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POLYCHLORINATED DIBENZO-p-DIOXINS (PCDD) AND POLYCHLORINATED DIBENZOFURANS (PCDF) IN
EMISSIONS FROM AN URBAN INCINERATOR. 2. CORRELATION BETWEEN CONCENTRATION
OF MICROPOLLUTANTS AND COMBUSTION CONDITIONS

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INTRODUCTION



In a previous paper (1) we reported the average and peak values of PCDD and PCDF emitted from an urban incinerator monitored over a 9-month period. We underlined the wide variability in the different sample concentrations and the need to study the possible correlation between the amount of micropollutants released and several combustion parameters.

Three hypotheses are currently supported about the presence of PCDD and PCDF in incinerator emissions. Lustenhower et al. (2) and Esposito et al. (3) suggested that these compounds are present in the burned waste and are not destroyed; Rappe et al. (4) considered chlorophenates and other similar compounds as the precursors of chlorinated dioxins and furans. Finally Dow Chemical Company (5) argued that there is a very large series of organic compounds that can be considered as precursors and so chlorinated dioxins and furans occur in all combustion processes.

In order to investigate the main parameters which may be involved in the formation and/or decomposition of PCDD and PCDF during combustion, incinerator operating temperature, fume temperature, stack flow and tons of refuse burned were recorded and, in addition to PCDD and PCDF, HCl, NO_x, SO₂, CO and particulate were also analyzed.

METHODS

The method of sampling (effected on two consecutive days each month) and analysis for PCDD and PCDF have already been described (1). HCl, SO₂ and particulate were collected during six hours in isokinetic conditions by a glass probe inside the stack. The analytical method for HCl, adsorbed on 0.1 N NaOH, was that reported by Zall et al. (6). SO₂ was analysed according to West and Gaeke (7), with the addition of sulfamic acid (8) and ethylenediamine tetraacetic acid (9). Particulate analysis was gravimetric.

Table 1 - Emissions from the stack and combustion conditions (I PART)

Sample	PCDD ^(a)	PCDF ^(a)	ln PCDD	ln PCDF	Minimal combustion temperature(°C)	Average combustion temperature (°C)
1	1064	_(c)	6.970	_(c)	1000	1032
2	2618	8036	7.870	8.992	_(c)	_(c)
3	1474	5648	7.296	8.639	_(c)	_(c)
4	117180	111916	11.671	11.626	320	627
5	104308	97328	11.555	11.486	460	903
6	3019	6763	8.013	8.819	1010	1062
7	1593	3354	7.373	8.118	820	1032
8	2026	2175	7.614	7.685	680	894
9	8951	9672	9.100	9.177	740	902
10	1563	1747	7.354	7.466	990	1041
11	8581	3968	9.057	8.286	950	1016
12	621	1109	6.431	7.011	960	1012
13	846	1048	6.741	6.955	960	1030
14	1130	2106	7.030	7.653	940	1010
15	870	1717	6.768	7.448	950	1027
16	2538	3304	7.839	8.103	1010	1039
17	1548	2171	7.345	7.683	1010	1038
18	5881	6959	8.679	8.848	600	833

a) $\mu\text{g}/\text{ton}$: μg emitted for one ton of waste combusted

c) Data not available

For NO_x six 30-minute samplings were carried out each day. The NO_x was determined with the Saltzman reagent (10); NO was oxidized with KMnO_4 to NO_2 and then analyzed as exposed.

For CO six spot samples were taken each day and CO was analyzed by GC after methanation (11).

Fume temperature and stack flow were recorded several times during each sampling. The combustion chamber operating temperature was recorded by an automatic thermocouple throughout sampling.

RESULTS AND DISCUSSION

Table 1 shows the results relative to each sampling; the possible correlation between all the analyzed parameters and PCDD or PCDF concentrations were investigated using a multiple regression method. The only significant correlation was found between PCDD or PCDF concentrations (logarithmic values) and the minimal combustion temperature reached during sampling (Fig. 1,2).

