Toward a Time Trend Analysis of Dioxin Emissions and Exposure

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Abstract

Old agrochemical samples were analyzed for their dioxin impurities. Some herbicides were contaminated with 2,3,7,8-chlorine-substituted dioxin congeners. Using these new data as well as impurity and emission data reported in the literature, the time trends for dioxin emissions from the use of chlorinated aromatic compounds and some incineration activities have been estimated. The results indicate that dioxin emission was high during 1960s and 1970s and then decreased in terms of both amount of dioxin (PCDD/Fs) and toxic equivalent (TEQ). Herbicides were the major sources in the high emission period. After the mid-1980s, incineration sources became major. The order of importance in terms of total dioxin emission into the environment during the past 40 years is estimated to be chloronitrophen (CNP) > pentachlorophenol (PCP) > municipal solid waste incineration (MSWI) $\cong$ industrial waste incineration (IWI) in terms of PCDD/Fs and PCP > CNP > PCB > MSWI $\cong$ IWI in terms of I-TEQ.

1. Introduction

In the last workshop, we showed that a fairly large part of the dioxin pollution in aquatic sediment in Japan was caused by herbicides used in the past (Masunaga, 1998). In the case of Tokyo Bay in terms of the amount of PCDD/Fs (tetra- to octa-chlorinated dibenzo-p-dioxins and dibenzofurans), pentachlorophenol (PCP), chloronitrophen (CNP), and atmospheric deposition (assumed to be the sum of aerial emission sources from combustion) were estimated to contribute about 50, 8, and 8 percent, respectively, to the total amount of PCDD/Fs accumulated in bottom sediment during the past 35 years. Both PCP and CNP were widely used as herbicides in rice fields in the past. In terms of I-TEQ (International-TEQ), however, the contributions of the PCP

and CNP decreased to 31 and virtually zero percent, respectively, and that of atmospheric sources increased to 45%. Most of the dioxin impurities in herbicides were reported to be either non-2,3,7,8-chlorine-substituted congeners or 2,3,7,8-chlorine-substituted congeners with low toxic equivalency factor (TEF) values. Especially in the case of CNP, the presence of toxic 2,3,7,8-chlorine-substituted congeners has not been reported (Yamagishi *et al.*, 1981; Morita, 1991). Thus, the contributions of CNP to dioxin pollution in terms of TEQ have been believed to be negligible. Reports of dioxin impurities in Japanese agrochemicals, however, have been very limited. For example, there have been no reports on Japanese PCP formulation. Here, we report the dioxin impurities in fifteen Japanese agrochemical samples obtained from farmers' barns. Using these new data, we present a revised estimation of dioxin emissions in this country.

It has been often said that dioxin pollution in Japan is more severe than in other developed countries. On the other hand, the concentration of dioxins and co-PCBs in Japanese mothers' milk in terms of I-TEQ is reported to be decreasing during the last twenty years (Ministry of Health and Welfare, 1998a). The real cause of these phenomena must be clarified to evaluate the current situation and to propose appropriate countermeasures. We are currently analyzing sediment cores sampled from the Japanese coast and lakes and will try to estimate the contribution of different dioxin sources in the past and present based on the composition of different dioxin congeners. We hope that these results together with time trend estimation presented here will provide a much clearer view of the dioxin problem in this country as well as give some suggestions to other countries.

2. Dioxin impurities in Japanese agrochemical formulations

Agrochemical samples were collected from barns in the Kanto area. Fifteen (six different active ingredients, all chlorinated aromatic compound) were analyzed. Dioxin impurities were detected in all samples at various concentrations (Table 1). Results are as follows:
PCP: Four samples of PCP were analyzed. The dates of validity on the labels showed that three of the four were estimated to be produced between 1964 and 1968 and coincided with the middle of the period when PCP was used extensively in Japan. The concentrations of PCDD/Fs and I-TEQ varied by two orders of magnitude among samples.
CNP: Five CNP samples were analyzed. From the dates of validity, the dates of production were estimated to be between 1975 and 1986. The reported data on dioxins in CNP shows that all the 2,3,7,8-chlorine-substituted congeners were below detection limit (0.1 ppb) in these formulation (Morita, 1991), which corresponds to 1.4 ppb in active ingredients. In this study, however, 2,3,7,8-chlorine-substituted congeners were detected in all five samples, and TEQ ranged from 3.9 to 7,100 ng I-TEQ/g, meaning that toxic congeners in CNP cannot be ignored.
Nitrophen (NIP): One sample of NIP was analyzed. The 2,3,7,8-chlorine-substituted congeners were detected. To my knowledge, this is the first report of toxic congeners in NIP.
Tetrachloro-iso-phthalonitrile (TPN): TPN has been used as fungicide. The two samples

