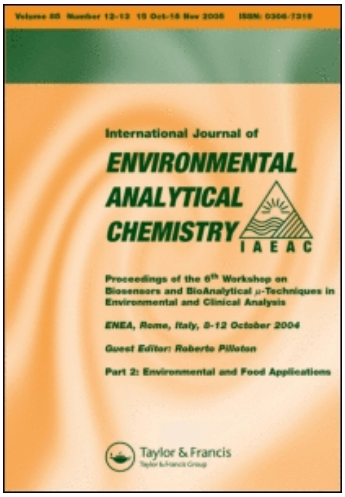


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# Daily Variations in Composition of Extractable Organic Compounds in Fly-Ash from Municipal Waste Incineration

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# Daily Variations in Composition of Extractable Organic Compounds in Fly-Ash from Municipal Waste Incineration

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The daily variations of organic compounds on fly ash from municipal waste incinerator are reported. Variations in composition over a one week sampling period were 1 to 8 μg/g for estimated total organic compounds, 57 to 220 ng/g for total polychlorinated dibenzo-*p*-dioxins, and 56 to 490 ng/g for total polycyclic aromatic hydrocarbons.

KEY WORDS: polychlorinated dibenzo-*p*-dioxin, municipal incineration, polycyclic aromatic hydrocarbons, GC/MS, Analysis.

## INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins (PCDD) have been identified on fly-ash from muncipal incinerators located in Canada, Japan, Switzerland, the Netherlands, France and the United States.[1–4] Although attention has focussed on the PCDD, benzene extractions

of fly-ash are complex mixtures of organic compounds that also include aliphatic hydrocarbons, polycyclic aromatic hydrocarbons and a very large variety of chlorinated compounds.[5–7] Total concentrations of organic compounds in these extracts were estimated using GC-FID. These varied between 1 to 60 ng/g of fly-ash. The composition of target organic compounds in fly-ash from a specific incinerator is generally constant, although the overall number and concentrations of different compounds may vary in time and in samples collected from the incinerator.

A recent study has attempted to characterize a specific incinerator for chlorinated aromatics over a limited time-period of 3 days.[8] Studies of this nature which include stack sampling are limited in terms of the number of days tested because of the very large expense involved in stack sampling. Indications of total incinerator emissions over longer time periods can be obtained at less expense by monitoring the precipitated fly-ash only. These samples comprise a large portion of the total organic emissions of an incinerator because the concentration of organic compounds in fly-ash particles in stack gases is greater than the precipitated fly-ash, particulates in these emissions only account for 1 to 5 per cent of the total fly-ash precipitated.

In a previous study, variations in organic concentrations from an Ontario, Canada municipal incinerator, sampled weekly over an 8-week period were presented.[7] In the present study, daily samples were taken from the same incinerator for one week in order to observe short-term variations in the concentrations of various organic compounds, including PCDD.



## EXPERIMENTAL

### Sample collection and storage

Samples of fly-ash were collected in kilogram quantities by personnel from the Ontario Ministry of the Environment from a refractory-type incinerator. Samples were taken from below the electrostatic precipitator and were stored in closed glass jars at room temperature and protected from light. Samples were taken Sept 9–14 (037–041), 16 (042–044) 17 (045), 24 (046–050) 1979.

## Gas chromatographic analysis

Samples were analyzed in duplicate or triplicate using procedures which have been described in an earlier study.[1] The procedures included: 16-h Soxhlet extraction of 20–30 g of sample with 200 mL benzene, concentration of extract to 100 $\mu$L using rotary evaporation with aspirator vacuum, and direct analysis by GC and GC/MS. A Hewlett-Packard 5830A was equipped with flame ionization detection and 2 m × 2 mm i.d. glass column packed with Aue packing.[9] The oven temperature program was 90°C to 250°C at 4°C/min and helium carrier gas flow rate was 40 mL/min. Injector temperature was 250°C and the detector temperature was 275°C. For calculation of retention indices, a normal hydrocarbon standard mixture was analyzed periodically. Retention indices were calculated by the Fortran program RICALC. GC peaks were displayed as bar graph plots using a Zeta plotter by the program GCPLOT.[10]



