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DISTRIBUTION OF PCDDs AND OTHER TOXIC COMPOUNDS GENERATED ON FLY ASH PARTICULATES IN MUNICIPAL INCINERATORS

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SUMMARY

A bulk fly ash sample from a municipal incinerator located in France has been separated into different particle size fractions by manual sieving using standard screens. Average particle sizes varied from 30 μm to over 850 μm. Separated fractions were extracted by ultrasonic agitation using benzene and analyzed by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) for polychlorinated dibenzo-*p*-dioxins, *n*-alkanes, phthalates, and selected polynuclear aromatic hydrocarbons. Differences were observed in the relative distribution of organics on the fly ash size fractions from the French incinerator and the distributions which were observed in fly ash from an Ontario (Canada) incinerator. No tetrachlorinated dibenzo-*p*-dioxins were detected on the French fly ash size fractions at a detection limit of 100 pg/g, although the concentration of octachlorodibenzo-*p*-dioxin was 120 ng/g for the 30-μm particles.

INTRODUCTION

There has been an increased interest in the use of municipal refuse incineration as a means of energy production. This is especially attractive since energy recovery facilities can be situated near large urban centres where fuel is readily available and there is a demand for energy. However, it has been shown that fly ash generated during this incineration contains hazardous organic compounds such as polynuclear aromatic hydrocarbons (PAHs) and polychlorinated dibenzo-*p*-dioxins (PCDDs)[1–4].

Most fly ash is collected by electrostatic precipitators or wet scrubbers and disposed of in landfill sites. About 1 to 5% of the fly ash particles remains uncollected and enters the environment with the stack gases. Knowledge of the distribution of hazardous organic compounds on different sized particles is important to estimate the transport of these substances in the environment and because particles of less than 30 μm are directly respirable by humans.

It has been demonstrated that PAHs are highly concentrated on the respirable fraction of atmospheric particulate matter[5,6]. Concentrations of PAHs for coke oven emissions also varied with particle size[7]. Recent data obtained on samples of fly ash from a Canadian municipal incinerator have shown that concentrations of various

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PCDD congeners varied with the different size fractions[8]. The results show that tetrachlorinated dibenzo-*p*-dioxins and pentachlorinated dibenzo-*p*-dioxins were more highly concentrated on the larger particles (550 μm), while octachlorodibenzo-*p*-dioxin was more concentrated on the smaller particles (30 μm). In this study, fly ash from a municipal incinerator located in France is separated into different size fractions as in the previous investigation. Concentrated extracts of each fraction containing the organic compounds are analyzed by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS). A comparative study of the patterns of total organics, PAHs and PCDDs between French and Ontario fly ash size fractions is presented. These studies are necessary to increase our understanding of the generation of toxic organic compounds during the combustion of municipal refuse.

EXPERIMENTAL

Sample collection and storage

A large grab-sample of fly ash was taken under one of the electrostatic precipitator hoppers in a municipal incinerator located in the south of Paris, France. The incinerator temperature at the top of the furnace was 950°C and the primary air-flow was 45,000 m^3/h. The sample was stored in glass jars at ambient temperature and was protected from light. After extraction, sample extracts were stored in a freezer at about −15°C.

Fractionation of fly ash

Six size fractions of fly ash were obtained using five Tyler sieves (W. S. Tyler, St. Catherines, Canada). The brass sieves had metal screens with openings of 850 μm, 250 μm, 150 μm, 106 μm and 63 μm. All sieves, including the top and bottom collector were cleaned by ultrasonic agitation using an aqueous solution of Alconox detergent for approximately 15 min. This was followed by rinsing with tap water, deionized water, methanol and then air drying. Hand sieving was performed and all fractions were stored in polypropylene containers equipped with polypropylene screw caps that had first been rinsed with small portions of benzene, then air dried.

Sample extraction and concentration

Extraction was performed by ultrasonic agitation using benzene[8,9]. Samples of 10 g were added to individual flasks with 100 ml of benzene and agitated for 1 h. After initial extraction the fly ash was allowed to settle and the benzene was decanted into fresh flasks through porous glass frits. This procedure was repeated two additional times with 50 ml of fresh benzene added each time and ultrasonic agitation for 30 min. After the third extraction cycle, the fly ash was transferred to the glass frit and rinsed three times with 10-ml portions of fresh benzene.