analyzed contained low concentrations of dioxins and had sub-ppb levels of TEQ.

2-Methyl-4-chloro-pehnoxyacetic acid (MCP): A fairly old MCP sample contained ng I-TEQ/g levels of dioxin.

2,4-Dichlorophenoxyacetic acid (2,4-D): Two relatively new 2,4-D samples had very low dioxin levels and had virtually no 2,3,7,8-chlorine-substituted congeners.

Table 1. Dioxin impurities in some agrochemicals

Chemical[1]	PCP	PCP	PCP	PCP	TPN	TPN	2,4-D	2,4-D
Date of validity[2]	1967.10	1970.10	1971.10	Unknown	1973.10	1993.10	1996.10	1998.10
Manufacturer	NSD	I	I	K	K	K	I	NSC
PCDDs [3]	11.4×10^6	168,000	32,600	6,300	194	173	0.22	0.42
PCDFs [3]	0.26×10^6	37,000	64,800	2,700	6.5	21	3.64	0.08
PCDD/Fs [3]	11.7×10^6	205,000	97,200	9,000	201	194	3.86	0.50
I-TEQ [4]	17,000	485	2,440	197	0.44	0.39	<0.005	<0.005
WHO-TEQ [4]	6,500	318	2,420	218	0.27	0.22	<0.005	<0.005
Major 2,3,7,8-congeners	OCDD, 1234678-HpCDD	OCDD, OCDF	1234678-HpCDD, OCDF	OCDD, 1234678-HpCDD	OCDD, 1234678-HpCDD	OCDD, OCDF	OCDD	ND

Chemical[1]	CNP	CNP	CNP	CNP	CNP	NIP	MCP
Date of validity[2]	1978.10	1983.10	1986.10	1987.10	1989.10	1969.10	1974.10
Manufacturer	M	S	S	S	S	TYC	NSC
PCDDs [3]	8.64×10^6	4.04×10^6	3.42×10^6	437,000	279,000	5,350	2,060
PCDFs [3]	0.28×10^6	0.14×10^6	0.01×10^6	736	744	7,710	27
PCDD/Fs [3]	8.92×10^6	4.18×10^6	3.43×10^6	438,000	279,000	13,100	2,090
I-TEQ [4]	7,100	1,280	62	3.9	4.9	1.5	2.1
WHO-TEQ [4]	12,000	2,130	67	5.4	5.6	2.2	0.54
Major 2,3,7,8-congeners	12378-PeCDD, 234678-HxCDF	12378-PeCDD, 123678-HxCDD	123678-HxCDD, 123789-HxCDD	12378-PeCDD, 2378-HxCDD	2378-TCDD, 123789-HxCDD	OCDD, 1234678-HpCDD	OCDD, OCDF

[1] PCP: pentachlorophenol, TPN: tetrachloro-iso-phthalonitrile, 2,4-D: 2,4-dichlorophenoxyacetic acid,
   CNP: chloronitrophen (2,4-dichlorophenyl-3'-methoxy-4'-nitorphenylether), NIP: nitrophen (2,4-dichlorophenyl-4-nitorphenylether), MCP: 2-methyl-4-chloro-phenoxyacetic acid.
[2] In general, date of production is three years prior to the date of validity.
[3] Concentrations are based on active ingredient (ng/g).
[4] Concentrations are based on active ingredient (ng I-TEQ/g or ng WHO-TEQ/g).

3. Time trends of dioxin emissions from chlorinated aromatic compounds in Japan

Using our new data as well as those found in the literature, the dioxin emission to the environment from chlorinated aromatic compounds was estimated.

