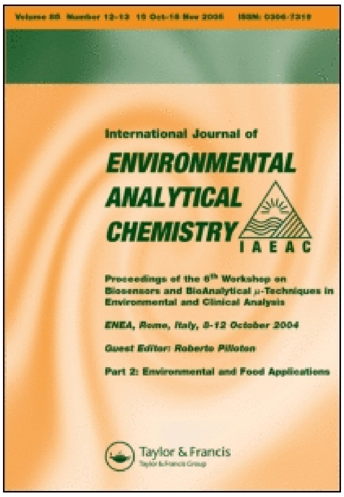

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Determination of Desorption Losses of Polychlorinated Dibenzo-p-Dioxins from Municipal Incinerator Flyash by Gas Chromatography/Mass Spectrometry

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Municipal incinerator flyash was heated in a pyrex tube under a flow of high-purity nitrogen. The levels of polychlorinated dibenzo-p-dioxins (PCDD) in the heated samples were determined using gas chromatography/mass spectrometry (GC/MS) and compared to levels in unheated samples.

In a time and temperature study where temperatures from 100° to 200°C and heating times from 16 to 48 hours were investigated, PCDD levels decreased to 10 to 30 percent of the levels in unheated samples. The final PCDD levels were independent of heating time and temperature under the above conditions. About 10 percent of the PCDD could not be desorbed and are thought to be chemisorbed on the surface of the flyash particles. Heating the flyash at 120°C for 2 to 6 hours desorbed 15 to 38 percent of the PCDD. The desorption rates for the PCDD homologues were estimated to be 0.037, 0.086, 0.15 and 0.23 ng/g/hr/L for tetrachloro-, pentachloro-, hexachloro- and heptachlorodibenzo-p-dioxins respectively. At constant temperature these rates appear to depend mainly on the amount of the particular PCDD homologue originally present on the flyash, not on physiochemical properties such as vapour pressure or dipole moment. When expressed as percent/hr/L, desorption rates for the PCDD homologues were not significantly different from each other. The average value was 0.78 percent/hr/L. Desorbed PCDD were adsorbed onto exhaustively extracted flyash placed in the tube downstream of the heated sample. There was no evidence of decomposition of the PCDD under the experimental conditions.

KEY WORDS: Polychlorinated dibenzo-p-dioxins, chlorinated dioxins, thermal desorption, flyash, gas chromatography/mass spectrometry.

INTRODUCTION

Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzo-furans are groups of compounds which are among the most toxic. Since 1977 it has been know that PCDD are a by-product of municipal garbage incineration.[1-6] Sampling of stack gases from incinerators has shown that PCDD are emitted into the atmosphere.[7] As a result, the Ontario Ministry of the Environment has set provisional guidelines for PCDD emissions from incinerators.[8]

For many years in the United States and Canada the EPA Method 5 Sampling Train has been used to monitor the gaseous and particulate emissions of incinerators.[9] With the inclusion of a cartridge with suitable solid sorbent, the Method 5 Trains can be used for PCDD sampling. In the sampling train a glass fiber filter to trap particulates is placed upstream of impingers and adsorbant cartridges. This filter is maintained at 120°C for the duration of sampling which can last anywhere from one to 24 hours. In the majority of sampling tests, a large portion of all PCDD is found in the impingers and adsorbant cartridges. Because of the unknown behaviour of adsorption and desorption of organic compounds on the trapped particulates it is not known whether the relative amounts of PCDD found on the filter and in the impingers is indicative of the relative amounts in the stack effluent. Sampling artifacts could be introduced by adsorption or desorption of PCDD on the particulate matter on the filter. It is important to know the true distribution between gas and particles as gaseous state PCDD are possibly a more potent health hazard than the particulate

PCDD. Also, this information will aid in understanding the mechanism of formation of PCDD during incineration and in specifying equipment for air emission abatement.

Therefore the purpose of this study was to investigate adsorption and desorption behaviour of PCDD on flyash particles. This report presents the results and recommendations for further studies into this problem.

MATERIAL AND METHODS

Materials

Flyash from a municipal incinerator was supplied by the Ontario Ministry of the Environment. All solvents were "distilled in glass" UV grade (Caledon Laboratories, Toronto, Ont., Canada). Unlabelled PCDD standards were purchased from Ultra Scientific Inc. (Hope, R.I., U.S.A.) and Cambridge Isotopes (Woburn, Ma., U.S.A.). Labelled PCDD standards, $[^{13}C_{12}]$ TCDD and $[^{13}C_{12}]$OCDD were supplied by the Ontario Ministry of the Environment.

Pyrex tubes 45 cm × 2 cm I.D. were constructed with a medium porosity glass frit.

All glassware was washed in an ultrasonic bath for approximately thirty minutes using a mild detergent. Following rinsing with deionized water, glassware was dried overnight in an oven at 275°C. Before use glassware was rinsed with benzene. Soxhelet extraction apparatus was rinsed by refluxing benzene for two hours. The rinse benzene was discarded and fresh benzene used for the flyash extraction. This procedure has been shown effective in removing background impurities from laboratory glassware.

Time and temperature studies

About 15 g of flyash was placed in the Pyrex tube on the upstream side of a glass frit. A plug of clean glasswool was used to retain the flyash. The tube and contents were placed in a modified gas chromatograph oven. A florisil trap was attached to the downstream end of the tube outside the oven to trap desorbed material. The flyash was heated under a flow of 100 mL/min high purity dry nitrogen at temperatures of 100, 150 and 200°C. At each temperature the flyash was heated for 16, 32 and 48 hours.

Time studies at constant temperature

Flyash was sieved and the 170–200 Mesh fraction was used for these experiments. About 15 g of the unextracted flyash was placed in the Pyrex tube on the upstream side of the glass frit. About 12 g of exhaustively extracted flyash was placed downstream of the unextracted flyash against the glass frit. Flyash was retained with glasswool plugs. The tube and contents were heated at 120°C for 2, 4, and 6 hours in duplicate under a 100 mL/min flow of high purity nitrogen. Any desorbed organic compounds not absorbed by the trap flyash were absorbed by a florisil guard trap. A flowchart of the experiment is shown in Figure 1.