Extracts were concentrated to 100 μl by rotary evaporation under aspirator vacuum and stored in 1.0 ml reacti-vials equipped with screw caps and PTFE liners as described previously[8]. All glassware, including reacti-vials and pipets, was cleaned by ultrasonic agitation for 30 min with Alconox detergent. After thorough rinsing with tap water and deionized water, glassware was then placed in an oven at 250°C for at least 1 h. All equipment was at ambient temperature before use. Solvents were "distilled-in-glass" grade (Caledon Labs., Georgetown, Canada). A 200-ml amount of benzene solvent was carried through the entire process as a procedure blank.

GC analysis

A Hewlett-Packard 5830A GC with flame ionization detector was equipped with a 2 m × 2 mm I.D. glass column packed with Aue packing[10]. A temperature program of 90°C initial temperature to 250°C final temperature at 4°C/min was employed for all sample extracts. Injection temperature was 250°C; detector temperature, 275°C; and the carrier gas flow-rate 37 ml/min, measured at 90°C. A slope sensitivity of 0.1 mV/min was used for peak detection.

For calculation of retention indices, a normal hydrocarbon standard mixture was analyzed periodically. Retention indices were calculated by the Fortran program RICALC[11]. GC peaks were displayed as bar-graph plots using a Zeta plotter by the program GCPLOT[11].

GC–MS analysis

Selected PAH and various PCDD congeners were analyzed by a Hewlett-Packard 5992A GC/MS/Calculator using selected ion monitoring (SIM). The ions monitored for the tetrachlorinated dibenzo-*p*-dioxins were 319.9 and 321.9. The ions selected for penta- through octachlorinated dibenzo-*p*-dioxins were 355.9, 389.8, 425.8 and 459.7, respectively. Chromatographic conditions were as described previously.

The series of congeners were quantified using a solution of 1,2,3,4-tetrachlorodibenzo-*p*-dioxin (1,2,3,4-TCDD) and octachlorodibenzo-*p*-dioxin (OCDD) standards. The intermediate congeners were quantified by using a linear interpolation of response factors between those of 1,2,3,4-TCDD and OCDD. Quantification of PAHs was performed by monitoring the ions 166.1, 202.1, 178.1 and 202.1 from a reference solution containing fluorene, fluoranthene, anthracene and pyrene. Six ions were monitored during each SIM analysis with a dwell time of 166 msec per ion. SIM areas were used for quantification. Normal alkanes and phthalate esters were determined by monitoring the ions 85.1 and 149.1.

Mass spectra were obtained by scanning from 500 to 50 a.m.u. at 330 a.m.u./sec. Spectra taken at the top of the eluting GC peaks were saved on floppy disk in addition to those at the lowest valley between peaks for later background subtraction. A user-developed program called Dual-Mode was employed which allowed storage of total ion abundances and mass chromatograms in addition to mass spectra[12]. Before operating in either scanning or SIM mode, the mass spectrometer was tuned daily by the manufacturer supplied program AUTOTUNE using a perfluorotributylamine calibration standard.

RESULTS AND DISCUSSION

Results of GC analyses of concentrated extracts of the different size fractions are shown in Fig. 1. This plot, termed GCPLOT, is a bar graph display of estimated GC peak concentrations *versus* Kovats' retention indices. The estimates are based on GC peak areas and an average organic compound response factor of 400 area counts per ng determined from previous work. The full-scale value is shown in the upper right hand corner of each plot. Any peak plotted to full-scale is estimated to have a concentration greater than or equal to the full-scale value. Visual comparison of plots for different size fractions indicates that the 30 μm and 80 μm size fractions contain

