POLYCHLORINATED BIPHENYLS AND POLYCHLORINATED DIBENZO-p-DIOXINS/FURANS: OBSERVATIONS FROM INCINERATION AND LABORATORY STUDIES

François A. Espourteille, Elmar R. Altwicker and Shannon Talbot
The Isermann Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy NY 12180

INTRODUCTION

Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/F) have been reported as contaminants on fly ash, flue gas and residues from municipal solid waste incinerators (MSW), (The National Incineration Testing and Evaluation Program: Two-stage Combustion (Prince Edward Island), 1985; Altwicker et al., 1989; Marklund et al.,1992; Funcke et al., 1995; Kaune et al., 1995), steel processing and reclamation plants (Aittola et al., 1992; Jager, 1993), and cement kilns (Reiner et al., 1995; Schreiber et al., 1995). Concentration levels of other contaminants, such as chlorobenzenes (CB), chlorophenols (CP), polyaromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) are occasionally reported. It has been demonstrated that CB and CP can act as precursors to PCDD/F formation, both in incinerators and in laboratory systems (Karasek and Dixon, 1987; Altwicker et al., 1989; de Leer et al., 1989; Altwicker et al., 1993; Fangmark et al., 1994) and that PCDD/F can also be formed by de-novo synthesis (Stieglitz et al., 1989a; Stieglitz et al., 1989b; Milligan and Altwicker, 1993). While information about PCDD/F in incinerators is plentiful, this is not the case for PCB. PCB are similar in structure to PCDD/F and could be formed along side PCDD/F in incinerators, possibly sharing formation mechanisms. In this paper, the literature on simultaneous PCB and PCDD/F observations during incineration is reviewed, and some new data on the relationship between the classes of compounds from a waste wood ash are presented.

CONCENTRATION OF PCB AND PCDD/F IN MSW AND SIMILAR ENVIRONMENTS.

One of the earliest report to quantify both PCB and PCDD/F in MSW was The National Incinerator Testing and Evaluation Program: Two-stage Combustion (Prince Edward Island), published in September 1985 (PEI Report). Comparative data is available for four different runs, a normal cycle (secondary chamber temperature 840 C), a long cycle (secondary chamber temperature 890 C), a high secondary chamber temperature run (1080 C), and a low secondary chamber temperature run (780 C). Stack flow rate varied between 7900 m^3/h and 11,000 m^3/h, stack temperature remained constant at about 184 C. Key operating parameters remained constant during the four runs. With the exception of the stack emission for the high secondary temperature run, all runs show PCB levels to be higher than PCDD or PCDF levels. In the case of the normal cycle run, the PCB value reported is almost one order of magnitude greater than the PCDD value. Most values for bottom ash were below detection limit.

Marklund et al. (1994) report on the emissions of polychlorinated compounds from a pilot scale incinerator simulating and MSW. A variety of fuel types were used and PCDD/F and PCB were quantified in the gas flue. The ratio of PCDD/F to PCB varied from 0.34 to 3.69, depending on the fuel used. Levels of coplanar PCB were usually, but not always, one order of magnitude below PCB levels (co-PCB/PCB ratio ranged from 0.02 to 0.58, depending on fuel mixture). PCDD/F and PCB levels were affected by the nature of the fuel which contained one or more of the following: bleached or unbleached paper, ink, aluminum foil, and waste pellets. No trend could be found to explain the co-PCB / PCB ratio variation. Paper, bleached or unbleached with or without ink and aluminum foil added to the fuel mixture, produced relatively constant amounts of PCDD. PCDF levels varied considerably more. Waste pellets yielded the largest flue concentration of PCDD/F but did not have the same effect on PCB concentration. Addition of ink or aluminum foil to bleached or unbleached paper

resulted in an increase in total PCB, culminating when both ink and foil were present. Unbleached paper produced less total PCB than bleached paper. This trend was found when waste pellets were added to unbleached paper, but not to bleached paper. A feed comprise of bleached paper, waste pellets, aluminum and ink resulted in a decrease in total PCB concentration when compared to a feed lacking ink and foil. Trends in co-planar PCB concentration did not follow those seen for total PCB.