## GC/MS analysis

Selected PAH were determined by GC/MS selected ion monitoring (SIM) using a Hewlett-Packard 5992 GC/MS/calculator. GC conditions were as described previously. The PAH monitored were biphenyl (m/z 154.1), fluorene (m/z 166.1), anthracene (m/z 178.1), fluoranthrene and pyrene (m/z 202.1), and benzofluoranthrene and the benzopyrenes (m/z 252.2).

Quantitative results were obtained by analyzing a standard mixture which contained biphenyl, fluorene, fluoranthrene, and benzo(a)pyrene. A relative response factor of 1 was assumed between benzopyrene and anthracene, pyrene and benzofluoranthrene. All calculations were based on peak areas from SIM analyses.

PCDD were also determined by SIM analysis. Ions monitored were: m/z 321.9, 355.9, 389.8, 425.8 and 459.7 for tetra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-*p*-dioxins, respectively. Since packed-column GC was employed, individual isomer determinations were not attempted. The total SIM area for all isomers having the same number of chlorine atoms was determined for each isomer group. The tetra- and octachlorinated dioxins were compared with areas from SIM analysis of standard solutions of 1,2,3,4,-tetrachlorodibenzo-*p*-dioxin (1,2,3,4-TCDD) and octachlorodibenzo-*p*-dioxin (OCDD), respectively. The penta-, hexa- and hepta-chlorinated

dioxins were based on the response of 1,2,3,4-TCDD with a relative response factor of 1, since representatives of these classes were unavailable in our laboratory at the time of this work.

## RESULTS AND DISCUSSION

Gas chromatographic (GC) analyses of concentrated extracts of municipal incinerator fly-ash samples are shown in Figure 1. For days on which samples were collected from more than one of the three furnaces of the incinerator, GC data from only one sample were chosen for display. Chromatograms are represented as bar graph plots of peak areas *versus* retention index, by the computer program GCPLOT, for which each bar height is proportional to a GC peak's chromatographic area. A peak plotted to full scale has an area greater than or equal to the value shown in the rectangle at the upper right corner of each chromatogram, and has an approximate concentration of 100 to 150 ng/g fly-ash. The same full-scale was chosen for all plots to facilitate comparisons between chromatograms and peak areas were normalized to the area per gram of fly-ash extracted before plotting.

Figure 1 shows that there are large variations between samples for the total amount of organic material extracted and in the number of components detected. Large fluctuations, even on consecutive days, can result from daily variance in the feedstock and incinerator operating conditions. However, data were not available in this investigation to assess these variables.

The incinerator from which samples were collected consists of three furnaces. The feedstock is not expected to vary significantly for any of the three furnaces for a specific day. During two of the sampling days, fly-ash was collected from each furnace. The chromatograms compared in Figure 1 were chosen to match the sampling location of as many of the samples as possible. Figure 2 shows chromatographic data from concentrated extracts of fly-ash from each of the three furnaces, sampled on the same day. All three chromatograms are similar in the number, pattern and concentration of components extracted. The small difference between chromatograms are of the same magnitude and demonstrate the reproducibility of this technique.