PCP: A total of thirty-three PCDD/F and nine I-TEQ concentrations were found including the four reported in this study.   Our four data sets almost cover the range reported in the literature. The distribution of logarithms of PCDD/F concentration indicated that they belong to two different populations.   This is reasonable because two different manufacturing processes have

been used for PCP. As a target of the estimation is the total dioxin load and as we could not identify the production date for most of the data reported, we decided to use the arithmetic mean as an impurity factor. The factor was calculated to be 742 μg/g for PCDD/Fs and 970 ng/g for I-TEQ. Then the time trend of dioxin emission was estimated by multiplying the amount of herbicide used and an impurity factor. The results are summarized in Fig. 1. Emissions from 1955 to 1994 totaled to around 120 tons PCDD/Fs or 470 kg TEQ.
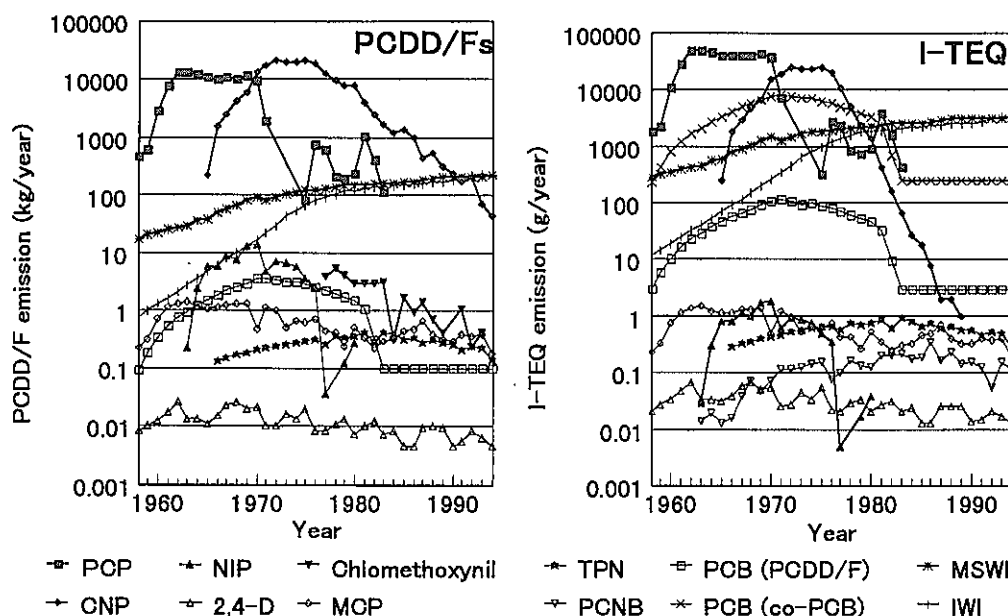

Fig. 1. Estimated time trends in PCDD/F and I-TEQ emissions from various sources in Japan

CNP: A total of 11 PCDD/F and 5 TEQ data sets for CNP were found including the five reported here. The dioxin concentrations decreased exponentially with the date of production estimated from the last date of validity. Thus, we assumed that the PCDD/F and TEQ emission factor for CNP depends on the date of production as shown in Fig. 2, and estimated the annual emission. We assumed the concentrations of impurities stay the same before 1977 (high end cut-off) to avoid an over estimation. Emissions from 1965 to 1994 totaled to about 200 tons PCDD/Fs or 190 kg TEQ, which is on the same order as PCP.

NIP: Three PCDD/F and one TEQ data sets on NIP were found including ours. Their arithmetic mean was used as impurity factor, and the annual emission was estimated. Emissions between 1963 and 1982 totaled to about 92 kg PCDD/Fs or 12 g TEQ.

Other agrochemicals: Using dioxin impurity data collected from the literature and by our analysis, dioxin emissions to the environment were estimated. They are summarized in Table 2 and Fig. 1.