Wilken et al. (1994), reported PCB concentration in the flue gas of an MSW to be 16 to 20 times, on average, the PCDD/F concentration over a five day run. Sakai et al (1992 & 1993) analyzed flue gas of a Japanese MSW for PCDD/F and PCB content. PCDD/F concentration from an MSW were 1,800 ng/m^3 for flue gas and 610 ng/g for fly ash while PCB displayed lower concentrations for both flue gas, 466 ng/ m^3, and fly ash, 28 ng/g. Co-planar PCB values were one order of magnitude lower than total PCB, with 22 ng/ m^3 for flue gas and 3.2 ng/g for fly ash. This last study show PCDD/F values much higher than total PCB, but the ratio between total PCB and co-planar PCB remains constant. Miyata et al. (1993) reported average daily emissions for PCDD, 922.82 mg/day, PCDF, 2419.55 mg/day, and co-planar PCB, 52.20 mg/day, for an MSW. No total PCB values were reported. The difference between total PCDD/F, 3342.37 mg/day, and co-planar PCB, 52.20 mg/day, is tow order of magnitude. Kawakami et al. (1993) sampled an MSW during different phases of functioning (start up, steady state, shutdown) along with sampling at steady state in different parts of the unit (furnace, gas cooler, bag filter in and out). While concentrations of PCDD/F and PCB in flue gas varied up to two orders of magnitude, the ratio between PCDD/F and PCB was always close to one order of magnitude (0.06-0.29); total PCB to co-planar ratio was equally stable at about one order of magnitude (0.03-0.20). Samples taken when steady state had been reached exhibited much closer ratio than samples taken during startup or shutdown of the unit. Analysis of PCDD/F and PCB at various places in the MSW revealed that while PCDD and PCDF concentrations increased both at the exit of the gas cooler and the bag filter, total PCB concentration increased at the gas cooler exit but decreased, nominally, at the bag filter exit. Co-planar PCB behaved more like PCDD/F than PCB and increased in both instances. Analysis of PCDD/F and PCB of MSW dust revealed different ratios; PCB concentration was about two orders of magnitude less than PCDD/F concentration, but the difference between PCB and co-planar PCB was only one order of magnitude. This information is summarized in Table 1.

Table 1.

Relationship of PCB and PCDD/F from Various Sources

Source	Incinerator type	PCDD/ PCB	PCDF/ PCB	PCDD+F/ PCB	coPCB/ PCB
The National Incinerator Testing and Evaluation Program (PEI)	MSW; normal cycle	0.125	0.175	0.3	na
PEI	MSW; long cycle	1.83	2.67	4.5	na
PEI	MSW; higher 2nd chamber temp.	pcb nd	pcb nd	pcb nd	na
PEI	MSW; low 2nd chamber temp.	0.92	0.77	1.69	na
Marklund et al. 1994	Pilot scale MSW	0.06-0.76	0.28-1.42	0.34-3.69	0.02-0.58
Wilken et al. 1994	MSW	na	na	0.063	na
Sakai et al. 1992 & 1993	MSW	0.53	0.34	0.86	0.04
Myiata et al 1993*		1.78	4.65	6.43	0.1
Kawakami et al. 1993	MSW	0.35-11.8	0.54-8.50	3.45-16.7	0.03-0.20
Jager 1993	Steel reclamation plant	0.0004-0.31	0.00004 2-1.03	0.0056-1.3	na

*Total PCB values not given and estimated at 10X co-planar PCB values given for ratio calculations.

