

### Dioxin Impurities in Old Japanese Agrochemical Formulations

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#### Introduction

The detailed analysis of dioxin congeners in environmental samples in Japan indicated that a significant portion of dioxins accumulated in soil and sediment originated from agrochemicals, especially pentachlorophenol and chloronitrofen (Masunaga *et al.*, 1998). However, little data have been published on the levels and characteristics of the dioxin impurities in these chemicals. Thus the estimation of the amount of dioxin emission into the environment in the past has been difficult. In this work, dioxin impurities in 15 agrochemicals are reported and amounts of dioxin emissions through these chemicals are estimated. The results indicate that annual emissions of dioxins from agrochemicals were far greater than that from combustion sources during the 1960s and 1970s.

#### Materials and Methods

**Agrochemicals:** We collected old agrochemical formulations from farms in the Kanto area in Japan. Some very old chemicals were found left unused in the corner of barns, which was very fortunate for our research purpose, although it is not a good practice for agrochemicals which were banned for safety reasons to be left unattended. Only the chemicals in original packagings were collected. The agrochemicals analyzed and their abbreviations are as follows: pentachlorophenol (PCP), 2,4,6-trichlorophenyl-4'-nitrophenyl ether (chloronitrofen, CNP), 2,4-dichlorophenyl-4'-nitrophenyl ether (nitrofen, NIP), tetrachloro-iso-phthalonitrile (chlorothalonil, TPN), 2-methyl-4-chloro-phenoxyacetic acid (MCP), and 2,4-dichlorophenoxyacetic acid (2,4-D).

**Analysis:** Different extraction procedures were adopted based on the characteristics of the formulations. Crude extracts of powder, granular and hydrate formulations (PCP, CNP, NIP, TPN and MCP) were prepared by Soxhlet extraction with dichloromethane for more than 8 hours and then they were transferred into a hexane solution. Emulsion formulations (CNP) were infiltrated into silica gel and eluted with hexane and then partitioned twice against 1N-KOH solution. The hexane layer was used as the crude extract. Liquid formulations (2,4-D) were partitioned twice with hexane and the hexane layer was taken as the crude extract.

Cleanup procedures were the same for all crude extracts. They were passed through a multilayered silica gel column (silica gel + 10%AgNO<sub>3</sub>/silica gel + silica gel + 22%H<sub>2</sub>SO<sub>4</sub>/silica gel + 44%H<sub>2</sub>SO<sub>4</sub>/silica gel + silica gel + 2%KOH/silica gel + silica gel). Before dioxin analysis, additional cleanup was performed with an activated-carbon column when required. The dioxins were analyzed by HRGC-HRMS (Shimadzu GC-14A-Shimadzu/Kratos CONCEPT32 type 1-S or HP6890GC-Micromass Autospec Ultima).

#### Results

The results of the analysis are shown in Table 1. PCP was extensively used as a paddy field

herbicide during the 1960s and the beginning of the 1970s. A total of about 170,000 tons of active ingredient were sprayed. The four samples analyzed in this study exhibited a wide range of dioxin impurity concentration from 8.7 to 11,000  $\mu\text{g/g}$  active ingredient, which almost covered the range of concentration reported over the world. The toxic equivalent values ranged between 170 and 14,000 ng I-TEQ/g (190 - 3,500 ng WHO-TEQ/g). The most abundant congeners were  $\text{O}_8\text{CDD}$ , 1,2,3,4,6,7,8- $\text{H}_7\text{CDD}$ ,  $\text{O}_8\text{CDF}$ , and 1,2,3,4,6,8,9- $\text{H}_7\text{CDF}$ .

