

INVESTIGATING LEVELS OF HALOGENATED AROMATIC COMPOUNDS IN A HIGHLY CONTAMINATED MUNICIPAL WASTE INCINERATOR FLY ASH SAMPLE

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Introduction

A significant amount of research has been dedicated to measuring and minimizing the formation of environmental pollutants during the incineration of municipal waste, specifically relating to polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)¹⁻⁷. However, even the most advanced municipal solid waste (MSW) combustion systems do not provide complete combustion⁸ and the public must rely on strict regulations in developed countries⁹ and monitoring elsewhere to protect them from exposure to unsafe levels. Unfortunately, controls were not always in place to minimize unwanted side-products of incineration. When the Commissioners Street Refuse Incinerator (pictured right) was opened in Toronto, Canada in 1955, it had a capacity of 900 imperial tons of waste per day and, as was customary during this time period, very few controls were in place to prevent the formation and release of harmful pollutants into the surrounding environment. This particular incinerator was closed in 1988 due to pressure arising from a Department of Public Health report on the high levels of PCDDs and other carcinogenic chemicals it was producing.¹⁰ In 1985, the Ontario Ministry of the Environment (MOE) compared PCDD and PCDF levels in precipitated fly ash from 9 Ontario waste incineration sources to values obtained from a total of 41 plants in 8 other countries. The compilation of global fly ash data revealed that Ontario fly ash contained significantly lower PCDD and PCDF concentrations (ng/g) compared to similar sources, with one notable exception – the Commissioners Street Refuse Incinerator.¹¹ The total PCDD/PCDF level measured in the Commissioners Street sample (reported as 20414 ng/g) was 3 times higher than the next worst sample.¹¹ Significant advances have been made in the capabilities of analytical instrumentation since this report was published. The objective of this work is to investigate levels of halogenated aromatic compounds in an archived sample of Commissioners Street fly ash using modern techniques and instruments.



Materials and Methods

Subsamples of an archived Commissioners Street fly ash sample were analyzed and the averaged values are reported. Fly ash samples were spiked with a surrogate mixture containing mass-labelled PCDDs, PCDFs, and polychlorinated biphenyls (PCBs) (Wellington Laboratories Inc., Ontario, Canada). Each sample was treated with HCl and filtered into a separatory funnel; the acid treated ash and filter were air-dried in the fumehood. The acid wash was extracted with dichloromethane (Caledon, Ontario, Canada) and the combined extracts were rotary evaporated (just to dryness). The dried ash and filter were Soxhlet extracted with toluene (Caledon, Ontario, Canada) at 50°C for 16-20 hours at a rate of 3-4 cycles per hour and the resulting extracts were rotary evaporated (just to dryness). The acid wash and Soxhlet extracts were combined and then acid treated and cleaned up using a multi-layer silica column. A PX21 carbon column was also used to isolate planar compounds. The resulting extracts were rotary evaporated to dryness, reconstituted with nonane (Caledon, Ontario, Canada) containing internal standards, and submitted for HRGC/LRMS and HRGC/HRMS analysis. All HRGC/LRMS experiments were conducted on an Agilent 7890A (HRGC)/5975C (LRMS) in splitless mode using a 30 m DB-5 column (0.25 mm id, 0.25 µm film thickness). Data were collected over a full scan range of 50-1000 amu in positive ion electron impact mode (EI+) or negative chemical ionization (NCI) using methane as the reagent gas. All HRGC/HRMS experiments were conducted on an Agilent 6890N gas chromatograph (HP6890) coupled with a Waters Autospec mass spectrometer (Ultima) using a 60 m DB-5 column (0.25 mm id, 0.25 µm film thickness). All data were collected in SIR mode at 10,000 mass resolution using positive ion electron impact ionization (EI+).