Extraction and concentration

The flyash was transferred to a glass thimble with a medium porosity glass frit. Twenty nanograms of $[^{13}C_{12}]$TCDD and 14 ng of $[^{13}C_{12}]$ OCDD internal standards in isooctane were added to the flyash in the time studies. Organic compounds were extracted with 200 mL benzene in a Soxhlet extractor for 18 hours. The extract was reduced to several mL by rotary evaporation under reduced pressure. In the event that particulate matter was suspended in the extract after rotary evaporation, the extract was transferred to a centrifuge tube and centrifuged to drive the particles to the bottom. The extract was transferred with rinsing to a pear-shaped flask and concentrated further. Final concentration to 300 uL was achieved by blowing a gentle stream of high purity nitrogen over the surface of the sample in a calibrated 1 mL reacti-vial.

Gas chromatographic analysis

Total organic compounds (TOC) were estimated by using gas chromatography–flame ionization detector (GC–FID) techniques. The Hewlett-Packard 5880 GC was equipped with a cool on-column injection, a fused silica WCOT column 30 m × 0.32 mm I.D. coated with a 0.25 μm thick DB-5 stationary phase (J&W Scientific, Rancho Cordova, CA., U.S.A.) and a Level 4 terminal-integrator. Chromatographic conditions were: Helium carrier gas flow 2.5 mL/min., temperature program 90°C to 300°C at 6°C/min. TOC were estimated using a response factor of 8 area counts/ng, based on average response factors for different compound classes.[10]

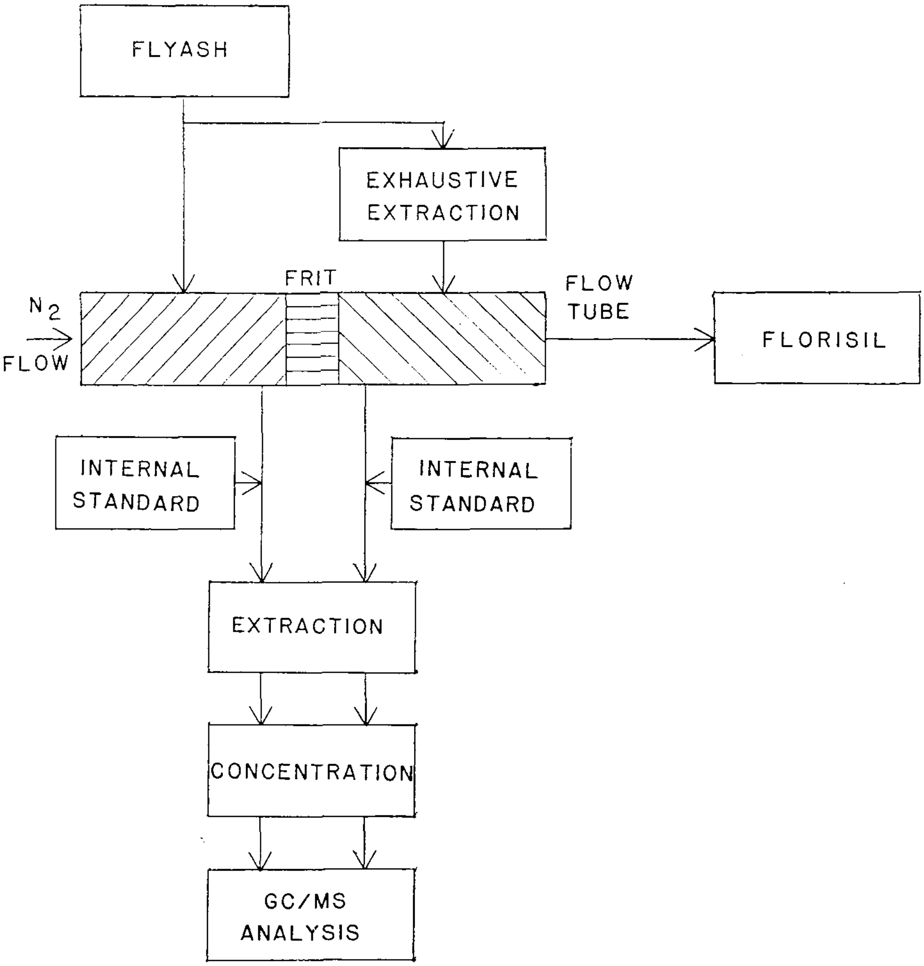

FIGURE 1 Flowchart of the flyash analysis. Flyash was heated at 120°C for 2, 3 and 6 hours under a 100 mL/min flow of high-purity nitrogen.

Gas chromatography/mass spectrometry analysis

Analyses were carried out on a Hewlett-Packard 5987A gas chromatograph/mass spectrometer (GC/MS) with an HP1000 data system. The HP5987A GC/MS has a mass spectra search system, Probability Based Matching (PBM) and Self Training Interpretive Retrieval

TABLE I

Instrument operating parameters

Chromatographic Conditions
Fused silica WCOT column 30 m × 0.32 mm I.D.
Stationary phase DB-5, 0.25 μm thickness
Helium carrier gas flow 2.5 mL/min.
Temperature program 90°C to 300°C at 6°C/min.

Linear Scan Mass Spectrometry
Scan range 50 amu–500 amu
Scan rate 630 amu/s

Selected Ion Monitoring Mass Spectrometry

Ions	M/Z	dwell (ms)
TCDD $[M+2]^+$	321.9	100
$[^{13}C_{12}]$TCDD $[M+2]^+$	333.9	100
P_5CDD $[M+2]^+$	355.9	100
H_6CDD $[M+2]^+$	389.8	100
H_7CDD $[M+2]^+$	425.8	100
OCDD $[M+2]^+$	459.7	100
$[^{13}C_{12}]$OCDD $[M+2]^+$	471.7	100

System (STIRS) based on over 70,000 reference spectra. The instrument was equipped with a cool on-column injector, a fused silica 30 m × 0.32 m I.D. DB-5 column (J&W Scientific, Rancho Cordova, CA., U.S.A.) and a direct inlet GC/MS interface. Instrument operating parameters are given in Table I.