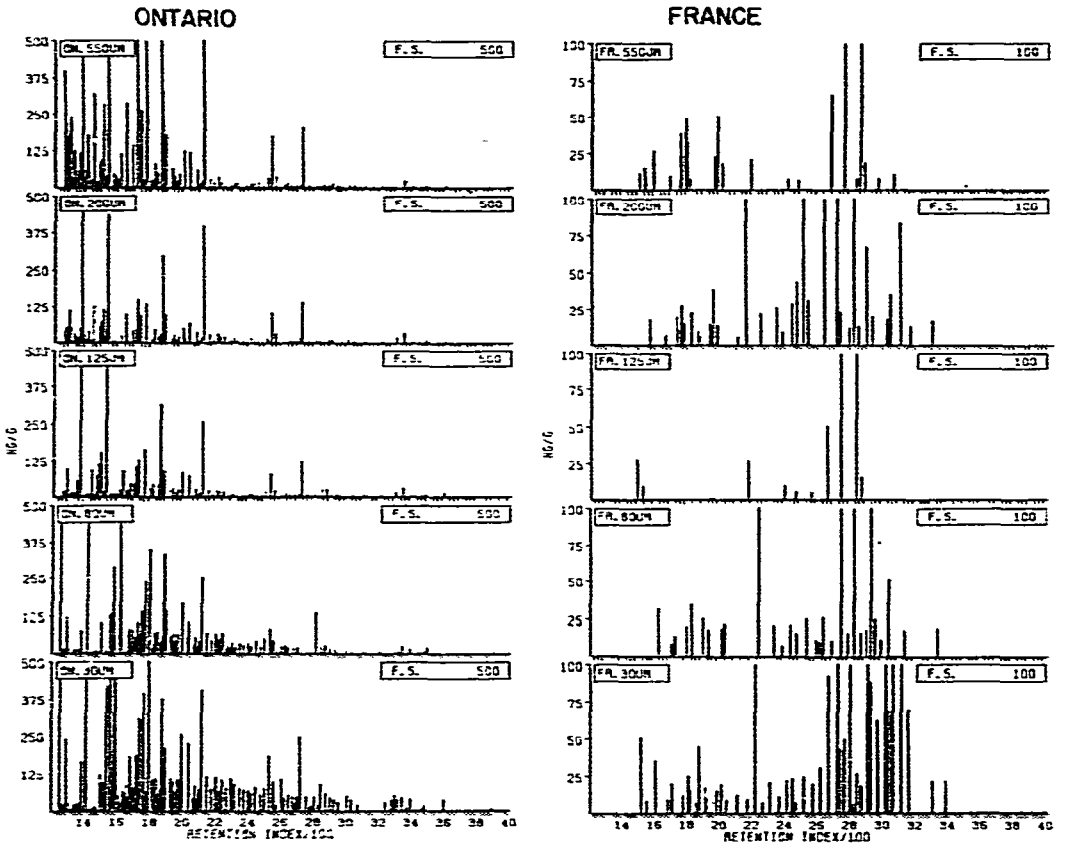

Fig. 1. GCPLOT comparison of chromatographic data from concentrated extracts of French and Ontario fly ash size fractions. Chromatograms are stacked in order of 550 μm size fraction (top of plot) to 30 μm size fraction (bottom of plot). All GC peak areas were converted to estimated concentrations (ng/g) before plotting.

the greatest numbers of components and in higher concentrations than the larger size fractions. The total organic compounds was estimated by using the average response factor of 400 area counts per ng and the sum of the GC integration values between retention indices 1100 and 4000. Estimates of total organic material extracted from the different size fractions for the French and Canadian fly ash samples are given in Table I. Procedure blanks included in these analyses showed contamination from two peaks at retention indices 2750 and 2850. These were identified by GC–MS analysis combined with computerized library search as dioctyl phthalate and farnesyl cyanide. The Ontario fly ash has more components than the French fly ash for each size fraction. Total concentrations of these components are also greater in the Ontario fly ash on each size fraction for the early eluting compounds. However, a greater number of later eluting compounds were detected in the French size fractions than in corresponding Ontario size fractions. Concentrations of the major identified components from each size fraction are given in Table II. These comprise more than 60% of the

TABLE I

ESTIMATED TOTAL ORGANIC MASS ON DIFFERENT SIZE FRACTIONS FOR FRENCH AND CANADIAN FLY ASH

Average particle size (μm)	*France (ng/g)*	*Ontario (ng/g)*
30	2500	97000
80	1600	64000
125	630	23000
200	1600	23000
550	900	55000
>850	22000	(1) 75000*
		(2) 3100

* The Ontario fly-ash large fraction consisted of two distinct types of particles: (1) black ash particles identical in appearance to those from the French fly-ash, and (2) large agglomerate particles.