Results

In order to determine the classes of compounds present in the Commissioners Street fly ash extract, it was run full scan by HRGC/LRMS (Figure 1). Spectral analysis revealed the presence of PCDDs, PCDFs, PCBs, polychlorinated naphthalenes (PCNs), and mixed brominated-polychlorinated compounds. Preliminary analysis hinted that high levels of phthalates were unevenly distributed throughout the Commissioner Street fly ash. It has been reported that the presence of plastics during combustion (specifically polyvinylchloride) can act as a source of PCDDs and PCDFs.¹² The high instrumental background noise that the phthalates created could also have inflated original measurements reported in 1985 by the MOE¹¹ since less precise instrumentation was utilized.

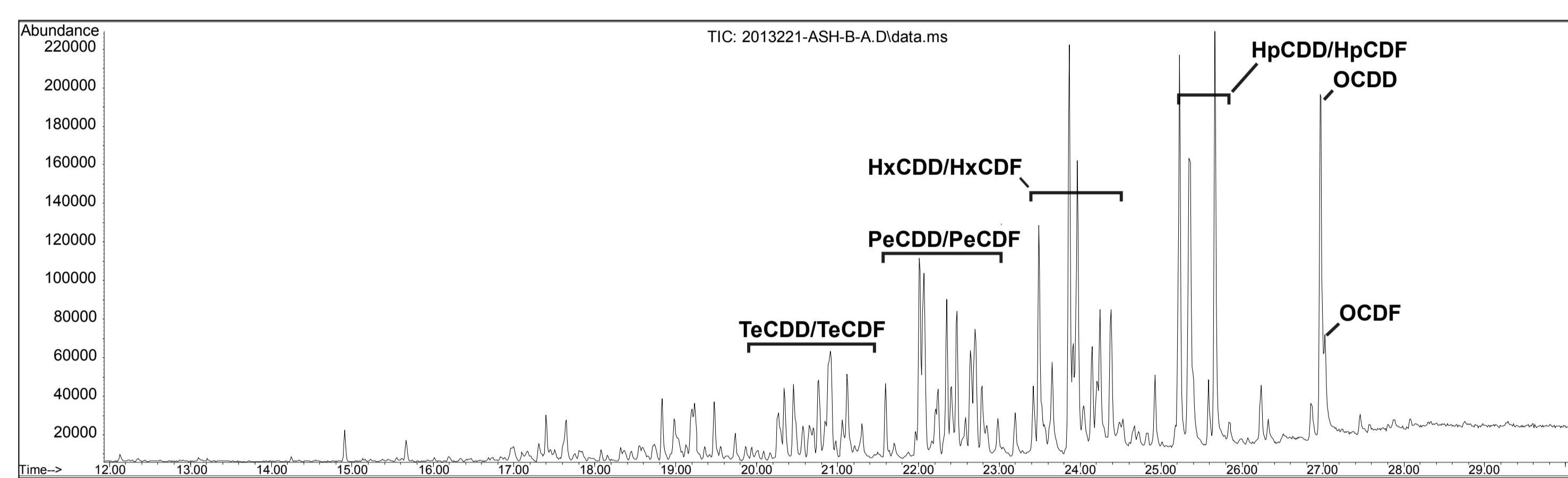


Figure 1: HRGC/LRMS chromatogram of Commissioners Street Fly Ash with PCDD and PCDF congener windows defined.

The elevated PCDD/PCDF values that were measured in this study for the Commissioners Street fly ash (total = 8000 ng/g) are much lower than those reported by Ozvacic et. al. in 1985¹¹ (total = 20414 ng/g). This difference could be due to a number of factors including the availability of mass-labelled internal standards as well as the instrumentation utilized.

The presence of PCNs in the full scan analysis (HRGC/LRMS) prompted a HRGC/HRMS comparison of the congeners present in the extract to those in a commercial material (Halowax 1014¹⁶). Very few similarities in congener patterns were noted between the sample and the commercial mixture. The visible difference across all congener groups warranted further investigation so a mixture of known PCNs was run to definitively identify some of the isomers. PCN congeners containing 2,3,6,7-substitution are known to be more toxic¹⁶ and it can be seen in Figure 2 that the relative concentration of 1,2,3,4,6,7-hexachloronaphthalene is significantly higher (approximately 14 times) in the incinerator sample. 1,2,3,6,7-Pentachloronaphthalene was also identified in the fly ash sample based on a relative retention time reported in the literature¹⁷. This indicates that potentially toxic PCN congeners were generated during the incineration process at the Commissioners Street facility and may have been subsequently released to the environment during the incinerator's operational years.