RESULTS AND DISCUSSION

Extraction of organic compounds

The precision of the extraction step was estimated by extracting the raw flyash in triplicate and determining the TOC in each extract. Two one-μL aliquots of each extract were injected into the GC.

The TOC analyses of the flyash extracts are presented in Table II. The response factor of 8 area counts/ng is an estimate which can vary between 4 and 14 area counts/ng, depending on the relative proportions of the different compound classes. The determination is quite reproducible (precision) but can only be considered semi-

TABLE II
Total organic carbon in flyash extracts

Extract		MOE I	MOE II	MOE III
Injection	1	16540[a]	18250	16170
Injection	2	16220	16320	17680

[a] ng/g flyash.

Average TOC is 17030 ng/g; pooled standard deviation (S.D.) is 738 ng/g; relative standard deviation (R.S.D.) is 0.043.

quantitive, with an error of 200 percent (accuracy). However, since the relative proportions of the compound classes are constant between replicates, the analyses can be used to determine if the three extracts were significantly different from each other.[11] Since the test indicated no difference between extractions, the pooled variance was used to determine the relative error of the extraction step, which was 4.3 percent.

Time and temperature study

There were few qualitative changes in the organic content of the flyash due to heating, as shown in Figure 2. The major peak at 28.2 minutes in the unheated sample was missing in the heated sample. This compound, identified by spectra library matching as molecular sulphur (S_8), likely decomposed during heating. Some of the major components detected in the undesorbed flyash were detected in the trap flyash chromatogram. The large peak at 45 minutes was identified as phthalate ester. This likely desorbed from the Tygon tubing used to connect the nitrogen gas supply to the flow meter.

The percent loss of each PCDD congener is shown in Table III and presented graphically in Figure 3. The data were tested for temperature and time effects by a 2-Way Model 1 analysis of variance (ANOVA) without replication.[11] Within each group of PCDD congeners there was no significant effect due to temperature or heating time at the ninety-five percent confidence level. The relative precision of the quantitation procedure was estimated from the ANOVA to be eight percent relative.

It had been expected that the amount of PCDD desorbed would increase with an increase in temperature with heating time held

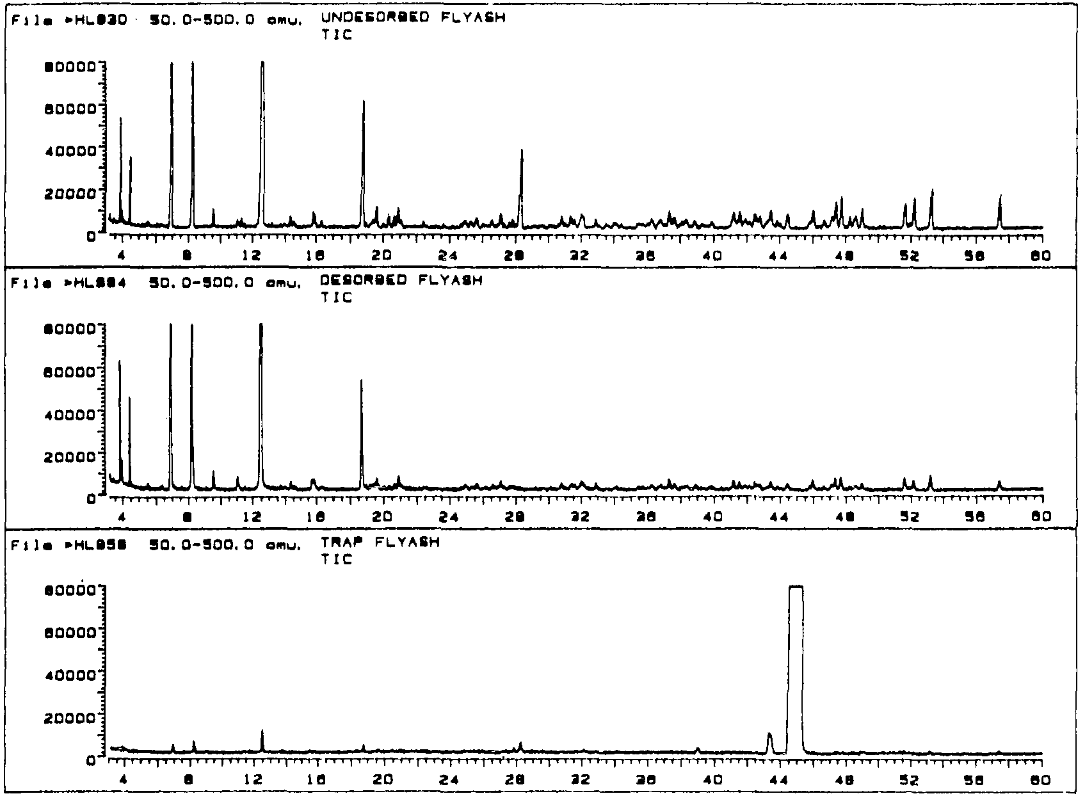

FIGURE 2 Linear scan GC/MS analyses of flyash. The top plot is of undesorbed flyash, the middle plot is of flyash heated at 200°C for 48 hours and the lower plot is of exhaustively-extracted flyash placed downstream to absorb desorbed material.

