Isomerspecific Analysis of Diphenyl Ether Herbicide (CNP) for Mono- to Octa-CDD/F at Sub-ppb Levels

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Introduction

The agrochemical formulations, which made from chlorophenols often, included polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) as impurities. The representative is the CNP (Chloronitrofen: 246-trichlorophenyl-4'-nitrophenyl ether), and it was applied on a paddy field as a herbicide from 1970's to 80's in Japan. Yamagishi *et. al.* (1981) reported that CNP included some dioxin isomers such as 1368-tetra-CDD, 1379-tetra-CDD and 2468-tetra-CDF. In fact, these dioxin isomers have been often detected from soils and sediments, and are ubiquitous pollutants in Japanese environment. In addition, it is reported that CNP contains toxic 2378-chlorine-substitute PCDD/F as well (Masunaga *et. al.*, 1999). These findings indicate that the dioxin impurity in CNP has various isomers regardless of the general recognition of being simpler in the constituent of the dioxins through the chemical synthesis process compared to those through the incineration process. However it has not come to clarifying all of dioxin component in CNP. Thus the isomer specific analysis was done to identify mono- to octa-CDD/F in the CNP formulations using HRGC/HRMS. This paper deals with the levels and composition of the dioxin isomers as well as the difference of isomer composition with year of production.

Materials and Methods

The three CNP formulations analyzed in this work were obtained from Mitsui Chemicals, Inc. They are the emulsifiable concentrate including 20% active ingredient produced in 1982, 1983 and 1985, and have been stored in the sealing condition in 500ml of brown bottle. The extraction and clean-up for mono- to octa-PCDD/Fs in three CNP emulsifiable concentrates were basically performed as described by Hagenmaier *et. al.* (1987). Briefly, the CNP sample diluted with 10% acetone in n-hexane was fortified with fifteen $^{13}C_{12}$-PCDD/F internal standards. The sample was saponificated in 1N potassium hydroxide in ethanol solution for 1 hr while the shaking was done, and then extracted with n-hexane. The hexane extract was cleaned up in order using a concentrated sulfuric acid and a disposable silica-gel cartridge column. If necessary, the additional clean-up was done using an alumina column chromatography. The dioxins were analyzed by HRGC/HRMS (HP5890GC/Micromass Autospec) at a resolution of 10,000 with SP-2331 (60m x 0.32mm, 0.2μm) for mono- to hexa-CDD/F and HP-5MS (60m x 0.32mm, 0.25μm) for hepta- and octa-CDD/F. Individual PCDD/F isomers on SP-2331 and HP-5MS were identified by retention behavior and the abundance ratio of two ions monitored. The isomers are assigned as described by Nakano *et.al.* (1999) for mono- to tri-CDD/F and Ryan *et.al.* (1991) for tetra- to octa-CDD/F.

Results and Discussion

The 83 isomers were identified in the three CNP formulations. The concentrations of individual isomers are given Table 1. The isomer patterns within the mono- to octa-CDD/F congener groups in CNP are illustrated in Figure 1, compared to flyash samples as a typical "incineration pattern". The total concentration of PCDD was clearly

higher compared to that of PCDF. The concentration of 1368-tetra-CDD was the highest with a range of 590 to 3,700 μg/g active ingredient. 1379-tetra-CDD and 24-di-CDF ranged from 140 to 1,300 and 0.97 to 62 μg/g, respectively. Among the toxic 2,3,7,8-chlorine-substitute isomers, 123678-hexa-CDD was the highest with a range of a range of 0.0025 to 0.077 μg/g. As to the mono to tri-CDD/Fs which become clear for the first time, the predominant isomers were 1- for mono-CDD, 13-, 27/23/28- and 18- for di-CDD, 136- and 138- for tri-CDD, 1- for mono-CDF, 24- for di-CDF, and 248- and 246- for tri-CDF. Those isomer patterns for di- to hexa-CDD/F were clearly different from "incineration pattern".