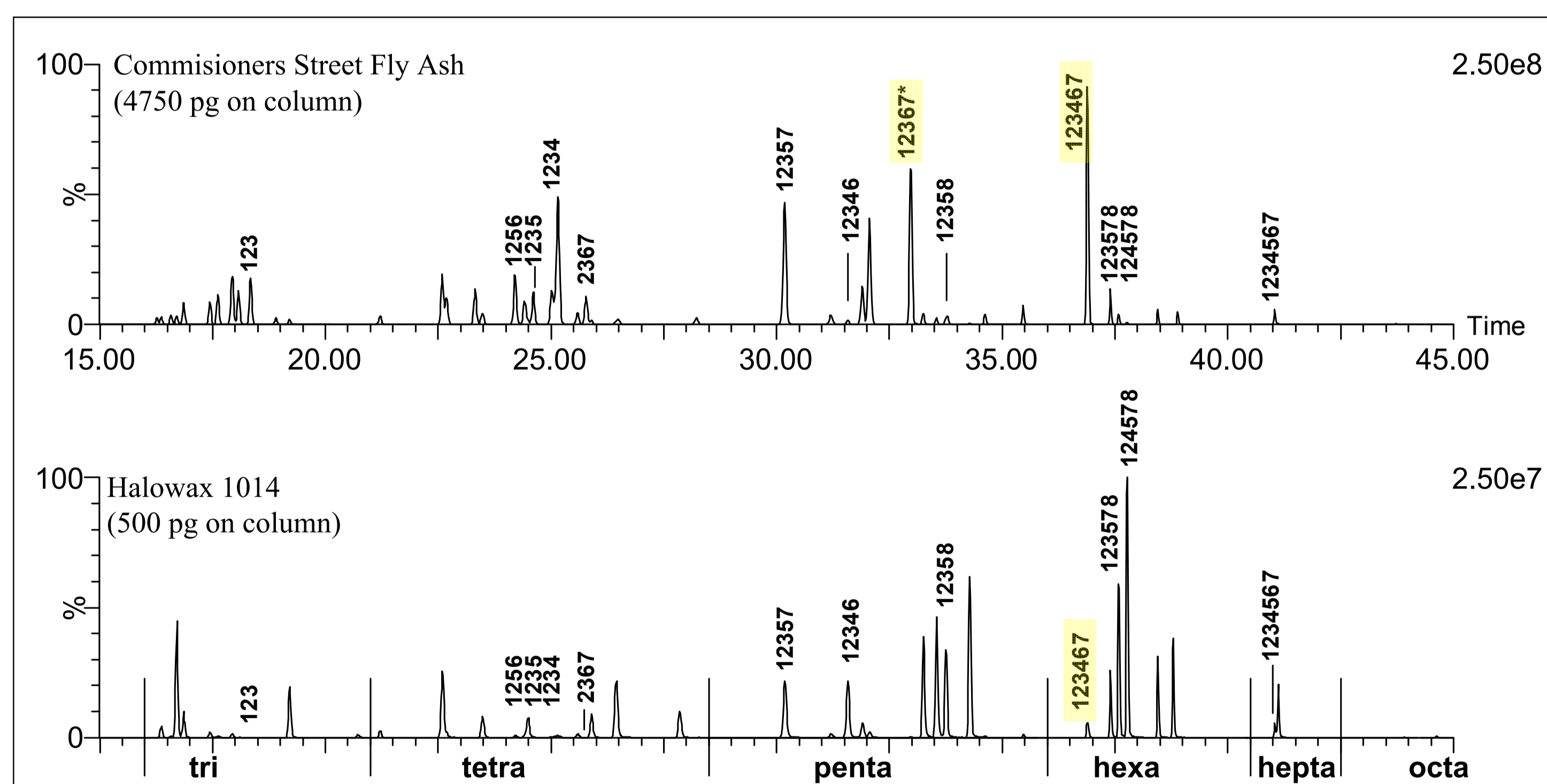


Figure 2: Comparison of the PCN congener patterns in Halowax 1014 and the Commissioners Street fly ash extract (* indicates the congener identification was based on a literature reference).