TABLE II

CONCENTRATIONS (ng/g) OF MAJOR ORGANIC COMPONENTS IN CONCENTRATED ORGANIC EXTRACTS OF FRENCH FLY ASH SIZE FRACTIONS

	Average particle size (μm)					
	30	*80*	*125*	*200*	*550*	*>850*
Butyl benzyl phthalate	240	—	—	—	65	1300
Dibutyl phthalate	190	190	10	100	21	820
Dioctyl phthalate	—	—	300	190	110	5500
Total alkanes	620	510	120	440	190	3300
Farnesyl cyanide	340	160	170	240	290	2600
Total	1400	860	600	970	680	14000
Per-cent of total estimated organic mass	56	54	95	61	76	64

total extracted organic mass. Butylbenzyl phthalate was found in the French ash but not in the Ontario ash. In the previous study, the large Ontario particles (>850 μm) were observed to consist of two distinct fractions, light ash and agglomerate ash[8]. The corresponding French fly ash size fraction was homogeneous in composition and was more concentrated in total organic material than any of the other French size fractions.

The concentrations of PCDDs for each size fraction are given in Table III. No tetrachlorodibenzo-*p*-dioxins (TCDDs) were detected in any size fractions of the French fly ash. The detection limits under the given experimental conditions were determined to be 100 pg/g for 1,2,3,4-TCDD and 200 pg/g for OCDD. The total PCDD concentration decreases with increasing particle size, unlike the Ontario sample in which this trend is reversed. This is illustrated in Fig. 2. It can be observed that there is a skewed pattern among the congeners towards the OCDD in the French

TABLE III

PCDD CONCENTRATIONS (ng/g) IN FRENCH FLY ASH SIZE FRACTIONS

ND = Not detected.

Mean particle size (μm)	*Total*	*T_4CDD*	*P_5CDD*	*H_6CDD*	*H_7CDD*	*OCDD*
30	160	ND	5	8	30	120
85	67	ND	0.8	8	20	39
125	25	ND	1	4	8	12
200	6	ND	0.6	1	ND	4.1
550	4	ND	0.4	0.8	0.4	2.3
>850	13	ND	ND	ND	4	8.4

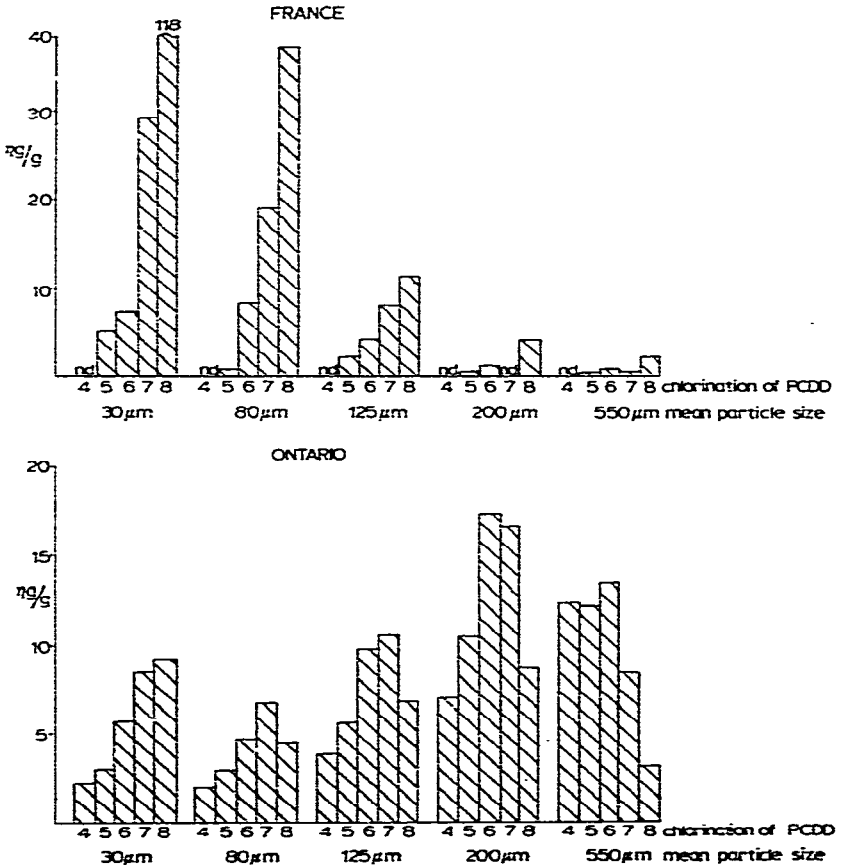

Fig. 2. Chlorinated dioxin concentrations on Ontario and French fly ash size fractions.

size fractions. This also differs from the Ontario sample, where there is a skewing towards OCDD in the smaller particles; but the larger sized particles are skewed towards TCDD. Additionally, the highest concentration of PCDD lies on the larger

particles of the Ontario sample. These differences may reflect the different incinerator conditions and designs as well as differences between France and Canadian incinerator feedstock.