The total PCDD/F concentration and TEQs in three CNP samples decreased as their year of production became newer. The total concentrations and TEQs of PCDD/F for the 1985 CNP sample decreased to1/7 and 1/9 for the 1982 sample, respectively. Such tendency agrees with the previous reports by Masunaga *et. al.* (1999). Moreover we found variations in the ratio of predominance isomers for tetra- to hepta-CDD. The ratio of 1368- and 1379-tetra-CDD changed from 3:1 to 4:1, 12368- and 12468-/12479- and 12379-petna-CDD changed from 3:3:1 to 1:3:1, 123468-/124679-/124689- and 123679-/123689-hexa-CDD changed from 8:1 to 3:2, 1234679- and 1234678-hepta-CDD changed from 1:1 to 1:3. We estimate these variations are as results of purified a raw material (246-trichlorophenol) and an improvement of the manufacturing method on CNP products. On the other hand isomer distribution of all PCDF congener and mono- to tri-CDD didn't vary for the most part among samples with year of production.

Table 1. Concentrations (μg/g active ingredient) of PCDD/F isomer in CNP samples

Isomer	CNP('82)	CNP('83)	CNP('85)	Isomer	CNP('82)	CNP('83)	CNP('8
2-MCDD	0.00069	0.00061	0.00060	1236-/1279-TeCDD	0.47	0.48	0.042
1-	0.00083	0.00081	0.00069	1469-1278-	<0.00003	<0.00003	<0.000(
total-	0.0015	0.0014	0.0013	1239-	<0.00003	<0.00003	<0.000(
13-DCDD	0.011	0.0079	0.0029	1269-	<0.00003	<0.00003	<0.000(
27-/23-/28-	0.0022	0.0019	0.0029	1267-	<0.00003	<0.00003	<0.000(
14-/17-	0.00057	0.00051	0.00066	1289-	<0.00003	<0.00003	<0.000(
18-	0.0017	0.0013	0.0023	total-	5000	4600	730
16-	0.00082	0.00083	0.0012	12468-/12479-PeCDD	46	43	0.32
12-	<0.00003	<0.00003	<0.00003	12368-	45	42	0.72
19-	<0.00003	<0.00003	0.00050	12478-	<0.00003	<0.00003	<0.000(
total-	0.017	0.012	0.010	12379-	15	13	0.22
137-TrCDD	0.48	0.44	0.047	12469-/12347-	0.075	0.072	0.006:
138-	1.2	1.1	0.13	12378-	0.020	0.018	0.002'
136-	1.3	1.2	0.12	12369-	0.057	0.053	0.000'
124-	<0.00003	<0.00003	<0.00003	12467-	0.0060	0.0038	<0.000(
139-/237-	0.0025	0.35	0.0096	12489-	0.020	0.017	<0.000(
147-	<0.00003	<0.00003	<0.00003	12346-	<0.00003	<0.00003	<0.000(
123-	<0.00003	<0.00003	<0.00003	12367-	0.012	0.011	0.000:
178-	<0.00003	<0.00003	<0.00003	12389-	0.014	0.013	0.001'
127-	<0.00003	<0.00003	<0.00003	total-	110	98	1.3
128-	<0.00003	<0.00003	<0.00003	123468-/124679-/			
146-	<0.00003	<0.00003	<0.00003	124689-HxCDD	3.9	3.6	0.022
126-	<0.00003	<0.00003	<0.00003	123679-/123689-	0.48	0.51	0.016
129-	<0.00003	<0.00003	<0.00003	123478-	<0.00005	<0.00004	<0.000(
total-	2.9	3.2	0.31	123678-	0.077	0.074	0.002:
1368-TeCDD	3700	3400	590	123469-	0.0050	0.0049	<0.000(
1379-	1300	1200	140	123789-	0.036	0.035	0.000:
1378-	0.12	0.14	0.014	123467-	0.0025	0.0028	0.000
1369-/1247-/1248-	5.6	6.4	0.34	total-	4.5	4.2	0.041
1268-	2.2	2.2	0.13	1234679-HpCDD	0.057	0.056	0.000:
1478-	<0.00003	<0.00003	<0.00003	1234678-	0.055	0.052	0.000'
2378-	<0.00003	<0.00003	<0.00003	total-	0.11	0.11	0.001(
1237-	0.069	0.069	0.0096	12346789-OCDD	0.012	0.012	0.000(
1234-/1246-/1249-/1238-	0.26	0.26	0.056	total-PCDDs	5100	4700	740