References

- Oh J-E, Gullett B, Ryan S, Touati A. (2007); *Environ. Sci. Technol.* 41(13): 4705-4710
- Luijk R, Akkerman DM, Slot P, Olie K, Kapteijn F. (1994); *Environ. Sci. Technol.* 28: 312-321
- Hatanaka T, Kitajima A, Takeuchi M. (2005); *Environ. Sci. Technol.* 39(24): 9452-9456
- Stammore BR. (2002); *Chemosphere* 47: 565-573
- Ryu J-Y, Mulholland JA, Dunn JE, Iino F, Gullett BK. (2004); *Environ. Sci. Technol.* 38: 5112-5119
- Gullett BK, Bruce KR, Beach LO. (1990); *Waste Management & Research* 8(3): 203-214
- Hagenmaier H, Kraft M, Brunner H, Haag R. (1987); *Environ. Sci. Technol.* 21: 1080-1084
- McKay G. (2002); *Chemical Engineering Journal* 86: 343-368
- UNEP Chemicals (1999, May). *Dioxin and Furan Inventories: National and Regional Emissions of PCDD/PCDF*. Retrieved May 27, 2013 from http://www.chem.unep.ch/pops/pcdd_activities/inventories/difurpt.pdf
- City of Toronto, Ontario Canada (2013). *Environmental Health*. Retrieved May 23, 2013 from <http://www.toronto.ca/archives/public-health/environmental.htm>
- Bradley J, McLeod R. *Scientific Criteria Document for Standard Development no. 4-84: Polychlorinated Dibenzo-p-dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs)*. Ontario Ministry of the Environment (1985)
- Christmann W, Kasiske D, Klöppel KD, Partsch H, Rotard W. (1989); *Chemosphere* 19: 387-392
- Schulz DE, Petrick G, Duinker JC. (1989); *Environ. Sci. Technol.* 23: 852-859
- van Bavel B, Fängmark I, Marklund S, Söderström G, Ljung K, Rappe C. (1992); *Organohalogen Compounds* 8: 225-228
- Schoonenboom MH, Tromp PC, Olie K. (1995); *Chemosphere* 30(7): 1341-1349
- Noma Y, Yamamoto T, Sakai S-I. (2004); *Environ. Sci. Technol.* 38: 1675-1680
- Jakobsson E, Asplund L. (2000). *Polychlorinated Naphthalenes (PCNs)*. In J. Paasivirta (Ed.), *The Handbook of Environmental Chemistry Vol. 3 Part K* (pp. 97-126). Berlin Heidelberg: Springer-Verlag
- Tong HY, Monson SJ, Gross ML, Huang LQ. (1991); *Anal. Chem.* 63: 2697-2705

With the intention of further characterizing the halogenated aromatic compounds present in the Commissioners Street fly ash, HRGC/HRMS analyses were carried out to determine the concentrations and identities of PCDDs, PCDFs, and PCBs in the sample. Indeed, it was found that significant levels of PCDDs, PCDFs, and PCBs (dioxin-like and total) were present in the sample (Table 1). In order to explore the PCB congener patterns generated during incineration, the percentages of dioxin-like PCBs present in the extract were compared to three Aroclor mixtures (1242, 1254, and 1260); the fly ash was most similar to Aroclor 1254. Further examination of the individual congener levels revealed that the relative concentration of PCB-126 was significantly higher in the incinerator sample compared to Aroclor 1254. It has been reported that Aroclor mixtures contain < 0.05% of PCB-126 (relative to total PCBs)¹³, however this particular congener was found to be present at 1.8% in the Commissioners Street fly ash. The formation of non-ortho PCBs (specifically PCB-77, -126, and -169) during incineration has been previously reported in the literature.^{14,15}

Table 1: Measured PCDD, PCDF, dioxin-like PCB, and total PCB levels by HRGC/HRMS analysis of the Commissioners Street fly ash sample.