TABLE III

Percent of Dioxins lost due to heating. Time and temperature study

	100°C			150°C			200°C		
Time	16 h	32 h	48 h	16 h	32 h	48 h	16 h	32 h	48 h
Dioxin									
TCDD	76[a]	82	74	81	78	68	76	86	83
P_5CDD	73	87	79	81	81	70	77	88	85
H_6CDD	78	86	78	80	81	68	73	89	86
H_7CDD	82	86	78	83	81	70	74	87	89

[a] Percentage of Original Amount.

constant and would increase with an increase in heating time with temperature held constant. The high amount of material desorbed, between 68 and 89 percent, and the lack of time and temperature dependence suggests that the PCDD were desorbed in a time shorter than 16 hours. Since all the PCDD were not desorbed even after heating for 48 hours at 200°C it is possible that some of the PCDD are more tightly bound (chemisorbed) to the surface of the flyash and would not desorb under the experimental conditions. The majority is just adsorbed through van der Waals forces (physisorbed). The presence of two different types of adsorption is supported by the data of Rordorf and Eiceman.[12,13] Rordorf measured the vapour pressure of 2, 3, 7, 8-TCDD to be $3.9–15.9 \times 10^{-2}$ Pa at 100°C and found its decomposition temperature in nitrogen to be between 850 and 1100°C. If this model is correct, the apparent rate of desorption (ng/g/hr/L) would have a finite value at the start of heating and would approach zero as the amount of physisorbed material approached zero. An illustration of this proposed model is shown in Figure 4.

Time study at constant temperature

Since the desorption behaviour was unknown, the initial experiments were conducted under high temperature, time and flow conditions. After obtaining positive results there, the next step was to obtain data under conditions nearer to those in stack sampling.

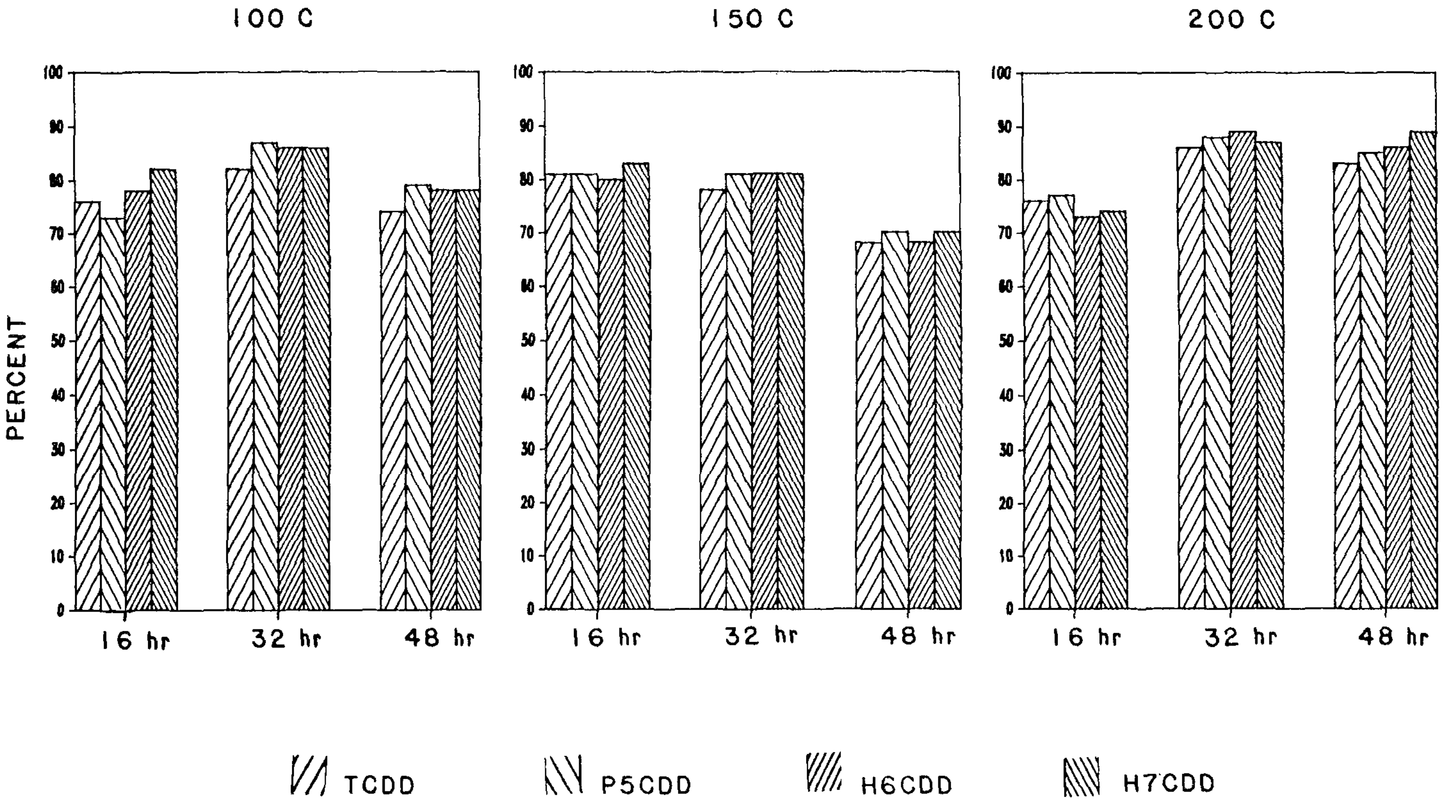

FIGURE 3 Data from GC/MS/SIM analyses of heated flyash showing the percentage of TCDD, P_5CDD, H_6CDD and H_7CDD lost due to desorption. The percentage lost was independent of heating time and temperature.