Table 1. - II. PART

sample	Mean stack flow (Nm ³ /h)	Waste combusted (tons/day)	Mean stack temperature (°C)	HCl ^(b)	SO ₂ ^(b)	CO ^(b)	NO _x ^(b)	Particulate ^(b)
1	28500	90	-(c)	-(c)	-(c)	-(c)	-(c)	-(c)
2	35700	90	203	1093	228	51	596	3.2
3	35700	130	196	1007	280	28	285	23.7
4	35000	30	185	7728	304	11477	1434	264.2
5	33000	80	200	2592	361	189	649	175.2
6	40450	90	204	662	444	182	563	713.0
7	39300	90	185	1824	1455	121	607	565.0
8	39650	70	143	4356	1033	322	808	62.5
9	35350	80	159	4666	630	30	445	107.5
10	31500	90	150	294	336	< 8.4	664	137.8
11	31000	90	159	248	438	< 8.4	545	62.8
12	32750	90	173	854	778	< 8.4	608	250.8
13	34450	90	175	686	974	< 8.4	698	210.4
14	34500	90	172	538	1030	< 8.4	254	232.8
15	38800	90	181	879	1365	< 8.4	675	336.0
16	35000	90	172	701	908	< 8.4	374	375.1
17	33900	90	173	474	958	< 8.4	446	361.9
18	32100	60	150	-(c)	-(c)	-(c)	-(c)	-(c)

(b) g/ton: g emitted for one ton of waste combusted

(c) data not available

The correlation between average combustion temperature during sampling and the amounts of micropollutants (logarithmic values) emitted was not significant. This suggests that the lowest temperature reached is the main factor affecting the amount of micropollutants emitted.

No significant correlation was found between fume temperature, stack flow, HCl, NO_x, SO₂, CO and micropollutants emitted.

The similarity between the amounts of PCDD (or PCDF) emitted on the two consecutive days every month (see Fig. 3,4), even when the other parameters change, stresses the importance of the materials burned in determining the composition of fumes emitted. In fact, the composition of the waste may well be similar on two consecutive days.

Combustion temperature and HCl could play a role even in the formation or destruction of the individual isomers. However no correlation was found between minimal combustion temperature

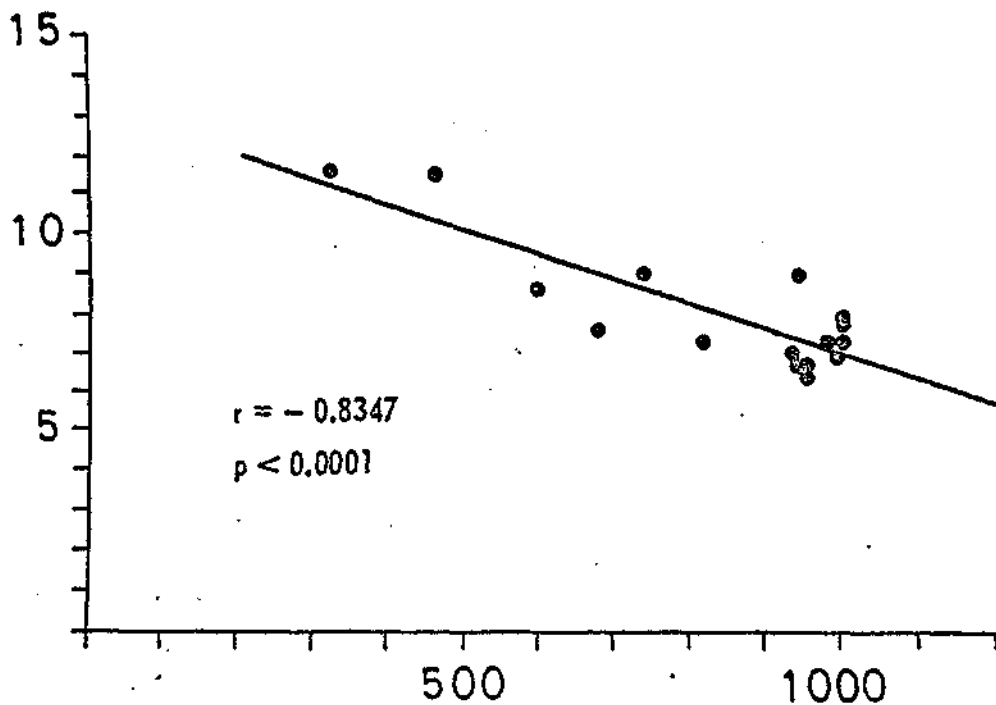


Fig. 1 - x = minimal combustion temperature reached during each sampling ($^{\circ}\text{C}$).
 y = PCDD emitted ($\ln \mu\text{g}/\text{ton}$)

