Characterisation of PCBs Formed During Thermal Processes.

T. Takasuga, T. Inoue, E. Ohi, N. Umetsu, P. Ireland & N. Takeda[☆].
Shimadzu Techno-Research Inc., 2-4 Nishinokyo-Sanjo Bocho, Nakagyo-ku, Kyoto 604, Japan.
[☆]Dept. of Environmental and Sanitary Engineering, Kyoto University, Kyoto 606, Japan.

1. Introduction.

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) can be formed during combustion processes, *e.g.* municipal solid waste (MSW) incineration. Recently, reports have appeared on the presence of non-*ortho* and mono-*ortho* substituted polychlorobiphenyls (PCBs) and polychloronaphthalenes (PCNs) during MSW incineration[1,2].

Commercial mixtures of PCBs have been synthesised by the chlorination of biphenyl and used in a wide variety of applications. There are 209 possible congeners and more than 100 have been found in commercial PCB preparations (*e.g.* Kanechlor, Aroclor). Japanese commercial PCB samples contain approximately 0.1~0.8% non-*ortho*PCBs, with commercial samples in the U.S.A. containing 0.3~0.6% non-*ortho*PCBs[3].

Previously an all congener specific, HRGC/HRMS analytical method for PCBs with HPLC clean-up was established[4]. This method has been used to monitor PCB levels and distributions in MSW samples (both gaseous and particulate phases). The results indicate that, in such samples, the relatively toxic non-*ortho* and mono-*ortho* PCBs predominate.

Model experiments were also performed in the laboratory by heating biphenyl in the presence of HCl and monitoring the formation of PCBs. This paper focuses on the characterisation of PCBs formed during thermal processes. Data for environmental air is also shown, and the possible sources of PCB in the air samples are discussed.

2. Materials and Methods.

The HRGC/HRMS method, including sample clean-up, is as previously described[4]. Assignment of PCB congeners was based upon previously published data[5].

MSW incinerators were sampled using standard procedures for PCDD/PCDF analysis[6].

Model experiments on the chlorination of biphenyl were performed on an Al_2O_3/SiO_2 support using a gas flow composition resembling that found during MSW incineration.

3. Results and Discussion.

Table 1 shows the major PCB congeners identified in samples from "thermal processes" (MSW incineration and model experiments) compared to those in a commercial PCB sample. Immediately noticeable is the tendency towards *meta*- and *para*- substituted PCBs in the "thermal processes" data, in comparison to the *ortho*- and *para*- substitution pattern for the commercial PCB sample.

Figure 1 shows the data for the relative abundances of non-*ortho*, and mono-*ortho* plus

Table 1. Predominant PCB Congeners Observed in Samples from Thermal Processes (MSW Incineration and Pyrolysis Experiments) and in Commercial PCB (Kanechlor).

