

Sources and Behavior of Dioxins in Japan

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Key Words: dioxins, polychlorinated dibenzo-*p*-dioxin (PCDD), polychlorinated dibenzofuran (PCDF), environmental behavior, source, mass balance, principle component analysis.

Abstract

Mass balances of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) during the past 35 years were estimated for the Tokyo Bay and Kasumigaura Lake basin based on detailed environmental analysis and past data on the use of chloroaromatic compounds. The major PCDD/F input to the basins was estimated to be from paddy-field herbicides and atmospheric deposition from combustion sources. However, sources of a considerable portion of the input remain unknown. Less than one percent of the PCDD/F entry to the basin as herbicide impurities was estimated to have accumulated in the bottom sediment of the two water bodies and the rest of the PCDD/Fs load most likely still remain in the soil in the fields. The direct atmospheric input to the water bodies, on the other hand, was equivalent to the amount accumulated in the sediment. The total amount of PCDD/Fs in the soil and in the sediment in the basin was estimated to correspond to hundreds of years of present atmospheric input.

1. Introduction

The problems caused by dioxin and its related compounds (dioxins) have been widely discussed in Japan since 1996, after number of soil and air pollution cases around municipal and industrial waste incineration plants were found. It is true that the percentage of waste incinerated in Japan is very high compared to other countries, but it must be clarified whether the level of present environmental dioxin pollution is really caused by waste incinerators. In this paper, the mass balance of dioxins in the Kanto region, Japan will be estimated and discussed based on the environmental monitoring data obtained in the present research project. The final goal of our analysis is to answer the following questions: (1) Is the proposed inventory of dioxin sources

consistent with the observed environmental pollution? (2) How have the dioxin sources and pollution changed during the past decades? (3) How effective will be the governmental plan of dioxin emission control from incinerators? Of course, it is difficult to satisfactorily answer these questions with such few observations and limited information, but the overall picture can be obtained based on bold assumptions.

2. Approach

One of the main features of this study is that non-2,3,7,8-chlorine substituted dibenzo-*p*-dioxin and dibenzofuran isomers as well as 2,3,7,8-substituted ones were quantified as precisely as possible in the environmental sample analysis. A detailed analysis requires much more energy and time than conventional procedures, but it provides far more information which can be used as an input to an extensive multivariate statistical analysis.

Japanese people consume much seafood, so sediment on sea and rivers beds is a very important environmental media because it transfers its pollutants to seafood consumers through the aquatic food chain. Sediment and soil are also conservative media for dioxins and they record the past pollution conditions. Thus, we selected sediment and soil as the objects of our analysis. Atmospheric deposition was also a focus of our analysis, since as a result of this process, dioxins are transferred from the incinerators to the aquatic and terrestrial environment. Incineration is considered to be one of the largest sources of dioxins.

In this study, the data regarding dioxin pollution in the conservative environmental media was analyzed in order to identify the contributions of different dioxin sources. Then the mass balances of dioxins were estimated based on both the atmospheric deposition measurement and the use of chlorinated chemicals in the study region.

3. Results and Discussion

3.1 Outline of dioxin monitoring results in the soil and sediment in the Kanto region

The isomer specific analysis of dioxins was carried out for sediments of Tokyo Bay and Kasumigaura Lake basin, paddy soil, and Tokyo urban soil samples (Sakurai *et al.*, 1998). The sampling points and some results of the analyses are shown in Figure 1. In general, the total concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) existed in the following order: marine sediments in the head of Tokyo Bay > lake sediments in Kasumigaura Lake > marine sediment at the entrance of Tokyo Bay > urban soil in Tokyo > paddy field soil > river sediment in Kasumigaura basin. This order was almost the same for the toxic equivalent (TEQ) concentrations, however, the ratios of TEQ/(Σ PCDD/Fs) showed some difference between sampling sites. The ratio of Σ PCDFs/(Σ PCDD/Fs) was higher in urban soil and Tokyo Bay sediment than in the Kasumigaura basin samples. The homologue profiles were relatively similar samples except for high tetrachlorodibenzo-*p*-dioxin (TCDD)