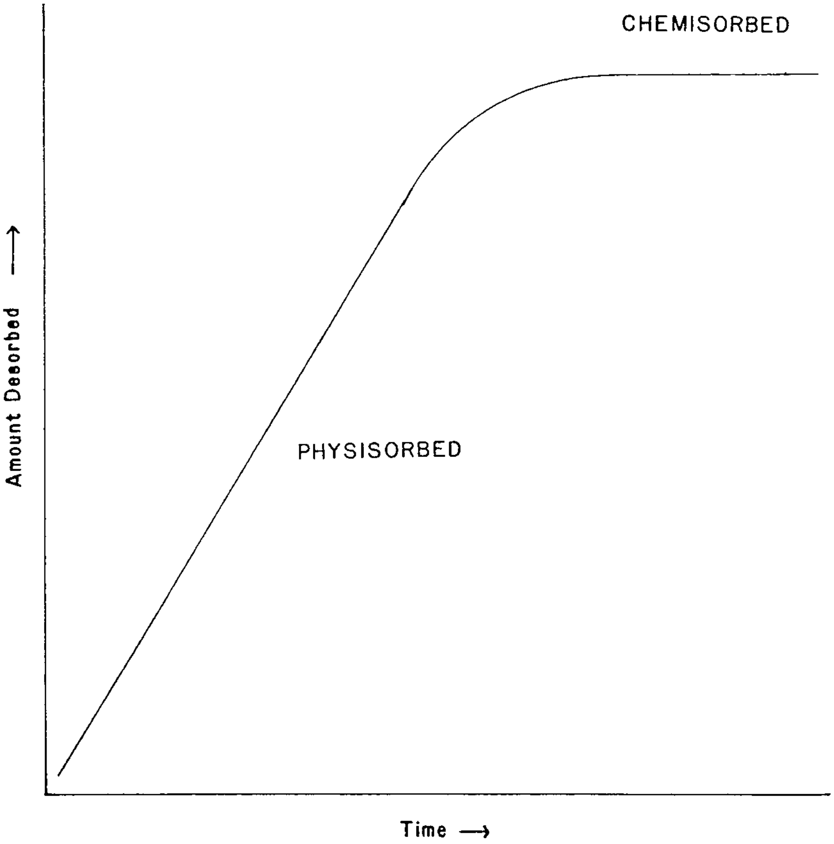

FIGURE 4 A proposed model of PCDD desorption from flyash. Physisorbed material could desorb under stack sampling conditions but tightly-bounded chemisorbed material would not desorb.

The percent loss of PCDD at 120°C after heating at 2, 4 and 6 hours in a 100 ml/min stream of dry nitrogen is presented in Table IV and shown in Figure 5. There are no apparent differences in PCDD lost after heating for 2 and 4 hours, which may be due to the relative errors of the analyses, which vary from 0.11 to 0.40.

These data, as illustrated in Figure 5 possess an interesting feature. The percent loss of PCDD due to heating decreases in order of TCDD, H_6CDD, P_5CDD, H_7CDD. If the desorption of physisorbed

TABLE IV

Dioxins desorbed due to heating. Time study at constant temperature

Time	Dioxin loss (percent of original amount) TCDD	P_5CDD	H_6CDD	H_7CDD
Original Am't	4.9[a]	9.9	18.1	24.0
2 h	24 ± 6[b]	16 ± 5	21 ± 4	15 ± 6
4 h	25 ± 6	15 ± 5	22 ± 4	15 ± 6
6 h	38 ± 6	33 ± 5	35 ± 4	20 ± 6

[a] ng dioxin/g flyash.

[b] Standard Error of the mean estimated from error mean square of analysis of variance, 2 replicates per sample.

material is governed solely by vapour pressure, the order would be expected to be that of increasing molar mass i.e. TCDD, P_5CDD, H_6CDD, H_7CDD. The switching of the order for P_5CDD and H_6CDD could be due to dipolar interactions. Both TCDD and H_6CDD homologue classes possess an even number of chlorine and hydrogen atoms and can form structures which possess no net dipole moment. Conversely, P_5CDD and H_7CDD have odd numbers of chlorine and hydrogen atoms and therefore are unable to form structures without a net dipole moment. We speculate that an increased average level of the van der Waals forces between the molecules results in greater retention of P_5CDD and H_7CDD congener classes. More exact and precise desorption data for each congener class is needed before any reliable conclusions can be reached.

A plot of desorption data taken from both studies is presented in Figure 6. The three sets of points below 10 hours, shown as circles, are taken from the time study at 120°C while points shown by squares are from the time and temperature study. The latter data are averages of data taken at the three temperatures. The data for 48 hours is omitted for clarity. The plot resembles the proposed model for PCDD desorption presented in Figure 4. The rising portion of the desorption curve represents the loss of physisorbed material from the flyash. The plateau of the curve for heating times greater than 16 hours represents the retention of material chemisorbed onto the surface of the flyash particles.

Desorption rates for PCDD have been estimated from data taken from both studies. Table V presents the PCDD loss data (ng/g) used