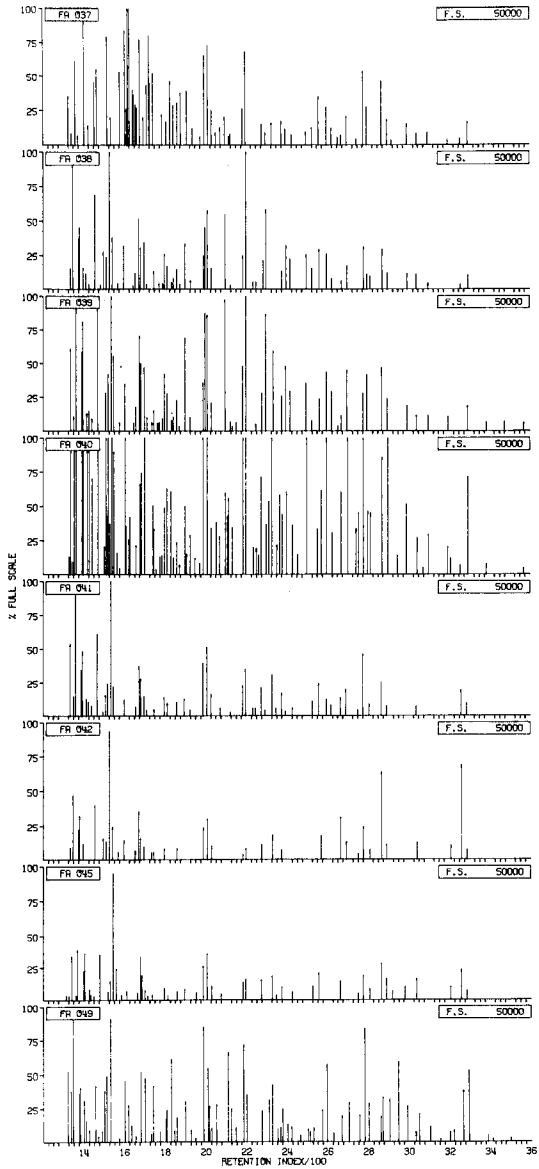


FIGURE 1. GC Plot of gas chromatographic analyses of extracts of fly-ash.

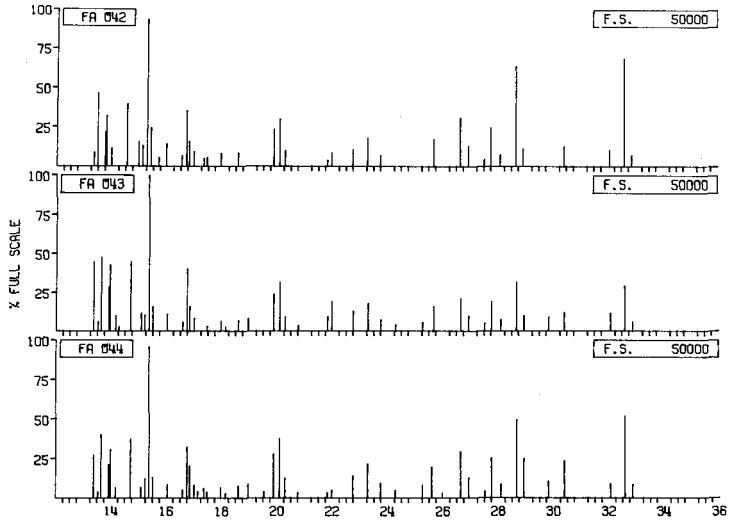


FIGURE 2. Chromatographic data from fly-ash extracts from each furnace sampled on the same day.

GC/MS analyses showed that the same target compounds were present on all samples of this study, although concentrations of individual components varied greatly. Table I is a partial summary of these data for the samples illustrated in figure 1. Some substances present at low concentrations were not included in this list. However, the listed compounds comprise over 80% of the estimated total organic content. All scanning GC/MS work was performed using the same MS electron multiplier voltage and corrected for injection volumes and weight of ash extracted. Therefore, the abundances of compounds in different samples are indicative of relative concentrations of the compounds in the sample extracts. Primarily, *n*-alkanes, phthalates, chlorobenzenes and polycyclic aromatic hydrocarbons were detected. No clear pattern in abundances of the compounds listed in Table I was observed during the short period of this study. Listed in Table I are the relative standard deviations from the means for each compound (RSD). This can be taken as a measure of the variation in concentration of these compounds. It can be seen that chlorobenzenes exhibit the smallest sample-to-sample variation of the listed compounds.