Table 2. Concentrations (μg/g active ingredient) of PCDD/F isomer in CNP samples (continued)

Isomer	CNP('82)	CNP('83)	CNP('85)	Isomer	CNP('82)	CNP('83)	CNP('85)
1-MCDF	0.0063	0.0038	0.0014	1249-/2368-TeCDF	<0.00003	<0.00003	<0.00002
3-	0.00020	0.000060	<0.00002	2467-	0.12	0.11	0.0039
2-	<0.00003	<0.00003	<0.00002	1239-	<0.00003	<0.00003	<0.00002
4-	0.00024	0.00011	<0.00002	2347-	<0.00003	<0.00003	<0.00002
total-	0.0067	0.0040	0.0014	1269-	<0.00003	<0.00003	<0.00002
13-DCDF	<0.00003	<0.00003	<0.00002	2378-	<0.00003	<0.00003	<0.00002
17-	<0.00003	<0.00003	<0.00002	2348-	0.014	0.014	0.00090
14-	<0.00003	<0.00003	<0.00002	2346-	0.0052	0.0050	0.0010
18-	<0.00003	<0.00003	<0.00002	2367-	<0.00003	<0.00003	<0.00002
16-	<0.00003	<0.00003	<0.00002	3467-	<0.00003	<0.00003	<0.00002
12-	<0.00003	<0.00003	<0.00002	1289-	<0.00003	<0.00003	<0.00002
24-	62	52	0.97	total-	2.6	2.3	0.38
37-	<0.00003	<0.00003	<0.00002	13468-PeCDF	0.0040	0.0039	0.00044
27-	<0.00003	<0.00003	<0.00002	12468-	0.18	0.17	0.017
23-	<0.00003	<0.00003	<0.00002	13678-	<0.00003	<0.00002	<0.00003
36-	<0.00003	0.0049	<0.00002	13479-	<0.00003	<0.00002	<0.00003
28-	<0.00003	<0.00003	<0.00002	12368-/13478-	0.0072	0.0053	0.00056
26-	<0.00003	<0.00003	<0.00002	12478-	0.0039	0.0039	<0.00003
19-	<0.00003	<0.00003	<0.00002	12479-/13467-	0.020	0.020	0.00037
34-	<0.00003	<0.00003	<0.00002	12467-	<0.00003	<0.00002	<0.00003
46-	<0.00003	0.0070	<0.00002	14678-/12347-	<0.00003	<0.00002	<0.00003
total-	62	52	0.97	12478-	0.0047	0.0048	<0.00003
137-TrCDF	<0.00003	<0.00003	<0.00002	12348-/12378-	0.012	0.011	0.00020
138-	<0.00003	<0.00003	<0.00002	12346-	0.00058	0.00061	<0.00003
136-	<0.00003	<0.00003	<0.00002	12379-	0.0014	0.0010	0.00024
134-	<0.00003	0.012	<0.00002	12367-	<0.00003	<0.00002	<0.00003
168-	<0.00003	<0.00003	<0.00002	12469-/12678-	0.00061	0.00071	0.000093
124-/147-/167-	<0.00003	0.0017	<0.00002	12679-	0.00072	0.00094	0.000082
178-/148-	<0.00003	0.0030	<0.00002	12369-	<0.00003	<0.00002	<0.00003