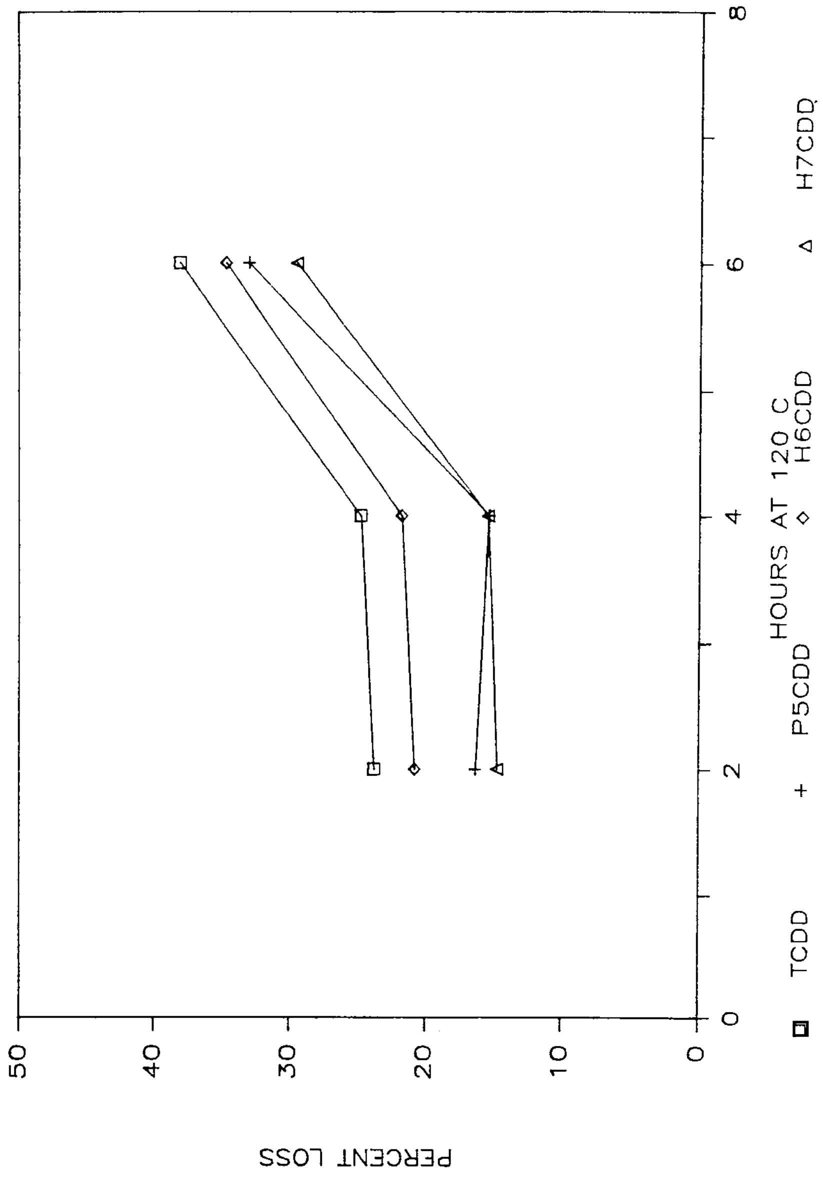

FIGURE 5 Data from GC/MS/SIM analyses of flyash heated at 120°C for 2, 4, and 6 hours showing the percent loss for TCDD, P_5CDD, H_6CDD and H_7CDD congeners.

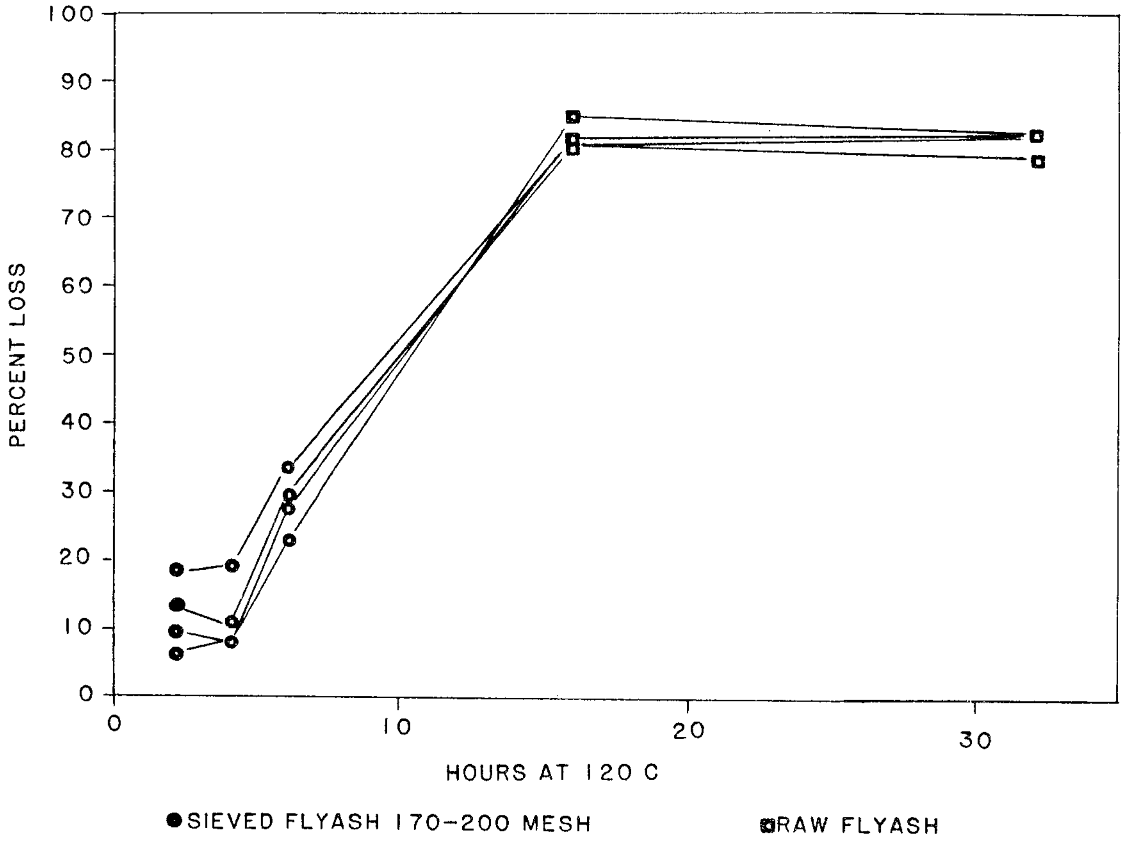

FIGURE 6 Percent loss desorption data selected from both studies shows that PCDD is desorbed at heating times less than 16 hours while some PCDD remains adsorbed even after heating for 32 hours. The plot is similar to the proposed model of PCDD desorption show in Figure 4.

TABLE V

Dioxins desorbed due to heating. Selected data from both studies

Time	Dioxin Loss (ng/g)			
	TCDD	P_5CDD	H_6CDD	H_7CDD
4 h	1.5	1.4	4.5	4.3
	1.2	2.0	4.2	3.9
6 h	2.2	3.8	7.2	7.5
	1.9	3.4	6.6	8.1
16 h	4.0[a]	7.8	15.5	21.5
	4.3	8.7	15.9	22.0
	4.0	8.3	14.4	19.4

[a] Data from Time Study are averages of the losses at the three temperatures at N_2 flow of 6 L/hr.

TABLE VI

Desorption rate of Dioxins[a]

Dioxin	Desorption rate	Intercept (ng/g/h/L)
TCDD	0.0368 ± 0.006[b]	0.584
P_5CDD	0.0865 ± 0.016	0.016
H_6CDD	0.147 ± 0.019	1.169
H_7CDD	0.229 ± 0.020	−0.965

[a] Data taken from Table V.