TABLE I

Compounds identified in fly-ash by GC-MS[a]

| Compound | Base peak abundances | | | | | | | | RSD |
|---|---|---|---|---|---|---|---|---|---|
| | 037 | 038 | 039 | 040 | 041 | 042 | 045 | 049 | |
| A. *Chlorinated aromatics* | | | | | | | | | |
| 1. tetrachlorobenzene | 1700 | 1800 | 3200 | 2500 | 1900 | 1200 | 1400 | 2600 | 0.32 |
| 2. pentachlorobenzene | 4300 | 4100 | 6500 | 5600 | 3900 | 2600 | 3100 | 6100 | 0.31 |
| 3. hexachlorobenzene | 1600 | 1400 | 1900 | 1700 | 1400 | 1000 | 800 | 2200 | 0.32 |
| B. *Polynuclear aromatic hydrocarbons* | | | | | | | | | |
| 1. methyl naphthalene | 600 | — | — | 2300 | — | — | — | — | 2.30 |
| 2. biphenyl | 500 | 400 | 600 | 2000 | 400 | — | — | 1400 | 0.75 |
| 3. fluorene | — | — | — | 200 | — | — | — | 100 | 1.00 |
| 4. anthracene | 900 | 700 | 1100 | 3900 | 900 | 400 | 500 | 4500 | 1.00 |
| 5. 9-fluoranthrene | 700 | 700 | 1000 | 1800 | 700 | 300 | 400 | 1200 | 0.57 |
| 6. fluoranthrene | 80 | — | — | 800 | — | — | — | 500 | 1.10 |
| 7. triphenyl benzene | 300 | 200 | 200 | 1500 | 200 | — | 100 | 3300 | 1.60 |
| C. *n-alkanes and phthalates* | | | | | | | | | |
| 1. tetradecane | 1000 | 500 | 400 | 2100 | 400 | 300 | — | — | 1.15 |
| 2. hexadecane | 900 | 700 | 800 | 1700 | 100 | 200 | — | 1100 | 0.81 |
| 3. heptadecane | 600 | 500 | 700 | 1500 | — | — | — | 900 | 1.00 |
| 4. octadecane | 400 | 400 | 700 | 700 | — | — | — | 600 | 0.90 |
| 5. nonadecane | 400 | 700 | 1800 | 600 | — | — | — | 400 | 1.20 |
| 6. cicosane | 300 | 1100 | 2100 | 600 | — | — | — | — | 1.50 |
| 7. heinecosane | 200 | 1500 | 2600 | 800 | — | — | — | — | 1.55 |
| 8. docosane | 300 | 1800 | 2400 | — | — | — | — | — | 1.45 |
| 9. tricosane | 300 | 1400 | 1900 | 1100 | — | — | — | — | 1.70 |

[a]includes most abundant components only; corrected for injection volume and weight of ash extracted.
( ) indicates compound was not detected by scanning GC/MS.

Data from SIM analyses of the fly-ash extracts are presented in Table II. Quantification of PCDD congeners and selected PAH are given. Since results for PCDD are based on 1,2,3,4-TCDD and OCDD standards, data for penta, hexa-, heptachlorodibenzo-*p*-dioxins are only semi-quantitative and are reported for comparison of the relative amounts among samples. As in the previous table, RSD is reported for each compound. Sone of the PAH are repeated from Table I but as concentrations. The similarity in corresponding RSD values indicates that both methods give comparable results. However, the PCDD vary within an experimental error of about