Concentrations of selected PAHs for each particle size fraction are given in Table IV. Fluorene was not detected in these fractions, contrary to those of the Ontario fly ash study[8]. Anthracene is more concentrated on the 850 μm size particles. Pyrene and fluoranthene concentrations were observed to decrease with increasing particle size. No trend was observed in the Ontario sample.

TABLE IV

CONCENTRATIONS (ng/g) OF SELECTED PAHs IN FRENCH FLY ASH SIZE FRACTIONS

ND = Not detected.

Mean particle size (μm)	*Total*	*Fluorene*	*Pyrene*	*Fluoranthene*	*Anthracene*
30	5.9	ND	3.0	2.9	ND
85	8.1	ND	1.9	1.7	4.5
125	3.4	ND	0.9	1.3	1.2
200	1.3	ND	0.8	0.5	ND
550	4.6	ND	0.7	1.0	2.9
>850	15	ND	3.4	1.7	10

The total PCDDs, PAHs and estimated total organic compounds are compared in Fig. 3. The PCDDs and total organic carbon (TOC) are most concentrated on the 30 μm size fraction which contains respirable particle sizes. A moderate amount of PAH is also associated with this fraction. The general pattern of the TOC is similar as that reported for the Ontario fly ash. However, for total PCDDs and PAHs greater concentrations were found on the larger particle sizes of the Ontario fly ash. These results suggest that no universal distribution of PCDDs is evident at the source and that the pathway of formation is variable. Previously it has been reported that constant ratios of PCDDs were not evident on whole fly ash[13]. It is apparent that this is also the case when fly ash is size-fractionated. In the previous study, matched patterns between the levels of pyrene and fluorene with total organic compounds were observed, while anthracene did not follow this trend[13]. These trends are also consistent with the size-fractionated particles in this study. Not only does the organic composition of the bulk fly ash differ between incinerators, but also the relative distributions of the organics on various size fractions. Many models could be hypothesized to explain these differences. However, there is insufficient data presented here to determine the most important factors. Further studies which include detailed records of incinerator operating conditions and estimates of bulk feedstock composition are needed. These data indicate that there are considerable differences between fly ash from different incinerators and only suggest areas of further exploration to provide understanding of the process of organic compound formation during combustion.

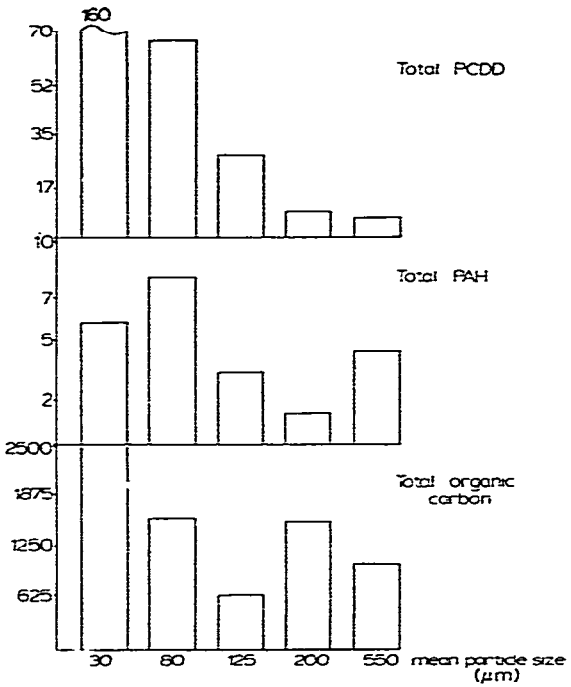

Fig. 3. Comparison of total PCDDs, total PAHs and estimated total organic carbon for French fly ash size fractions.

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