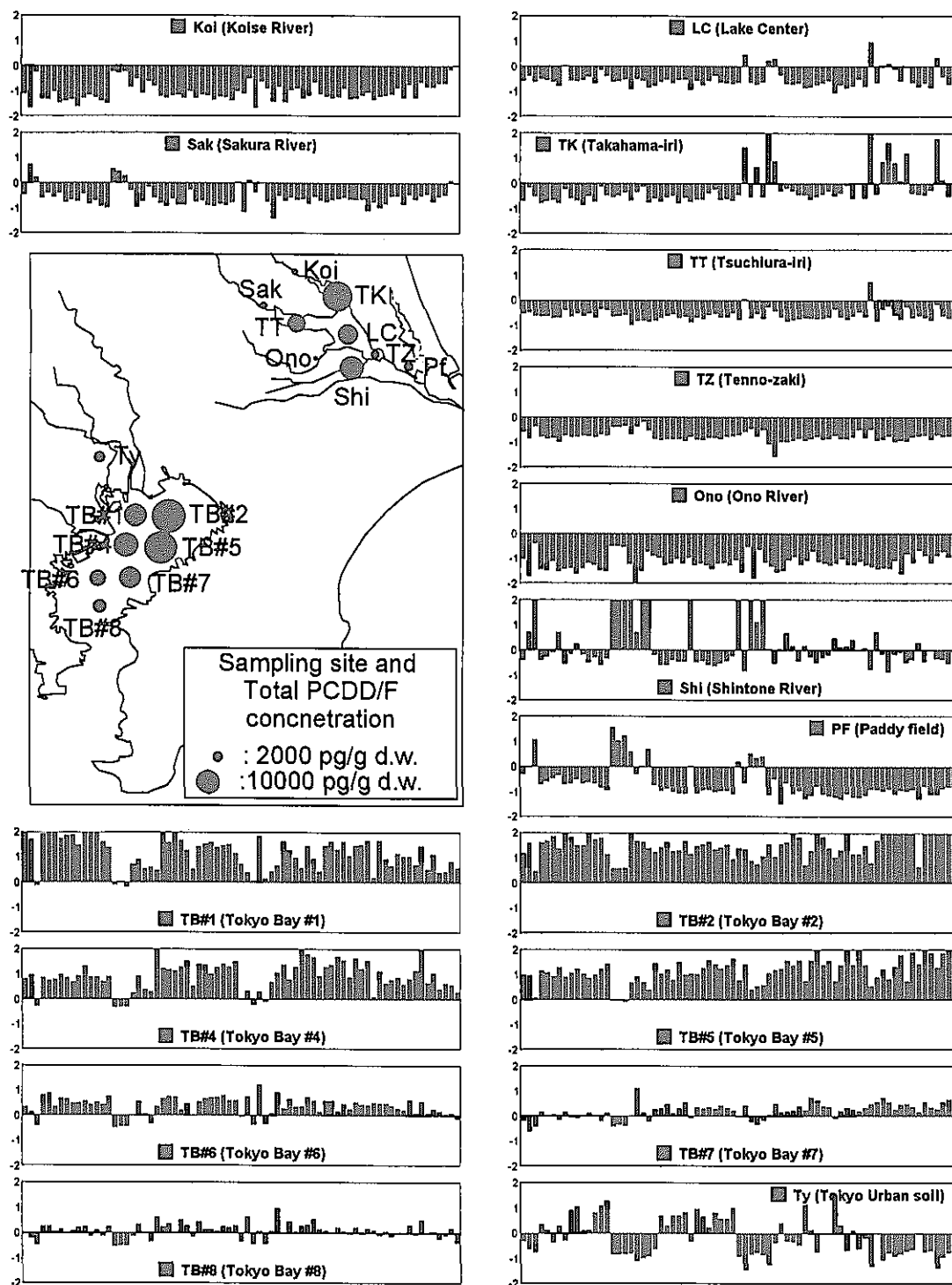


Figure 1 Location of sampling sites, total PCDD/F concentration and isomer profile

Tokyo Bay sediment: TB#1, TB#2, TB#4, TB#5, TB#6, TB#7, TB#8. Tokyo urban soil: Ty.
 Kasumigaura Lake sediment: LC, TK, TT, TZ. River sediment: Koi, Sak, Ono, Shi.
 Paddy field soil: Pf.