Jager (1993) reported on PCDD/F and PCB emissions from steel plants. Feeds containing varying amounts of waste metal of different origins yielded different concentrations of chlorinated wastes. Municipal Waste Incinerator (MWI) scrap produced 41.8 ng/m^3 PCDD, 81.9ng/ m^3 PCDF (total PCDD/F 124 ng/m3) and 155 ng/m3 PCB in flue gas; dust samples contained 69.3 ng/g PCDD, 203.4 ng/g PCDF (total PCDD/F 273 ng/g) and 776 ng/g PCB. Similar analysis for shredder scrap refuse yielded 1.0 ng/m3 PCDD, 2.89 ng/m3 PCDF (total PCDD/F 3.89 ng/m3) and 673 ng/m3 PCB; dust samples contained 31.9ng/g PCDD, 106.4 ng/g PCDF (total PCDD/F 138 ng/g) and 103 ng/g PCB. Shear scarp refuse produced 0.3 ng/m3 PCDD, 6.0 ng/m3 PCDF (total PCDD/F 6.4 ng/m3), and 701 ng/m3 PCB; dust samples contained 22.8 ng/g PCDD, 107.3 ng/g PCDF (total PCDD/F 130 ng/g), and 152 ng/g PCB. PCDD/F to PCB ratios varied considerably, from 0.0056 for shredder scrap flue gas to 1.3 for shredder scrap dust. Ratios for MWI were 0.8 and 0.35 for flue gas and dust, respectively. Shear scrap ratios were 0.009 and 0.86 for flue gas and dust, respectively. In all cases but one PCB levels were higher than PCDD/F levels.

LABORATORY MEASUREMENTS OF PCB AND PCDD/F IN COMBUSTION, POST COMBUSTION EXPERIMENTS

Eklund et al (1986) have presented evidence that combining phenol and HCl in the presence of heat (550C) results in the formation of chlorinated organic compounds, including chlorobenzenes, PCDD, PCDF, and PCB, among others. Leer et al. (1989) oxidized toluene in air at 525 C. in the presence of fly ash and a chlorine source and obtained a large variety of chlorinated organics, among them PCDD/F and PCB. They concluded that PCB could be formed by "de-novo" synthesis, along with PCDD/F. Blaha and Hagenmaier (1985) have shown that formation of PCDD/F occurs rapidly on model fly ash. PCB formation was low and remained constant over time which lead them to dismiss PCB as a direct precursor in the formation of PCDD/F. Schoonenboom et al (1993) reported on the formation of co-planar PCB from particulate organic carbon in a fly ash model system via "de novo" synthesis. Formation maxima for both PCB and PCDD/F occurred around 350 C. Fangmark et al. (1994) determined that PCB and PCDD/F formation exhibited similar dependency on temperature and residence time, thus suggesting similar formation mechanisms. Greater concentration were obtained at 340 C. and at the longest residence time, 2.9 seconds.

EXPERIMENTAL

Laboratory work to characterize a fly ash from a waste wood incinerator was undertaken. The dependency of PCDD/F and PCB formation was studied simulating the post combustion region of an incinerator. A comprehensive description of the apparatus, methods and analytical procedures can be found in Milligan and Altwicker (1993) and Talbot et al. (1996). The principal parameters investigated were temperature, oxygen concentration and residence time. The four graphs show below summarize the data. PCDD/F and co-planar PCB formation exhibit dependency to the same variables. Both PCDD/F and co-planar PCB increase with increasing temperature; formation peaks at 10.3 % oxygen and decreases at higher oxygen concentration. Formation of both PCDD/F and co-PCB display a near linear time dependency, but concentration reaches a plateau after 60 mn possibly due to competing degradation reactions. While co-planar PCB and PCDD/F exhibit similar behavior, absolute concentrations are usually two order of magnitude apart.

DISCUSSION

Laboratory data seems to agree with field MSW data. Incinerator feed plays a very important role in the formation of PCDD/F and PCB which might explain why incinerators burning feed high in metal or other unusual material differ from MSW in terms of PCDD/F and PCB generation.