123-	<0.00003	<0.00003	<0.00002	23468-	0.25	0.22	0.040
127-	<0.00003	<0.00003	<0.00002	12369-	0.0017	0.0012	<0.00003
146-	0.34	0.31	0.00019	12489-	<0.00003	<0.00002	<0.00003
247-	0.023	<0.00003	<0.00002	23478-	0.0017	0.0016	0.00025
128-	<0.00003	<0.00003	<0.00002	12389-	<0.00003	<0.00002	<0.00003
126-	<0.00003	<0.00003	<0.00002	23467-	0.0031	0.0030	0.00053
248-	0.18	0.17	0.012	total-	0.49	0.45	0.059
246-	0.072	0.76	0.020	123468-HxCDF	0.073	0.068	0.0047
237-/149-	<0.00003	0.56	<0.00002	134678-/134679-	<0.00002	<0.00002	<0.00002
234-/238-	<0.00003	<0.00003	<0.00002	124678-	0.0061	0.0056	0.00072
347-/236-	<0.00003	<0.00003	0.00035	124679-	<0.00002	<0.00002	<0.00002
267-	<0.00003	0.045	0.0019	123478-/123479-	<0.00002	<0.00002	<0.00002
129-	<0.00003	<0.00003	<0.00002	123678-	0.00074	0.00072	0.00013
346-	<0.00003	<0.00003	<0.00002	124689-	0.0015	0.0014	0.00018
total-	0.62	1.9	0.034	123467-	<0.00002	<0.00002	<0.00002
1368-TeCDF	0.0056	0.015	0.00074	123679-	<0.00002	<0.00002	<0.00002
1378-/1379-	<0.00003	<0.00003	<0.00002	123469-/123689-	0.00023	0.00023	<0.00002
1347-	<0.00003	<0.00003	<0.00002	123789-	<0.00002	<0.00002	<0.00002
1468-	<0.00003	<0.00003	<0.00002	123489-	<0.00002	<0.00002	<0.00002
1247-/1367-	<0.00003	<0.00003	<0.00002	234678-	0.023	0.020	0.0027
1348-	<0.00003	<0.00003	<0.00002	total-	0.10	0.096	0.0084
1346-/1248-	<0.00003	<0.00003	<0.00002	1234678-HnCDF	0.0012	0.00098	0.00014
1246-/1268-	<0.00003	<0.00003	<0.00002	1234679-	<0.00001	<0.00001	<0.00002
1478-1369-/1237-	<0.00003	<0.00003	<0.00002	1234689-	0.00028	0.00031	<0.00002
1678-/1234-	<0.00003	<0.00003	<0.00002	1234789-	0.000024	0.000028	<0.00002
2468-/1238-/1467-/1236-	2.4	2.2	0.37	total-	0.0015	0.0013	0.00014
1349-	<0.00003	<0.00003	<0.00002	12346789-OCDF	<0.00014	<0.00014	<0.00022
1278-	<0.00003	<0.00003	<0.00002	total-PCDFs	66	57	1.4
1267-/1279-	<0.00003	<0.00003	<0.00002	PCDDs+PCDFs	5200	4800	740
1469-	<0.00003	<0.00003	<0.00002	TEQs	0.036	0.033	0.0034