Graphs are PCDD/F isomer profiles for each site. The horizontal axis indicates the gas chromatographic peaks which correspond to one isomer or the sum of several isomers. The vertical axis indicates the normalized concentration (number of how many standard deviations away from the mean).

content in paddy-field soil and Shintone River sediment. The isomer profiles based on GC peaks are shown in Figure 1. These profiles are drawn using transformed data with variance normalized to unity for each peak among the samples. The samples from the same area, such as sediment of Tokyo Bay and that of Kasumigarua Lake, had similar isomer profiles.

3.2 Principle component analysis (PCA) of isomer profiles of soil and sediment samples

Many different processes and products such as combustion, chloroaromatic production, pulp and paper bleaching and chloroalkali processes, have been cited as the sources of dioxins, however, there is no reliable data on the relative importance and dioxin composition of these sources. Thus, principle component analysis, which does not require the source composition data, was applied to the isomer-specific data obtained in this project. Seventy-three gas chromatographic peaks (individual isomer or the sum of a few isomers) and 17 samples were considered as the variables and cases, respectively. The variance of each peak was normalized to unity and the obtained correlation matrix was used as an input for PCA. The details of the analysis and results are described by Sakurai *et al.* (1998). The results showed that four principle components (PCs) accounted for over 95% of the total variance (Table 1). The obtained PCs were interpreted by comparing their isomer compositions with the reported compositions of different dioxin sources. As a result of similarity to the isomer profile of atmospheric deposition monitored in the Kanto region (Ogura, 1998), PC-1 was attributed to atmospheric deposition. PC-2 could not be attributed due to the lack of reports on similar isomer profiles. Yamagishi *et al.* (1981) reported 1,3,6,8- and 1,3,7,9-TCDD and 2,4,6,8-tetrachlorodibenzofuran (TCDF) as the impurities of herbicide, 1,3,5-trichloro-2-(4-nitrophenoxy) benzene (CNP), which corresponded well with PC-3. PC-4 was attributed to the impurity of pentachlorophenol (PCP) based on the report by Hagenmaier & Brunner (1987).

Table 1 Results of the principle component analysis

PC	Contribution	Characteristic compounds ¹⁾	Origin attribution
PC-1	52 %	most of the tetra- to hexa-CDFs	atmospheric deposition
PC-2	17 %	penta- to hepta-CDDs with 1269-Cl substitution	unknown
PC-3	16 %	tetra- to penta-CDD/Fs, especially with 1368- or 1379-Cl substitution	CNP
PC-4	9 %	some of the hexa- to octa-CDD/Fs	PCP

1) Isomer or isomer-cluster peaks with high loading values ($r > 0.7$).

3.3 Potential dioxin sources in Japan

In order to confirm if CNP and PCP have been the primary dioxin sources in Japan, the dioxin load from different sources was estimated. Dioxins from combustion processes such as municipal, industrial and medical waste incineration, sewage-sludge incineration, electric power generation, iron manufacturing and from automobiles can be categorized into one large group of

atmospheric-dioxin-emitters. Thus the emission from this group can be represented by our atmospheric deposition monitoring. On the other hand, direct dioxin emission sources to soil and water bodies are the production and use of chloroaromatic compounds and pulp and paper bleaching. Among these, the sources considered to be important are listed in Table 2 and their dioxin inputs to the environment were estimated. Pulp and paper processes still remain to be studied.

The content of dioxins in pesticides varies depending on the manufacturer, production lot and year. The number of analyzed data reported is also limited. Thus, the estimated amount of dioxins formed as impurities of chloroaromatics are highly uncertain. For example, dioxin impurities in PCP have been reported relatively frequently, however, the difference between concentrations measured are over the order of two magnitudes and it is very difficult to estimate the average with this type of range. In spite of these uncertainties, the relative importance of these sources apparently does not seem to change and is estimated to be CNP > PCP > PCB. This supports our PCA results.