Laboratory data seems to indicate that co-planar PCB form using pathways similar to those responsible for the formation of PCDD/F; the important difference in absolute concentrations between these compounds would suggest that other variables are at play, such as individual reactivities of precursors. On the basis of the observed relative yields for the waste wood ash it seems doubtful that PCB act as

precursor to PCDF, but further studies may be needed, since other findings (cf. Table 1) suggest that PCB > PCDD/F. A definitive study could be performed using carbon 13 labeled co-planar PCB and to subsequently analyze for carbon13 labeled PCDF.

ACKNOWLEDGEMENT

Partial support of this work by the Georgia-Pacific Corporation is gratefully acknowledged.

BIBLIOGRAPHY

Aittola, J-P., Paasivirta, J., and Vattulainen, A. 1992. Measurements of Organochloro Compounds at a Metal Reclamation Plant. 12th International Symposium on Chlorinated Dioxins and Related Compounds (Dioxin '92) August 1992; Tampere, Finland.

Altwicker, E.R., Konduri, R.K.N.V., Lin, C., and Milligan, M.S. 1993. Formation of Precursors to Chlorined Dioxin/Furans under Heterogeneous Conditions. Combust. Sci. and Tech., 88, pp. 349-368.

Altwicker, E.R., Schonberg, J.S., Konduri, R.N.V.K., and Milligan, M.S. 1989. Polychlorinated Dioxin/Furans Formation in Incinerators. Haz. Waste & Haz. Mat., 7 (1), pp. 73-87.

Altwicker, E.R., Konduri, R.N.V.K., and Milligan, M.S. 1989. The Role of Precursors in Formation of Polychloro dibenzo-p-dioxins and polychlorodibenzofurans During Heterogeneous Combustion. 9th International Symposium on Chlorinated Dioxins and Related Compounds (Dioxin'89), September 1989, Toronto, Ontario.

Blaha, J., and Hagenmaier, H. 1995. Time Dependence of the *de novo* Synthesis of PCDD/PCDF and Potential Precursors on a Model Fly Ash. Organohalogen Compounds 23 (Dioxin '95), pp. 403-406.

Eklund, G., Pedersen, J.R., and Strömberg, B. 1986. Phenol and Hcl at 550 C yield a large variety of chlorinated toxic compounds. Nature 320 (6058), pp. 155-156.

Fangmark, I., Stromberg, B., Berge, N., and Rappe, C. 1994. Influence of Postcombustion Temperature Profiles in the Formation of PCDDs, PCDFs, PCBzs and PCBs in a Pilot Incinerator. Environ. Sci. Technol. 28, pp. 624-629.

Funcke, W., Hovemann, A., Philipp, C., Mark, F.E., Kerber, G., and Dresch, H. (1995). PCDF/D in Input Material, Solid Residues and Flue Gas from a Municipal Waste Incinerator during the Co-Combustion of Mixed Separate Plastic Waste. 15th International Symposium on Chlorinated Dioxins and Related Compounds (Dioxin'95), Edmonton, Canada, 1995.

Jager, J. 1993. PCDD/F and PCB Emission from Steel Producing, Processing and Reclamation Plants with Varying Input. Toxicology and Environmental Chem. 40, pp. 201-211.

Karasek, F.W., and Dickson, L.C. 1987. Model Studies of Polychlorinated Dibenzo-p-dioxins Formation During Municipal Refuse Incineration. Science, 237 (4816), pp. 754-756.

Kaune, A., Lenoir, D., Nikolai, U., Schramm, K.-W., and Kettrup, A. (1995). Seven-year Decreasing Trend of PCDD/F Emission in the Flue Gas of Waste Incinerator Showing Importance of Primary Measures. 15th International Symposium on Chlorinated Dioxins and Related Compounds (Dioxin'95), Edmonton, Canada, 1995.

Kawakami, I., Matsuzawa, Y, Tanaka, M., Sakai, S. and Hiraoka, M. 1993. Emission Level of Co-PCBs from MSW Incinerators. 13th International Symposium on Chlorinated Dioxins and Related Compounds (Dioxin'93), Vienna, Autria. September 1993. pp 375-380.

de Leer, E.B.W., Lexmond R.D., and de Zeeuw, M.A. 1989. "De Novo"-Synthesis Of Chlorinated Biphenyls, Dibenzofurans and Dibenzo-p-Dioxins in the Fly Ash Catalyzed Reaction of Toluene with Hydrochloric Acid. Chemosphere, 19 (8/9), pp. 1141-1152.