As a replacement for PCP, CNP came into extensive use as a paddy field herbicide in Japan during the 1970s. The total dioxin concentration in five CNP samples decreased as their expiry date became newer. The date of production is generally three years prior to the expiry date on the label. Likewise, TEQ of CNP decreased, but at a much faster rate than the total dioxin concentration (Figure 1). There has been no report of 2,3,7,8-chlorine-substituted congeners being detected in CNP, and it is generally believed that only non-2,3,7,8-substituted congeners are present. This new finding came to light probably because fairly old samples were analyzed by modern analytical techniques. The CNP sample with the highest dioxin concentration was produced in around 1975, which coincides with the period when CNP was most extensively used in Japan. Some of the most abundant congeners in CNP were 1,3,6,8- $\text{T}_4\text{CDD}$ , 1,3,7,9- $\text{T}_4\text{CDD}$  and 1,2,3,6,8- $\text{P}_5\text{CDD}$ .

NIP has a molecular structure similar to that of CNP, however, its dioxin concentration was lower than that of CNP even though an old sample was analyzed. TPN has been used as a fungicide. Relatively old and relatively new TPN samples had similar levels of total dioxin and TEQ, indicating that dioxin concentrations in TPN have been low since the 1970s. A sample of MCP from the early 1970s had ng/g level of TEQ based on active ingredient. Two 2,4-D samples with relatively new expiry dates had very low total dioxin concentrations and virtually no TEQ.

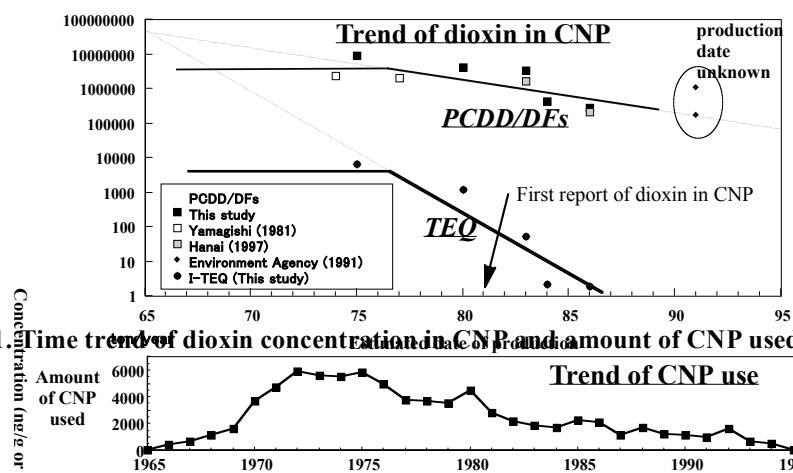


Figure 1. Time trend of dioxin concentration in CNP and amount of CNP used in Japan

### Discussion

Dioxin emission through agrochemicals: The amount of dioxin released into the environment through CNP use was estimated based on the data presented here. The time trend of dioxin concentration was assumed to follow the regression line drawn in Figure 1. We assumed that, before 1977, the dioxin concentration stayed at the same level as that in 1977 in order to avoid overestimation. The sum of the estimated emissions was about 200 ton PCDD/DFs or 190 kg

I-TEQ between 1965 and 1994. We could not obtain any typical time trend of dioxin concentration in the active ingredient for PCP. Since wide spread use of PCP in Japan was terminated at the beginning of the 1970s, it is probable that no attention was paid to its dioxin content during the period of its use. Thus, we calculated the emission based on the average concentrations of dioxin in PCP reported here and also by others (Buser & Bosshard, 1976; Rappe *et al.*, 1978; Rappe *et al.*, 1979; Hagenmaier & Brunner, 1987; Schecter *et al.*, 1997). The averages were around 740 µg/g for total dioxin and 2300 ng TEQ/g for I-TEQ. As the total amount of PCP used is about 170,000 tons of active ingredient, total dioxin emissions are estimated to be around 120 ton for total dioxin and 400 kg I-TEQ. Compared to these two herbicides, other agrochemicals contributed much less to dioxin emissions.