PCBs (polychlorinated biphenyls): Over fifty thousand tons of PCBs was used in Japan from 1952 to 1972 as insulating fluid in electric appliances (69%), heat exchanger fluid (16%), pressure sensitive paper (10%) and open use (5%) (Isono, 1975). Their use was banned in 1972,
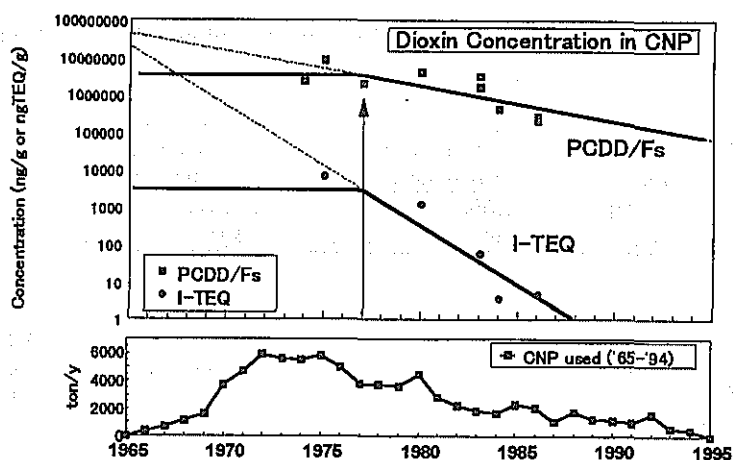
Fig. 2. Dioxin impurities and amount of CNP used in Japan

and PCB-containing wastes were order to be stored. Over twenty years of storage, some of them had been lost. PCB emission to the environment was estimated under the following scenario: Twenty percent of the PCBs in electric appliances went into the waste stream ten years after production and the remaining 80% was stored. Thirty percent of PCBs in heat exchangers went into the waste stream during ten years of use (3%/year). The remaining 70% was stored after ten years. Ninety percent of PCBs used in pressure sensitive papers went into waste stream in ten years and the remaining 10% was stored. Openly used PCBs were emitted to the environment 100% during their ten years of use. The stored PCB waste was lost and went into the waste stream at a rate of 0.35%/year based on the survey by Ministry of Health and Welfare (MHW) in 1992 (Environment Agency, 1997). Those PCBs that went into the waste stream may have been burned or discarded directly into the environment. Emission rates at this stage were assumed to be 10%; this is just a rough estimate used in the report of Environment Agency (EA) (Environment Agency, 1997), and no supporting data are available. The impurity factors for PCBs were calculated based on the reports by Wakimoto *et al.*, 1988 and Takasuga *et al.*, 1995. The calculated emission based on this scenario is shown in Fig. 1 and Table 2.

The relative importance among chlorinated aromatic compounds as a dioxin source is evident. PCP and CNP by far are the major emission sources of PCDD/Fs and TEQ.

3. Rough estimate of dioxin emission from industrial processes

In order to compare relative importance of chlorinated aromatic compounds as dioxin sources, a rough estimate of dioxin emission from incineration sources has been attempted.

Municipal solid waste incineration (MSWI): Dioxin concentrations in flue gas of MSWI facilities were recently measured nationwide (Ministry of Health and Welfare, 1998b).

Table 2. Estimation of dioxin emission from chlorinated organic compounds for the past 40 years in Japan