Marklund, S., Soderstrom, G., Ljung, K., Rappe, C., Kraft, M., and H. Hagenmaier (1992). Parallel sampling techniques at a Swedish municipal solid waste incinerator. Waste Management & Res. 10, pp. 21-36

Marklund, S., Wilkstrom, E., Lofvenius, G., Fangmark, I., and Rappe, C. 1994. Emissions of Chlorinated compounds in Combustion of Biofuels. Chemosphere 28(10), pp. 1895-1904.

Milligan, M.S. and Altwicker, E.R. 1993. The Relationship Between *de Novo* Synthesis of Polychlorinated dibenzo-p-dioxins and Dibenzofurans and Low-Temperature Carbon Gasification in Fly Ash. Env. Sci. & Tech., 27 (8), pp. 1595-1601.

Miyata, H., Aozasa, O., Mase, Y., Ohta, S., Khono, S., and Asada, S. 1993. Real Situation on Emission of PCDDs and Non-ortho Chlorine Substituted Coplananr PCBs via Flue Gas fom Urban Waste Incinerators in Japan. 13th International Symposium on Chlorinated Dioxins and Related Compounds (Dioxin'93), Vienna, Autria. September 1993. pp 253-256

Reiner, E.J., Gizyn, W.I., Khurana, V., Kolic, T.M., MacPherson, K.A., Waddell, D.S., and Bell, R.W. (1995). Environmental Impact of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans from a Cement Kiln. 15th International Symposium on Chlorinated Dioxins and Related Compounds (Dioxin'95), Edmonton, Canada, 1995

Sakai, S., Hiraoka, M., Takeda, N., and Shiozaki, K. 1992. Coplanar PCBs and PCDDs\PCDFs in Municipal Waste Incineration. 12th International Symposium on Chlorinated Dioxins and Related Compounds (Dioxin '92), v.9, pp. 215-218.

Schoonenboom, M., Tromp, P.C., and Olie, K. 1993. The Formation of coplanar PCBs, PCDDs and PCDFs in a fly-ash model system. 13th International Symposium on Chlorinated Dioxins and Related Compounds (Dioxin'95), Vienna, Austria, 1993.

Schreiber, R.J., Jr P.E., Evers, J.J., and Winders, W.H. 1995. Dioxins emissions and cement kiln operations. 15th International Symposium on Chlorinated Dioxins and Related Compounds (Dioxin'95), Edmonton, Canada, 1995

Stieglitz, L., Zwick, G., Beck, J., Roth, W., and Vogg, H. 1989. On the De-Novo Synthesis of PCDD/PCDF on Fly Ash of Municipal Waste Incinerator. Chemosphere 18, pp. 1219-1226.

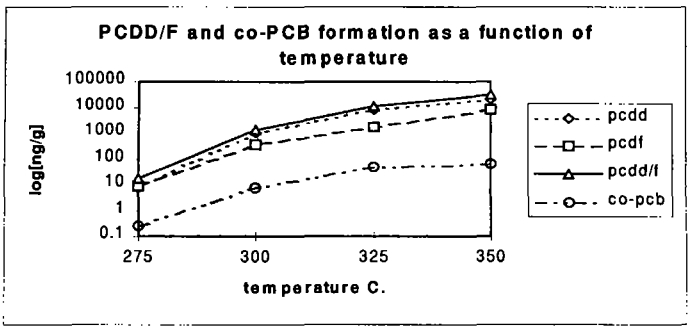
Stieglitz, L., Zwick, G., Beck, J., Bautz, H., and Roth, W. 1989. Carbonaceous Particles in Fly Ash - A Source for the De-Novo Synthesis of Organochlorocompounds. Chemosphere 19, pp. 283-290.