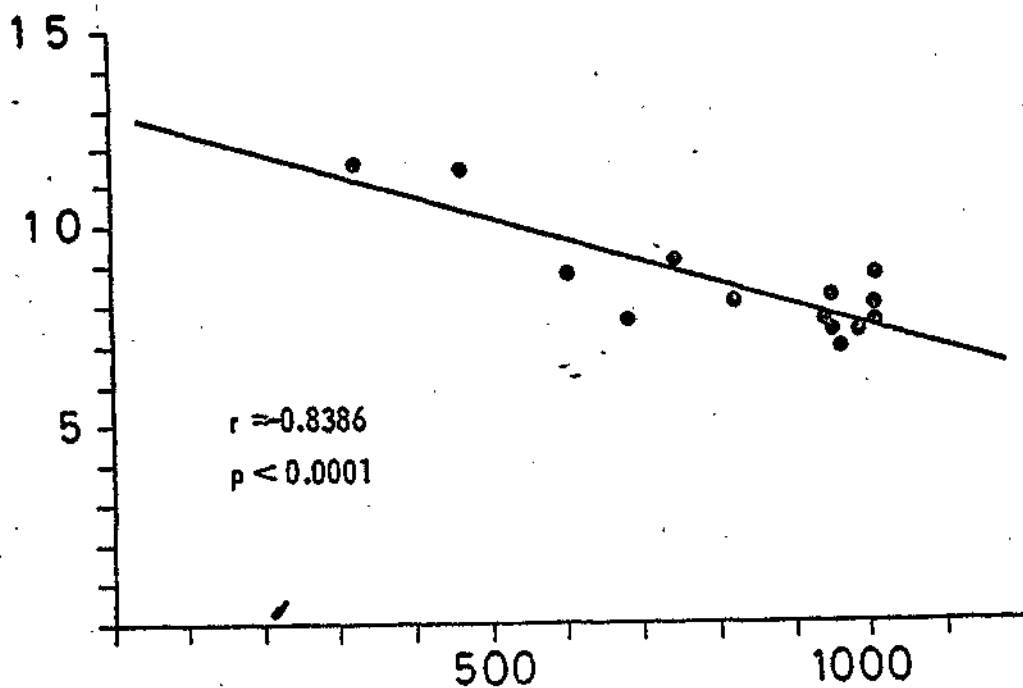


Fig. 2 - x = minimal combustion temperature reached during each sampling ($^{\circ}\text{C}$).
 y = PCDF emitted ($\ln \mu\text{g}/\text{ton}$)