Chemical	Period of produc -tion or use	Total production or use [- 1995] (ton)	Impurity factor[1] Arithmetic mean (Range) No. of data		Estimated emission during the past 40 years		Source of data on impurity factor
			PCDD/Fs (μg/g)	I-TEQ (ng TEQ/g)	PCDD/Fs (kg)	I-TEQ (g TEQ)	
PCP	1955 - (1974)	175,700[3]	742 (5.36- 11,700) n=33	970 (84 - 167,00) n=9	120,000	470,000	This study Buser & Bosshard, 1976 Rappe et al., 1978a Rappe et al., 1979 Hamgenmaier & Brunner, 1987 Sechter et al., 1997
2,4,5-T	1965 - 1974	160[3,4]	1.25 (0.1 - 6.1) n=8	2,3,7,8-TCDD: 1,040 (ND - 6,100) n=29	0.20	976	Rappe et al., 1978b Norstrom et al.,1979 Smith & Pearce, 1986
NIP	1963 - 1982	7,465[3]	11.6 (10.3 - 13.0) n=3	1.53 n=1	92	12	This study Yamagishi et al., 1981
CNP	1965 - (1994)	82,359[3]	2,280 (213 - 8,920) n=11	1,690 (3.9 - 7,100) n=5	200,000 time trend estimation	190,000 time trend estimation	This study Yamagishi et al., 1981 Morita, 1991 Hanai, 1997
2,4-D	1950 - now	11,400[3]	0.045 (0.00050 - 0.124) n=5	0.114 (ND - 0.827) n=10	0.51	1.3	This study Morita, 1991 Schecter et al., 1997 Schecter et al., 1998.
chlorome- thoxynil	1973 - (1996)	15,226[3]	2.51 (0.53 - 6.3) n=3	No data available	34.5	No estimation available	Yamagishi et al., 1981 Morita, 1991
MCP	1953 - now	12,700[3]	2.09 n=1	2.03 n=1	26	26	This study
TPN	1965 - now	44,000[3]	0.20 (0.19 - 0.20) n=2	0.41 (0.39 - 0.44) n=2	8.8	18	This study
PCNB	1956- (1996)	28,000[3]	No data available	0.15	No estimation available	4.3	Environment Agency, 1998
PCB	1954 - 1972	57,300[2]	10.8[5]	PCDF: 330[5] co-PCB: 24,000[5]	50	PCDF: 1,500 co-PCB: 110,000	Wakimoto et al., 1988 Takasuga et al., 1995

[1] Based on active ingredient. PCDD/Fs: Total of tetra- to octa- chlorinated PCDDs and PCDFs.
[2] Environment Agency, 1998.
[3] Ministry of Agriculture, Forestry and Fisheries, 1980-1997.
[4] Uemura et al., 1988.
[5] Weighted average of Kanechlor 300, 400, 500 and 600 based on each production amount.

Arithmetic means for different treatment systems, namely batch, mechanical batch, semicontinuous, and continuous systems, were calculated. These values together with the time trend of waste incinerated and the capacity of different systems were used to estimate the trend of dioxin emissions from MSWI. The results are shown in Fig. 1. The total PCDD/Fs and TEQ emitted between 1955 and 1994 were estimated to be 4500 kg PCDD/F and 72 kg TEQ. These are probably conservative estimates because the installation of air pollution control devices must have been lower in the past.

Industrial waste incineration (IWI): There are no reliable statistics on industrial waste incineration in the past. Thus, we used the MHW's recent survey of industrial waste incineration and trends in number of IWI facilities to estimate the amount of industrial waste incinerated in the past (Ministry of Health and Welfare, 1997). The EA's recent report (Environment Agency, 1998) on emission factors in sludge and other industrial waste incineration was used to estimate emissions. The total PCDD/F and TEQ emissions between 1955 and 1994 were calculated to be 3600 kg PCDD/F and 55 kg TEQ, respectively. It should be noted that these values are very rough estimate.

4. Contributions from different dioxin sources

Estimated total dioxin emissions during the past 40 years from sources studied here are summarized in Fig. 3.
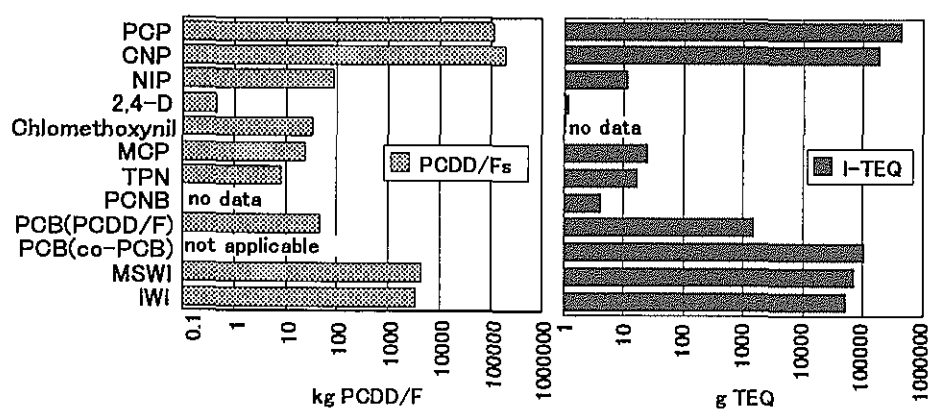