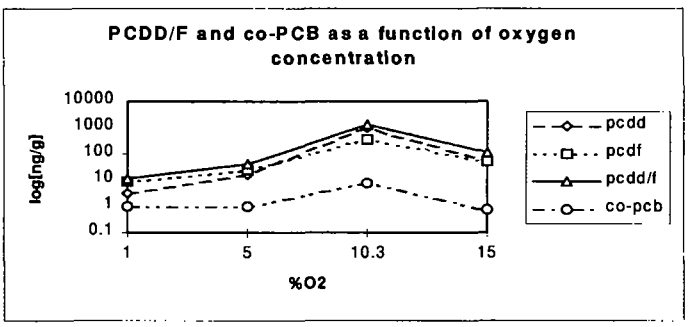
Talbot, S., Altwicker, E.R. and Espourteille, F.A. 1996. Polychlorinated Dibenzo-p-Dioxin/Furan (PCDD/F) Formation Potential of Wood Waste Incinerator Fly Ashes.

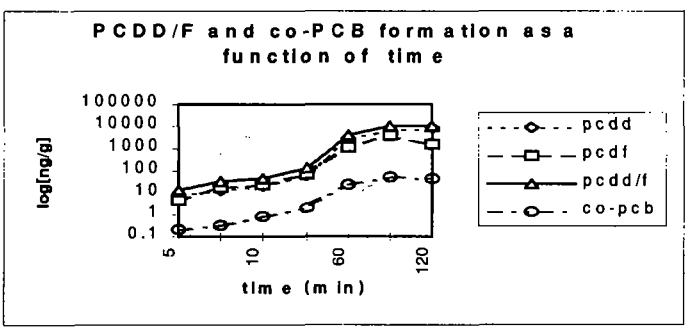
The National Incineraton Testing and Evaluation Program: Two-stage Combustion (Prince Edward Island). Urban Activities Division, Environmental Protection Service, Environment Canada. Report EPS 3/UP/1, September 1985.

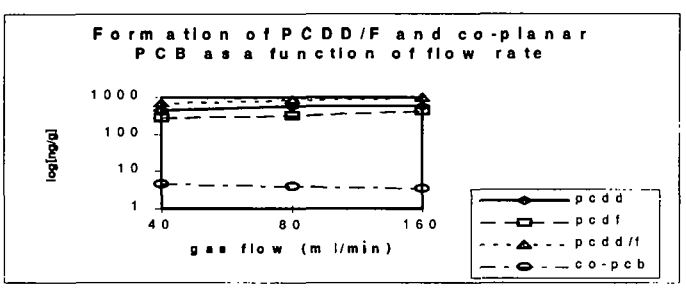
Wilken, M., Boske, J., Jager, J., and Zeschmar-Lahl, B. 1994. PCDD/F , PCB, Chlorbenzene and Chlorophenol Emissions Of A Municipal Solid Waste Incineration Plant (MSWI) - Variation Within A Five Day Routine Performance And Influence Of $Mg(OH)_2$ - Addition. Chemosphere 29 (9-11), pp. 2039-50.

SOUR (po)


PCDD/F and co-PCB formation as a function of temperature
log[ng/g]
100000
10000
1000
100
10
1
0.1
275
300
325
350
temperature C.
pcdd
pcdf
pcdd/f
co-pcb


PCDD/F and co-PCB as a function of oxygen concentration
log[ng/g]
10000
1000
100
10
1
0.1
1
5
10.3
15
%O2
pcdd
pcdf
pcdd/f
co-pcb


PCDD/F and co-PCB formation as a function of time
log[ng/g]
100000
10000
1000
100
10
1
0.1
5
10
60
120
time (min)
pcdd
pcdf
pcdd/f
co-pcb


Formation of PCDD/F and co-planar PCB as a function of flow rate
log[ng/g]
1000
100
10
1
40
80
160
gas flow (ml/min)
pcdd
pcdf
pcdd/f
co-pcb