[b] 95% confidence interval for desorption rate.

to calculate desorption rates (ng/g/hr/L). The data from the 2 hour experiments was suspect and therefore omitted. The calculated desorption rates for each congener class are presented in Table VI. The slope was calculated using linear regression techniques. The values listed under intercept do not have any physical meaning as no PCDD would be desorbed at 0 hours. The regression lines and confidence belts for the regression analysis of this data is presented in Figure 7. The 95% confidence belts are calculated for mean predicted values. The desorption rates increase from TCDD to H_7CDD. This increase is more likely due to the relative amounts of each congener found on flyash rather than an effect of increasing molar mass.

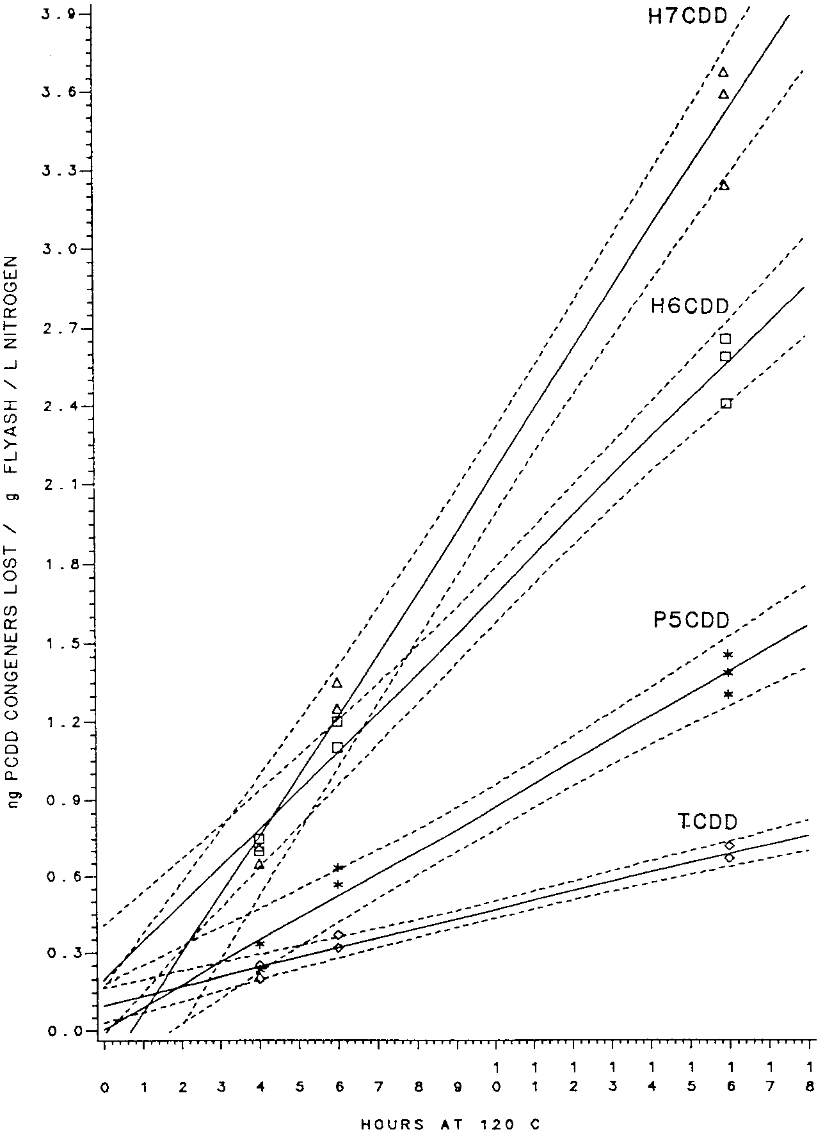

FIGURE 7 Plot of PCDD loss (ng/g flyash/L nitrogen) versus heating time at 120°C. The data is taken from Table V. The linear regression lines and 95% confidence belts for mean predicted values are overlayed on the data points.

Table VII presents desorption data, expressed as percentages of the original amount on the flyash. The data selected corresponds to the desorption data presented in Table V. These data were used to calculate desorption rates, expressed as percent/hr/L, and are shown in Table VIII. The desorption rates for the congener are equal, within experimental error. Therefore, the data for the four congener classes were combined and a desorption rate based on the combined data was calculated. These data and the best-fitting line are presented in Figure 8. The 95% confidence belts were calculated for mean

TABLE VII

Dioxins desorbed due to heating. Selected data from both studies

	Dioxin loss (percentage of original amount)			
Time	TCDD	P_5CDD	H_6CDD	H_7CDD
4 h	28	13	23	16
	23	19	21	15
6 h	42	35	36	29
	36	32	33	31
16 h	76[a]	73	78	82
	81	81	80	84
	76	77	73	74

[a] Data from Time and Temperature Study are averages of the losses at the three temperatures.

TABLE VIII

Desorption rate of dioxins[a]

Dioxin	Desorption rate (percent/h/L)	Intercept
TCDD	0.694[b] ± 0.112[c]	11.01
P_5CDD	0.803[b] ± 0.146	0.114
H_6CDD	0.745[b] ± 0.093	5.86
H_7CDD	0.870[b] ± 0.112	−3.65
Combined	0.778[d] ± 0.067	3.33

[a] Data taken from Table VII.

[b] 7 data points.

[c] 95% confidence interval for desorption rate

[d] 28 data points.