Fig. 3. Total dioxin emissions from different sources for the past 40 years in Japan

In terms of PCDD/Fs, it is certain that contributions of chlorinated aromatic compounds, especially PCP and CNP, are far larger than other sources. Similarly, PCP and CNP dominate as I-TEQ emission sources; however, contributions of MSWI and IWI are noted. As emissions from incinerators are estimated conservatively, they may contribute as much as half of the total emission. It should be also noted that I-TEQ from co-PCB in PCB formulations may be

significant.

5. Discussion

The time trends of dioxin emissions from different sources in Japan have been estimated. Other possible sources exist. For example, other industrial combustion sources have not been studied here, but they are probably not as significant as waste incineration processes. The estimation reported here is far from perfect; especially because the emission factors in the past are not available and emission factors measured recently have be used, which tends to lead to conservative estimate for the past. Nevertheless, the result here gives some new insights into the dioxin pollution problem.

Two kinds of herbicides, PCP and CNP, are the most significant sources of dioxin. We have already pointed this out at the last workshop (Masunaga, 1998). The origin of sediment contamination was estimated by statistical analysis based on congener composition. Although the change is small, revised results are shown in Fig. 4 using the new TEQ concentration data in CNP. The difference between the amount of emission and the amount accumulated in sediment is notable. It seems that atmospheric emission (combustion sources) can be accumulated in sediment more easily than herbicides which were applied to soil. Dioxin from the older herbicide, namely PCP, could also be found more than from the new herbicide, CNP. This indicates that a large part of the dioxin from CNP is still in agricultural fields. Another possible explanation of the discrepancy may be the shortcoming of using surface sediment to estimate the origin of dioxin for a longer period of time.

As for the time trends of dioxin emissions, the load was at a maximum during 1960s and 1970s and then decreased both in terms of PCDD/Fs and TEQ. Herbicides were the major sources during the maximum period, and after the mid-1980s, incineration sources became major.

We are currently analyzing the sediment cores which should provide information on the dioxin contamination in the aquatic environment. This will yield data on the trends in dioxin loads from different emission sources. Together with the trend in emissions presented here, we hope that this will present a clearer view of dioxin pollution in Japan over time.
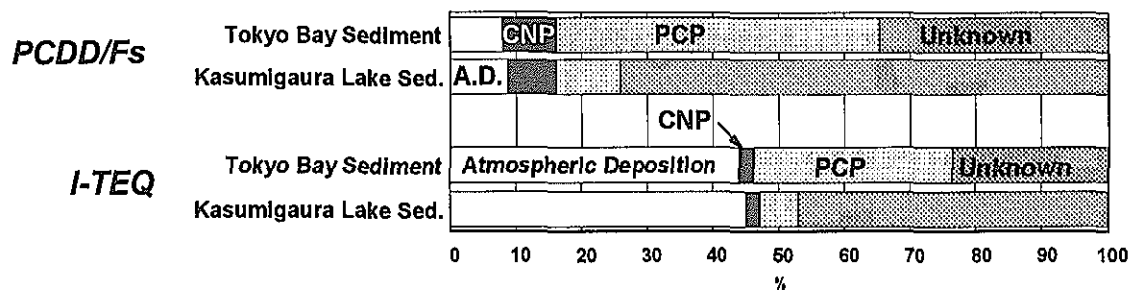

Fig. 4 Origin of dioxins sedimented in Tokyo Bay and Kasumigaura Lake for the past 35 years

6. Conclusion

Old agrochemical samples were analyzed for their dioxin impurities. The results showed that some herbicides were contaminated with 2,3,7,8-chlorine substituted dioxin congeners. Based on these new data as well as the impurity and emission data reported in the literature, time trends of dioxin emissions from chlorinated aromatic compounds and incineration processes have been estimated. The results indicate that dioxin emission was maximum during 1960s and 1970s and then decreased both in terms of PCDD/Fs and TEQ. Herbicides were the major sources in the maximum period whereas incineration sources became major after mid-1980s.

5. Acknowledgment

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