*Time trend of dioxin emission in Japan:* Based on the above estimate, dioxin emissions into the environment, especially agricultural land, were above 10 kg I-TEQ/year between 1961 and 1976 from PCP and CNP alone. The maximum annual emission was estimated to be nearly 40 kg I-TEQ/year. These amounts are greater than the recent national dioxin source inventories.

### Conclusions

The significance of dioxin emission through the past use of agrochemicals was studied by analyzing old formulations in Japan. Two herbicides, PCP and CNP, were found to be major sources in terms of both total dioxin and TEQ. Annual emissions to agricultural land from these two herbicides were above 10 kg I-TEQ/year during the 1960s and early 1970s. Further research needs to be conducted to survey how these dioxins have been circulating or accumulating and what effect they might have had or will continue to have.

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Table 1. Dioxin impurities in Japanese agrochemical formulations

Year of active ingredient	PCP 1967	PCP 1970	PCP 1971	PCP ?	CNP 1978	CNP 1983	CNP 1986	CNP 1987	CNP 1989	CNP 1969	NIP 1973	TPN 1993	MCP 1974	2,4-D 1996	2,4-D 1998
Manufacturer	NSD	I	I	KHC	M	S	S	S	S	TYC	KC	KC	NSC	I	NSC
Concentration in formulation	25%	13%	13%	25%	9%	20%	20%	20%	20%	7%	75%	50%	1.2%	50%	50%
<b>Concentration in formulation</b>															
TCDD	ng/g <50	<0.1	<1	2.5	<2	<15	<2	<0.4	<0.6	<0.01	<0.01	<0.01	<0.004	<0.01	<0.01
PCDD	ng/g <50	<0.1	<1	12	880	340	1.9	0.62	0.27	0.11	<0.01	<0.01	<0.004	<0.01	<0.01
-H6CDD	ng/g <50	1.5	7.3	160	25	28	<0.02	0.023	<0.02	<0.02	<0.02	<0.02	<0.004	<0.02	<0.02
-H6CDD	ng/g 860	2.6	140	8.3	530	300	65	0.54	1.4	0.061	0.064	0.058	0.0048	<0.02	<0.02
-H6CDD	ng/g 62	0.39	6.3	8.6	180	130	24	0.23	0.52	0.034	<0.02	<0.02	<0.004	<0.02	<0.02
3-H7CDD	ng/g 41,000	200	2,900	410	130	75	7.2	0.19	0.25	0.14	2.9	1.6	0.19	<0.02	<0.02
TCDF	ng/g 2,800,000	22,000	9,600	740	9.2	1.6	0.61	<0.05	0.083	9.1	140	84	21	0.079	<0.05
PCDF	ng/g <50	<0.1	<1	<0.1	11	<0.1	0.1	0.015	0.023	<0.01	<0.01	<0.01	<0.004	<0.01	<0.01
PCDF	ng/g <50	1.6	15	9.9	<0.1	<0.1	<0.01	0.038	0.078	0.039	<0.01	<0.01	<0.004	<0.01	<0.01
PCDF	ng/g <50	<0.1	1.3	3.4	69	<0.1	<0.01	0.04	0.029	0.037	<0.01	<0.01	<0.004	<0.01	<0.01
-H6CDF	ng/g 210	73	99	11	4.3	<0.1	<0.02	<0.02	<0.02	0.016	<0.02	0.042	<0.004	<0.02	<0.02
-H6CDF	ng/g 130	70	18	40	14	<0.1	5.5	0.027	0.16	0.021	<0.02	0.023	<0.004	<0.02	<0.02