PCDF Congeners and Group Totals	Concentration (ng/g)	PCDD Congeners and Group Totals	Concentration (ng/g)	Dioxin-like and Total PCBs	Concentration (ng/g)
2378TCDF	118	2378TCDD	11.1	81	5.47
Total TCDFs	660	Total TCDDs	411	77	27.3
12378PeCDF	54.3	12378PeCDD	88.3	123	3.32
23478PeCDF	93.8	Total PeCDDs	906	118	49.8
Totals PeCDFs	976	123478HxCDD	87.9	114	4.25
123478HxCDF	254	123678HxCDD	126	105	25.6
123678HxCDF	108	123789HxCDD	229	126	27.1
234678HxCDF	132	Total HxCDDs	1300	167	12.4
23789HxCDF	4.90	1234678HpCDD	630	156	25.7
Total HxCDFs	1040	Total HpCDDs	1090	157	7.04
1234678HpCDF	469	OCDD	795	169	10.7
1234789HpCDF	32.0			189	14.0
Total HpCDFs	671			Total PCBs	1530
OCDF	152				
		Total PCDD/PCDF (ng/g)	8000	Total DL-PCBs (ng/g)	213
		2005 WHO TEQ PCDD/PCDF (ng/g)	247	2005 WHO TEQ DL-PCBs (ng/g)	3.04

Similarly, a HRGC/HRMS investigation into the presence of mixed brominated-polychlorinated compounds was carried out. It was found that the incinerator fly ash contained monobromopolychlorinated dibenzo-p-dioxins and monobromopolychlorinated dibenzofurans along with smaller amounts of dibromopolychlorinated dibenzo-p-dioxins/furans (the approximate ratio of Br₁Cl₄DD: Br₂Cl₄DD was 7:1 and Br₁Cl₄DF: Br₂Cl₄DF was 20:1). These compounds have also been previously reported in a municipal waste incinerator fly ash sample.¹⁸ Totals of each congener group were determined semi-quantitatively assuming equal response to PCDDs and PCDFs and are reported in Table 2. It is interesting to note that total halogenation of these compounds was in-line with what was observed for the PCDDs and PCDFs (Table 1) with the highest and lowest degrees of halogenation being the least represented. In terms of overall formation, the mixed bromochlorodibenzo-p-dioxins (PXDDs) and mixed bromochlorodibenzofurans (PXDFs) observed only amounted to approximately 4 % of the total halogenated dioxins and furans formed.

Table 2: A semi-quantitative analysis of monobromo-polychlorodibenzodioxins/furans and dibromo-polychlorodibenzo-p-dioxins/furans detected in the Commissioners Street fly ash.

Group	Congener Groups	% of Group Total	Approximate Concentration (ng/g)	
Monobromo-polychlorodibenzo-p-dioxins	Br-Cl ₃	13	18	
	Br-Cl ₄	29	44	
	Br-Cl ₅	32	62	
	Br-Cl ₆	18	43	
	Br-Cl ₇	7	25	
	Br-Cl ₈	1	3.4	
	Monobromo-polychlorodibenzofurans	Br-Cl ₃	21	19
Br-Cl ₄		36	37	
Br-Cl ₅		30	39	
Br-Cl ₆		12	19	
Br-Cl ₇		1	3.4	
Dibromo-polychlorodibenzo-p-dioxins		Br ₂ -Cl	10	0.7
		Br ₂ -Cl ₂	32	2.2
	Br ₂ -Cl ₃	33	2.5	
	Br ₂ -Cl ₄	15	1.4	
	Br ₂ -Cl ₅	11	1.3	
	Dibromo-polychlorodibenzofurans	Br ₂ -Cl	16	1.9
Br ₂ -Cl ₂		58	6.8	
Br ₂ -Cl ₃		21	3.0	
Br ₂ -Cl ₄		3	0.5	
Br ₂ -Cl ₅		2	0.4	

The presence of mixed bromo/chloro species in the Commissioners Street fly ash sample is not surprising since brominated flame retardants were in use during the operation of this incinerator. Additional work needs to be completed to fully identify the remaining unknowns in the sample.