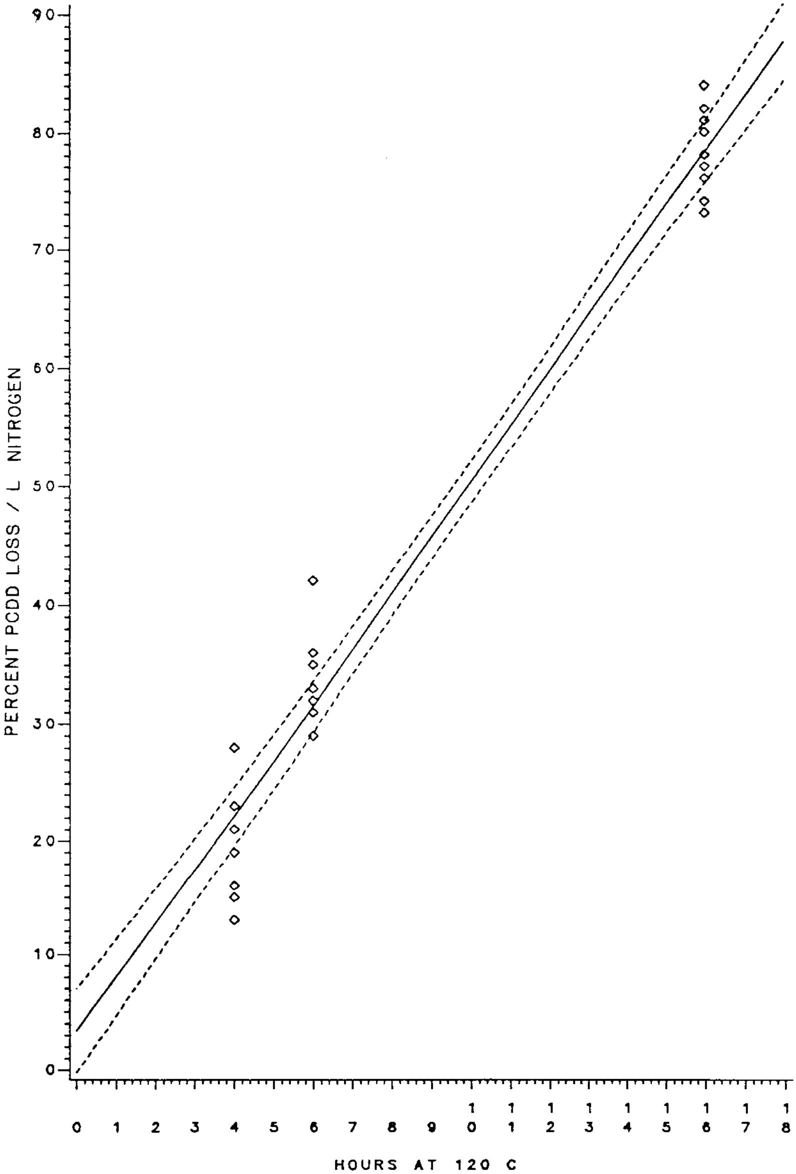

FIGURE 8 Plot of percent PCDD loss per L of nitrogen versus heating time at 120°C. The data is taken from Table VII. The linear regression line and 95% confidence belts for mean predicted values are overlayed on the data points.

predicted values. These data show that desorption rates in percent/hr/L are equal for each congener. This confirms our speculation that desorption rates expressed as ng/n/hr/L are more dependent upon the amount of physisorbed material in the flyash than on the molar mass.

Table IX shows the amount of PCDD found on the trap flyash just downstream of the desorbed flyash. The listed values are from single analyses so the variances are high. The apparent trend follows the desorption data, with increasingly larger amounts recovered with an increasingly larger amount desorbed.

Table X compares the amount desorbed to the amount absorbed on unextracted flyash. The data indicate that the PCDD were desorbed from flyash and reabsorbed downstream without significant decomposition. It is far more difficult to obtain reliable adsorption data than to obtain desorption data due to condensation of PCDD on the surface of the flow tube and absorption by the glass frit.

TABLE IX

Amount of Dioxins on trap flyash Dioxin (ng/g)[a]

Time	TCDD	P_5CDD	H_6CDD	H_7CDD
2 h	ND[b]	ND	ND	6
4 h	2	3	5	8
6 h	2	4	8	11

[a] OCDD not quantitated.
[b] Not detected.

TABLE X

Amount of Dioxins desorbed compared to amount of Dioxins absorbed on unextracted flyash

Time	TCDD		P_5CDD		H_6CDD		H_7CDD	
	Loss	Trap	Loss	Trap	Loss	Trap	Loss	Trap
2 h	18[a]	ND[b]	26	ND	61	ND	56	75
4 h	15	25	22	29	56	48	51	76
6 h	31	26	55	52	106	104	118	143

[a] ng dioxin.
[b] not detected.

Further experiments must be carefully designed before useful adsorption data can be produced.

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References

1. K. Olie, P. L. Vermeulen and O. Hutzinger, *Chemosphere,* **6,** 455 (1977).
2. G. A. Eiceman, R. E. Clement and F. W. Karasek, *Anal. Chem.* **51,** 2343 (1979).
3. R. E. Clement, G. A. Eiceman, F. W. Karasek, W. D. Bowers and M. L. Parsons, *J. Chromatogr.* **189,** 53 (1980).
4. G. A. Eiceman, R. E. Clement and F. W. Karasek, *Anal. Chem.* **53,** 955 (1981).
5. R. E. Clement and F. W. Karasek, *J. Chromatogr.* **234,** 395 (1982).
6. F. W. Karasek, *Canadian Research,* **13** (5) (1980).
7. A.S.M.E. Research Comm. on Industrial and Municipal Wastes, *Study on the State of the Art of Dioxin from Combustion Sources* (1980).
8. Ministry of the Environment, *Ambient Air Quality Provisional Guideline Criterion and Point of Impingement Provisional Guideline for Chlorinated Dibenzodioxins and Dibenzofurans.*
9. Ministry of the Environment, Report No. ARB-TDA-66-80, *Source Testing Code* Version no. 2 (November 1980).
10. H. Y. Tong and F. W. Karasek, *Anal. Chem.* **56,** 2124 (1984).
11. J. H. Zar, *Biostatistical Analysis,* (Prentice-Hall, New York, 1974).
12. B. F. Rordorf, *Thermodynamic and Thermal Properties of Polychlorinated Compounds: The Vapour Pressures and Flow Tube Kinetics of Ten Dibenzo-p-Dioxins,* Abstracts of 4th International Symposium on Chlorinated Dioxins and Related Compounds, Ottawa, Ontario, Canada (October 1984).
13. G. A. Eiceman and V. J. Vandives, *Atmosph. Environ.* **17,** 461 (1983).