Chlorine No.	Thermal Processes	Commercial PCB (Kanechlor)
Cl_1	3- (#2) 4- (#3) > 2- (#1)	2- (#1) 4- (#3) >> 3- (#2)
Cl_2	34- (#12) >> 35- (#14) 33'- (#11) 44'- (#15)	24'-/23- (#8) (#5) >> 22'-/26- (#4) (#10) 44'- (#15) 23'- (#6)
Cl_3	233'-/2'34- (#20) (#33) 345- (#38) 33'4- (#35) 344'- (#37)	24'5- (#31) 244'- (#28) 22'5- (#18) 2'34- (#33) > 22'3-/24'6- (#16) (#32) > 234'- (#22)
Cl_4	**33'44'**- (**#77**) 2344'-/233'4'- (#60) (#56) **33'45**- (**#78**) **33'45'**- (**#79**) **344'5**- (**#81**) 234'6- (#64)	22'55'- (#52) 23'4'5- (#70) 23'44'- (#66) > 22'45'- (#49) 22'35'- (#44) 234'6- (#64) 244'5- (#74) 2344'-/233'4'- (#60) (#56)
Cl_5	**33'44'5**- (**#126**) **233'44'**-/**33'455'**- (**#105**) (**#127**) **23'44'5**- (**#118**) > **233'4'5**-/**233'45'**- (**#107**) (**#108**) 233'4'6- (#110) **2344'5**- (**#114**) **2'33'45**- (**#122**) 22'33'4- (#82)	233'4'6- (#110) 22'455'- (#101) 22'35'6- (#95) **23'44'5**- (**#118**)
Cl_6	**33'44'55'**- (**#169**) **233'44'5**- (**#156**) 22'344'5'- (#138) 233'44'6- (#158) **233'44'5**- (**#157**) 22'34'5'6- (#149) **23'44'55'**- (**#167**)	22'34'5'6- (#149) 22'44'55'- (#153) 22'344'5'- (#138)
Cl_7	**233'44'55'**- (**#189**) 22'33'44'5- (#170) 233'44'56- (#190) > 233'44'5'6- (#191)	22'344'55'- (#180) 22'34'55'6- (#187) 22'33'456'- (#174) 22'33'566'- (#179) 22'33'44'5- (#170)
Cl_8	22'344'55'6-/22'33'44'5'6- (#203) (#196) 22'33'44'55'- (#194) 233'44'55'6- (#205)	22'33'45'66'- (#199) 22'344'55'6-/22'33'44'5'6- (#203) (#196) 22'33'44'55'- (#194)
Cl_9	22'33'44'55'6- (#206)	22'33'44'55'6- (#206)

IUPAC Number for each congener given in brackets below.

" / " Indicates isomers unresolved under GC conditions used.

Mono*ortho* and non-*ortho* congeners with >Cl_3 **highlighted**.

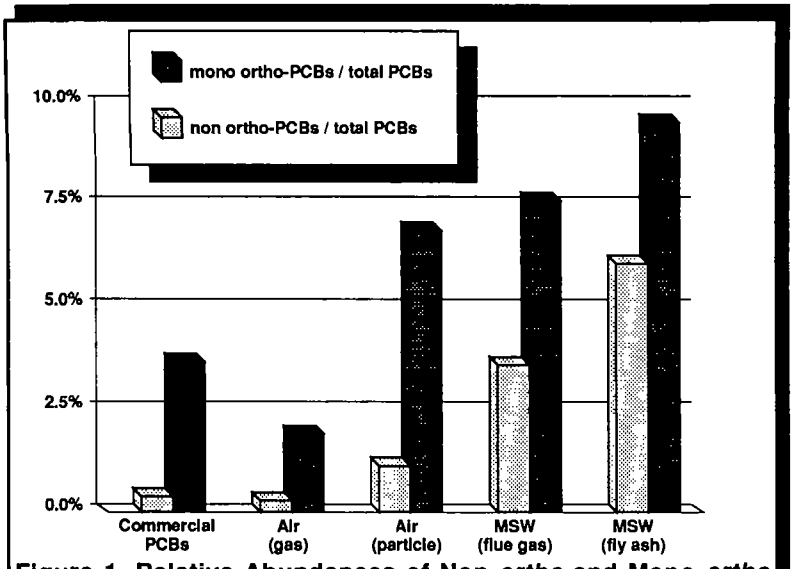
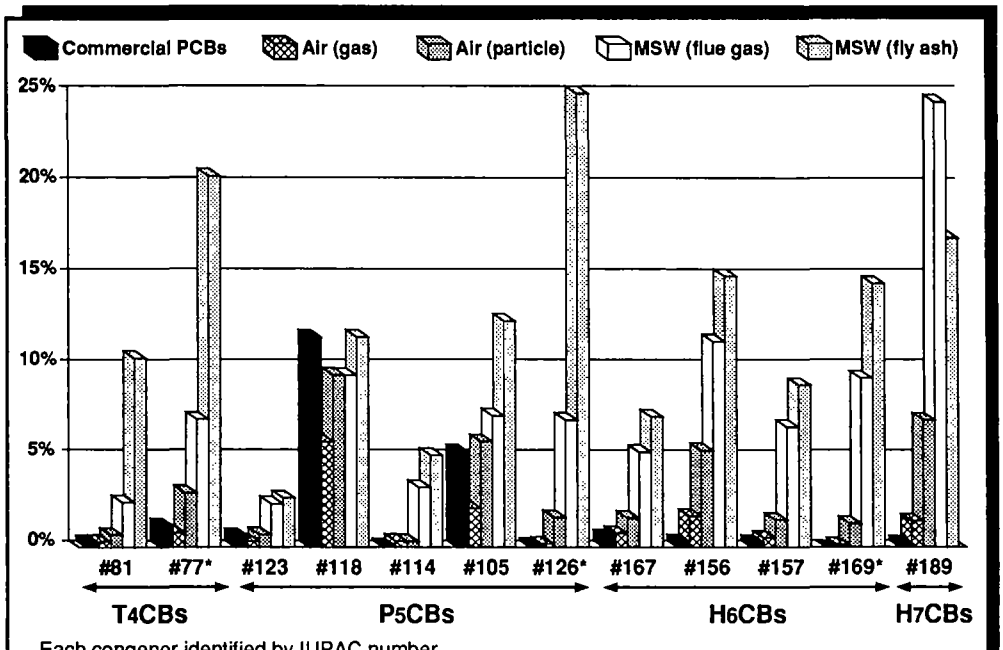