-H6CDF	ng/g 220	28	22	26	800	250	2.8	0.27	0.28	0.033	<0.02	0.033	<0.004	<0.02	<0.02
-H6CDF	ng/g 120	<0.1	25	13	2	<0.1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.004	<0.02	<0.02
3-H7CDF	ng/g 2,700	290	890	68	19	9.8	0.42	<0.02	0.024	0.035	0.18	0.13	0.014	<0.02	<0.02
3-H7CDF	ng/g 600	190	200	16	0.24	0.2	0.024	<0.02	<0.02	<0.02	<0.02	<0.02	<0.004	<0.02	<0.02
3-H7CDF	ng/g 35,000	2,900	3,000	100	0.41	0.63	0.11	<0.05	<0.05	0.092	2.4	8.2	0.14	<0.05	<0.05
TEQ (ND=0)	ngTEQ/g 3400	49	86	43	630	240	11	0.44	0.39	0.10	0.18	0.13	0.024	<0.005	<0.005
TEQ (ND=0)	ngTEQ/g 890	27	74	48	1100	410	12	0.75	0.53	0.15	0.051	0.042	0.0046	<0.005	<0.005
TCDD	ng/g 3,400	550	12	7.2	520,000	730,000	650,000	87,000	55,000	360	1.9	0.64	3.4	0.014	0.21
PCDD	ng/g 610	26	<1	160	250,000	73,000	33,000	360	700	4.7	0.11	0.081	0.19	<0.01	<0.01
-H6CDD	ng/g 1,700	9.1	290	220	7,400	4,300	750	19	26	0.36	0.15	0.11	<0.02	<0.02	<0.02
-H6CDD	ng/g 48,000	240	4,000	450	160	88	12	0.31	0.42	0.2	3.6	1.9	0.27	<0.02	<0.02
3-H7CDD	ng/g 2,800,000	22,000	9,600	740	9.2	1.6	0.61	<0.05	0.083	9.1	140	84	21	0.079	<0.05
PCDFs	ng/g 2,900,000	23,000	14,000	1,600	780,000	810,000	680,000	87,000	56,000	370	150	87	25	0.093	0.21
PCDF	ng/g 170	<0.1	11	<0.1	17,000	22,000	1,400	100	140	520	0.027	0.046	0.054	0.95	0.016
PCDF	ng/g <50	15	40	13	7,600	4,700	240	5.8	7.5	9.2	<0.01	<0.01	0.016	0.78	<0.01
-H6CDF	ng/g 2,900	440	1,700	290	1,700	820	26	1.2	1.1	0.28	0.32	0.47	0.017	0.015	<0.02
-H6CDF	ng/g 17,000	1,700	5,100	190	26	12	0.65	<0.02	0.072	0.083	0.99	1.5	0.066	0.031	0.023
3-H7CDF	ng/g 35,000	2,900	3,000	100	0.41	0.63	0.11	<0.05	<0.05	0.092	2.4	8.2	0.14	<0.05	<0.05
TEQ (ND=0)	ngTEQ/g 55,000	5,100	9,900	590	26,000	28,000	1,700	110	150	530	3.7	10	0.29	1.8	0.039
TEQ (ND=0)	ngTEQ/g 3,000,000	28,000	24,000	2,200	810,000	840,000	680,000	87,000	56,000	900	150	97	25	1.9	0.25
<b>Concentration based on active ingredient</b>															
TEQ (ND=0)	ngTEQ/g 14,000	370	640	170	7,000	1,200	54	2.2	2.0	1.5	0.24	0.25	2.0	<0.01	<0.01
TEQ (ND=0)	ngTEQ/g 3,500	200	550	190	12,000	2,100	59	3.8	2.6	2.2	0.069	0.084	0.39	<0.01	<0.01
TCDDs	ng/g 11,000,000	170,000	100,000	6,400	8,700,000	4,100,000	3,400,000	440,000	280,000	5,400	200	170	2,100	0.19	0.42
PCDFs	ng/g 220,000	37,000	73,000	2,400	290,000	140,000	8,000	550	750	7,600	4.9	20	24	3.6	0.079
TEQ (ND=0)/DFs	ng/g 11,000,000	210,000	180,000	8,700	9,000,000	4,200,000	3,400,000	440,000	280,000	13,000	200	190	2,100	3.8	0.50