Conclusion

We identified of the 83 isomers for mono- to octa-CDD/F in the three CNP formulations. Those isomer patterns were clearly different from "incineration pattern", therefore it is available we estimate the origin of PCDD/F in environmental samples. The total PCDD/F concentration and TEQs in three CNP samples decreased as their year of production became newer. Moreover we found variations in the ratio of predominance isomers for tetra- to hepta-CDD. On the other hand isomer distribution of all PCDF congener and mono- to tri-CDD didn't vary for the most part among samples with year of production.

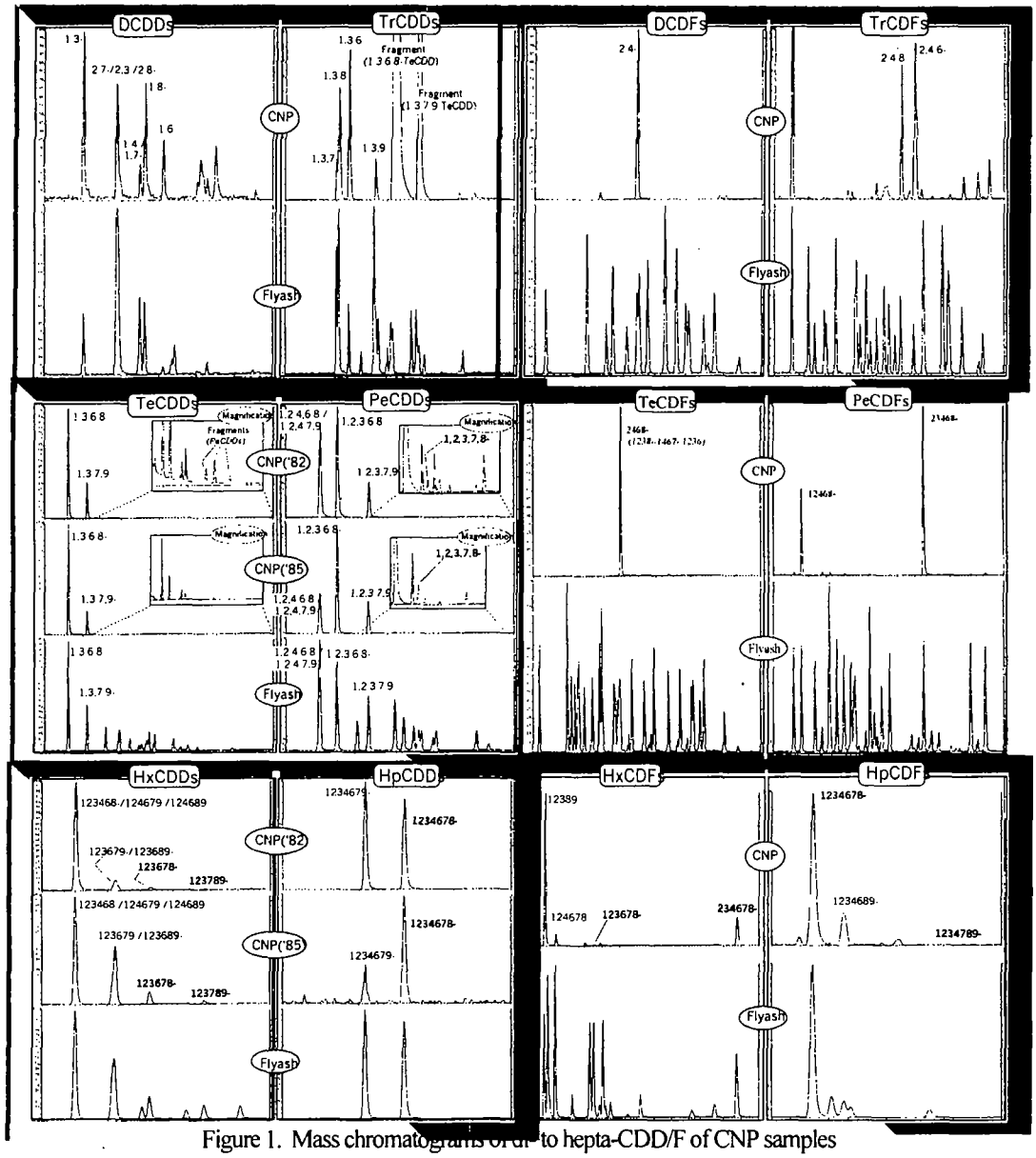

Figure 1. Mass chromatograms of di- to hepta-CDD/F of CNP samples
(Di- to Hexa-CDD/F: SP-2331 column, Hpta-CDD/F: HP-5MS column)

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