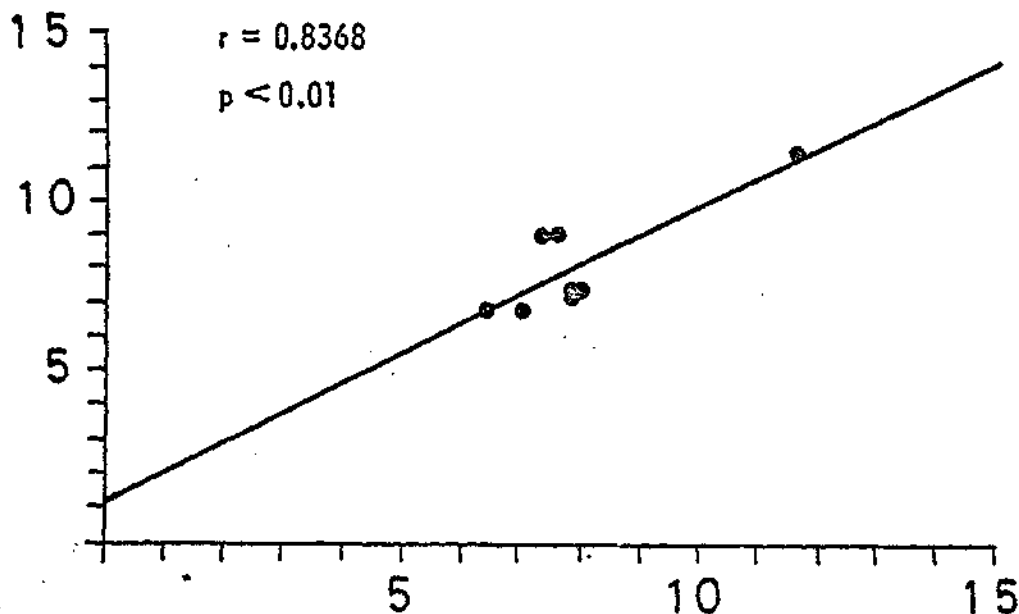


Fig. 3 - x = PCDD released the first sampling day of each month (ln µg/ton)
 y = PCDD released the second sampling day of each month (ln µg/ton)
 Samplings 1 and 18 are missing because only one sample was taken in those months.

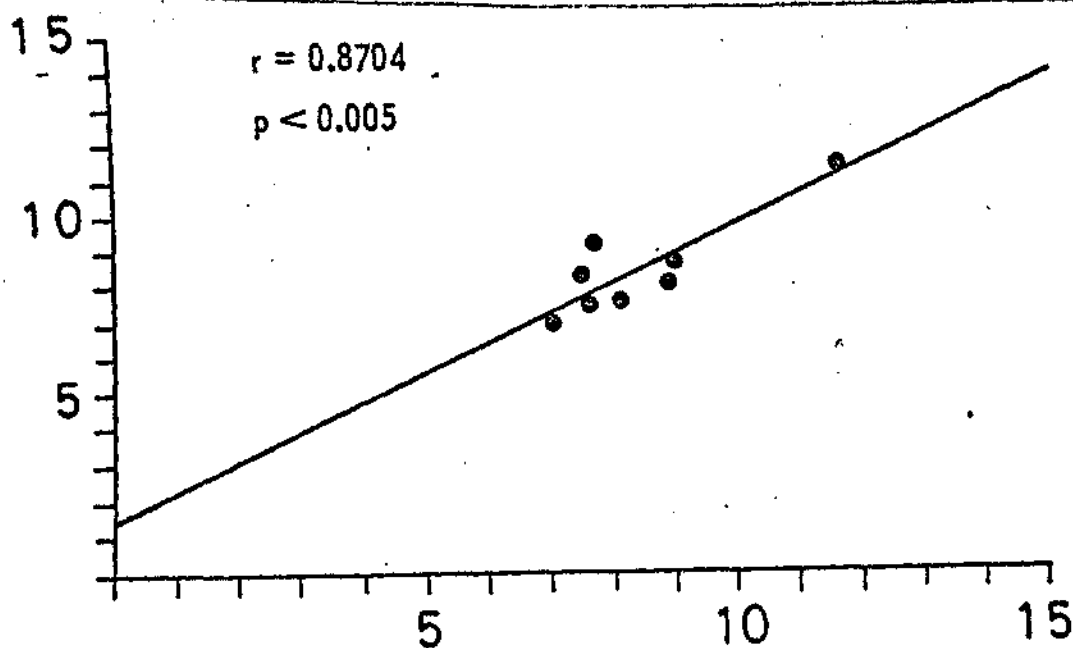


Fig. 4 - x = PCDF released the first sampling day of each month (ln µg/ton)
 y = PCDF released the second sampling day of each month (ln µg/ton)
 Sampling 18 is missing because only one sample was taken in the month.

and the ratios HexaCDD/OctaCDD or Tetra CDF/OctaCDF. HexaCDD and TetraCDF are the most abundant isomeric classes for PCDD and PCDF, respectively, and OctaCDD and OctaCDF are the least abundant. Similarly it was not possible to find any correlation between the amount of HCl and the ratios HexaCDD/OctaCDD and TetraCDF/OctaCDF. Moreover the ratio between individual classes of isomers was not affected by the fume temperature, indicating that selective condensation of individual

classes does not occur in the stack at least in these particular operating conditions.