TABLE II

Variations in PAH and PCDD concentrations in fly-ash by GC/MS/SIM

| | Sample concentrations (ng/g) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Compound | 037 | 038 | 039 | 040 | 041 | 042 | 045 | 049 | RSD |
| TCDD | 20 | 20 | 27 | 68 | 18 | 15 | 17 | 25 | 0.66 |
| P5CDD | 22 | 23 | 30 | 73 | 19 | 17 | 22 | 28 | 0.62 |
| H6CDD | 13 | 16 | 19 | 46 | 13 | 15 | 18 | 22 | 0.52 |
| H7CDD | 3 | 5 | 5 | 12 | 4 | 6 | 8 | 13 | 0.53 |
| OCDD | 4 | 5 | 5 | 18 | 3 | 20 | 21 | 31 | 0.78 |
| Total PCDD | 62 | 69 | 86 | 220 | 57 | 73 | 86 | 120 | 0.55 |
| Biphenyl | 45 | 40 | 59 | 140 | 29 | 21 | 18 | 110 | 0.77 |
| Fluorene | 3 | 1 | 2 | 49 | 2 | 1 | 1 | 20 | 1.70 |
| Fluoranthrene | 5 | 6 | 8 | 53 | 7 | 6 | 7 | 68 | 1.30 |
| Pyrene | 1 | 2 | 1 | 44 | 1 | 2 | 1 | 24 | 1.70 |
| Anthracene | 58 | 45 | 70 | 200 | 39 | 26 | 31 | 200 | 0.90 |
| Total PAH | 110 | 94 | 140 | 490 | 78 | 56 | 58 | 420 | 0.95 |



15%. This error is demonstrated in Table III, in which concentrations of samples taken on the same day and quantitated for PCDD using GC/MS/SIM are compared. The total PCDD was found to vary from 0.11 to 0.22 RSD. This range is similar to other reported results on quantitation of PCDD.[11] Variations in data in Table III also include furnace-to-furnace variation and sampling location variations. These data show the variations in organic compounds can occur even in samples taken on the same day from an incinerator, and that concentrations determined on a single grab-sample may not reflect the composition of the bulk of the precipitated fly-ash. However, the variation in the PCDD for the 5 samples taken on the same day was low and can be used as representative of the bulk fly-ash.

In both Tables I and II it is seen that PAH have an RSD about twice that of PCDD. As was observed in Table I, aliphatic hydrocarbons also show a large variation while PCDD and chlorobenzenes vary less than these groups. The variations in Tables I and II do not suggest large swings in incinerator conditions, since the analytical, sampling and feedstock daily variations could account for the observed sample-to-sample differences. However, PCDD and

TABLE III

Comparison of PCDD concentration for samples taken the same day[a]

| | Sample concentrations (ng/g) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Compound | 042 | 043 | 044 | RSD | 046 | 047 | 048 | 049 | 050 | RSD |
| TCDD | 15 | 15 | 18 | 0.11 | 28 | 21 | 31 | 25 | 35 | 0.19 |
| P5CDD | 17 | 17 | 21 | 0.12 | 34 | 25 | 33 | 28 | 30 | 0.12 |
| H6CDD | 15 | 15 | 19 | 0.14 | 32 | 17 | 17 | 22 | 24 | 0.28 |
| H7CDD | 6 | 7 | 8 | 0.14 | 7 | 5 | 4 | 13 | 11 | 0.48 |
| OCDD | 20 | 14 | 18 | 0.18 | 8 | 3 | 2 | 31 | 27 | 0.97 |
| Total PCDD | 73 | 68 | 84 | 0.11 | 109 | 71 | 87 | 119 | 127 | 0.22 |
| Total PAH | 60 | 40 | 60 | 0.21 | 180 | 80 | 290 | 420 | 350 | 0.51 |

[a]042, 043, 044 sampled Sept. 16.
046–050 sampled Sept. 24.



chlorobenzenes have smaller RSD values than the PAH compounds, which may suggest different mechanisms are involved in their formation.

Synthesis of PCDD and chlorobenzenes could occur from chemical reactions in the flame.[12,13] An understanding of these reactions and their rates could lead to control of emissions of these compounds from municipal waste incinerators.

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