high heating value material. These large emissions were expected due to the high Btu content of PE and the batch nature of the tests. The use of an afterburner substantially lowered PAH emissions. Further investigation of this type of technology could lead to a reduction in the potential environmental and health risks associated with incinerators.

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