Figure 1. Relative Abundances of Non-*ortho* and Mono-*ortho* PCBs in Air Samples, MSW Samples and a Commercial Sample.



Each congener identified by IUPAC number.

* Indicates a co-planar PCB.

Data is % relative abundance for each congener compared to total abundance for its congener group.

Figure 2. Relative Abundances of Individual Non-*ortho* and Mono-*ortho* PCB Congeners in Air Samples, MSW Samples and a Commercial Sample.

non-*ortho*, expressed as a percentage of total PCBs, for various samples. Air samples were taken at a number of different city locations in Japan, and each MSW sample (either fly ash or flue gas) came from a different site. Thus, it is assumed that the data are "average" data, and reflect a general trend, rather than a specific case for one incinerator or one site.

Both MSW sample types (flue gas and fly ash: averaged data from 10 and 20 samples, respectively) exhibit higher relative abundances of both non-*ortho* and mono-*ortho* PCBs when compared to the commercial PCB sample. Non-*ortho* and mono-*ortho* PCB relative abundances in air (both gas and particulate: averaged data from 5 samples) are intermediate between the levels seen for the MSW samples and the commercial PCB mixture.

Figure 2 is a more detailed analysis of the PCB composition for the same samples. Levels of individual non-*ortho* and mono-*ortho* PCBs are presented for tetra- through to heptachlorobiphenyls, encompassing the congeners having the highest toxicity. Apart from PCB isomers #118 and #105 (IUPAC numbers), levels of non-*ortho* and mono-*ortho* PCBs are relatively low in the commercial PCB sample. The levels of non-*ortho* and mono-*ortho* PCBs are relatively high in the MSW samples. Data from the laboratory experiment, in which biphenyl was subjected to conditions similar to those present during MSW incineration, produced a profile similar to that seen for MSW samples.

Although these data indicate that non-*ortho* and mono-*ortho* PCBs appear to be formed in higher proportions during "thermal processes" than seen in commercial PCB samples, past contamination by commercial PCBs possibly accounts for much of the non-*ortho* and mono-*ortho* PCBs now present in the environment. However, it is possible that, even as total PCB levels decrease, the proportion of non-*ortho* and mono-*ortho* PCBs in ambient air may actually increase due to contributions from "thermal processes", such as vehicle exhausts, MSW incineration and other combustion processes.

Continued monitoring of environmental samples is required to further define the contribution of combustion processes to the levels of non-*ortho*, mono-*ortho*, and total PCBs in the environment.

4. References.

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