The amounts of PCDD and PCDF in the different samplings were very similar (see Fig. 5). This suggests that both PCDD and PCDF concentrations depend on common factors.

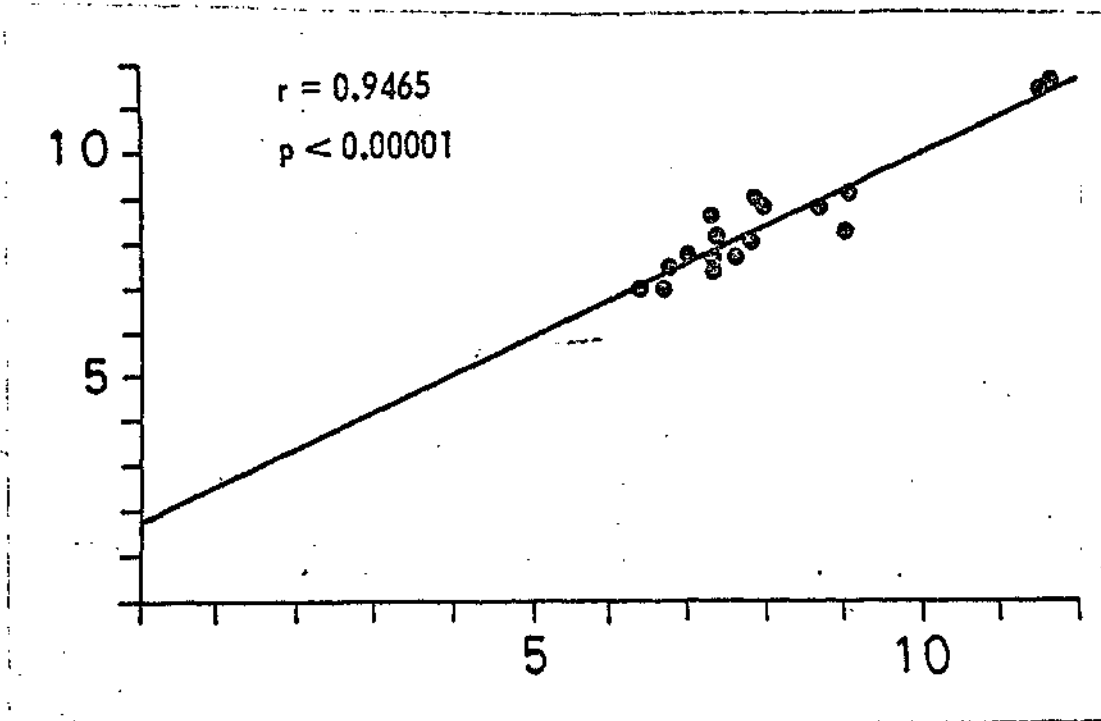


Fig. 5 - x = PCDD emitted during each sampling (ln µg/ton)
y = PCDF emitted during each sampling (ln µg/ton)

The data presented here confirm that the emission of PCDD and PCDF from urban waste incinerators is inversely related to the combustion temperature; this agrees with observations by other authors, who report that TCDD decomposes at temperatures higher than 800°C (12,13) and that no PCDD can be measured in incinerators operated at high temperatures (<1200°C) (14). However no information can be drawn from these results on the mechanism by which the combustion temperature influences the amount of PCDD and PCDF emitted. A low operating temperature could increase the probability of formation of polychlorinated compounds, reduce the rate of degradation of these compounds once formed or act in both directions.

Further investigations are required to clarify the processes of formation and the destruction of polychlorinated pollutants in urban incinerators, but some practical indications on the possibility of drastically reducing the amount of PCDD and PCDF released into the environment can already be drawn from the data presented here.

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