Table 2 Sources emitting dioxins to soil and water bodies over the past 30 - 40 years in Japan

Chemical or Process (use)	Period of production or use	Total production or use [up to 1994] (ton)	Σ PCDD/Fs concentration ¹⁾ [base on active ingredients] (ppm)	Σ PCDD/Fs formed (kg)	Characteristic PCDD/F composition
PCB (insulation oil, etc.)	1954 - 1981	57,300 ²⁾	1.4 - 38 ³⁾	80 - 2,177	PCDFs ¹⁰⁾
24-D (herbicide)	1950 - now	10,785 ^{3,4)}	PCDD: 0.02 - 1.752 ⁵⁾	0.22 - 19	1368/1379-TCDD, 2468-TCDF ¹⁰⁾
245-T (herbicide)	1965 - 1974	160 ^{3,4)}	2378-TCDD: <100 ⁵⁾	< 16	2378/1378-TCDD ¹⁰⁾
PCP (paddy field herbicide, etc.)	1955 - (1974)	175,700 ^{3,4)}	500 (5 - 1000) ⁷⁾	87,850 (880 - 176,000)	12468-PeCDF, HxCDD/Fs, HpCDD/Fs, OCDD/F ¹⁰⁾
nitrophen [NIP] (herbicide)	1963 - 1982	7,465 ^{3,4)}	10.3 & 11.4 ⁶⁾ (average=10.9)	81 (77 - 85)	?
CNP (paddy field herbicide)	1965 - (1994)	82,359 ^{3,4)}	2090, 2450 ⁶⁾ , 81.9, 513 ⁸⁾ , 209, 1730, 4850 ⁹⁾ (average=1700)	140,300 (17,200 - 202,000)	1368-TCDD, 1379-TCDD ⁶⁾
chlomethoxynil (paddy-field herbicide)	1973 - now	15,226 ^{3,4)}	6.3 ⁶⁾ , 0.53, 0.72 ⁸⁾ (average=2.52)	8.1 - 96	TCDFs ⁶⁾
pulp & paper bleaching					2378-TCDF/D, 12378-, 123789-HxCDD ¹⁰⁾

1) Total of tetra- to octa- chlorinated PCDD/Fs. 2) Environment Agency, 1988. 3) Ministry of Agriculture, 1980-1995. 4) Uemura *et al.*, 1988. 5) IARC, 1997. 6) Yamagishi *et al.*, 1981. 7) consulted with the following: IARC, 1997; USEPA, 1991; Morita, 1991. 8) Morita, 1991. 9) Sakurai & Hanai, 1997. 10) Evers *et al.*, 1993.

3.4 Contribution of different dioxin sources at each sampling point

The PC score at each sampling point could be derived from the PCA previously described, however, it only showed the deviation from the mean and did not represent the actual concentration. As PC-1 to -4 accounted for over 95% of the total contribution, it is safe to assume that contributions from sources other than these four were negligible. Thus, the contribution of the four sources were calculated by multiregression analyses (MRA) using the dioxin isomer profiles of atmospheric deposition (Ogura, 1998), CNP (Sakurai & Hanai, 1997) and PCP (Hagenmaier & Brunner, 1987) and that of PC-2 which was reconstructed by multiplying each variable with its standard deviation. The results of this MRA are shown in Table 3.

These results creates a different picture from the contributions obtained from PCA (Table 1) because PCA used normalized variables, whereas MRA used actual concentrations. The MRA results showed that atmospheric deposition was very important for urban soil and that CNP was important for paddy soil and river sediment, which are both very reasonable.

Table 3 Contribution of different dioxin sources at each sampling point

Samples Sources	TB#1	TB#2	TB#4	TB#5	TB#6	TB#7	TB#8	Ty
Atmos. Dep. ¹⁾	12.4	5.8	11.2	6.8	11.8	7.5	11.5	100.2
CNP	10.6	10.2	7.4	7.3	7.0	6.9	6.8	0.0
PCP	46.2	57.5	47.2	59.1	37.0	49.1	38.0	17.5
Unknown	30.8	26.5	34.2	26.8	44.2	36.6	43.8	-17.7

Samples Sources	LC	TK	TT	TZ	Koi	Sak	Ono	Shi	Pf
Atmos. Dep. ¹⁾	8.6	5.2	11.1	14.2	.9	8.0	9.4	5.9	6.5
CNP	7.2	5.7	8.0	26	24.4	38.9	25.1	57.8	60.3
PCP	9.1	14.9	9.0	11.4	20.9	27.0	23.9	12.2	2.2
Unknown	75.2	74.2	71.9	48.4	48.8	26.1	41.6	24.1	31.0

1) Atmospheric deposition.

3.5 Total amount of dioxins present in the sediment of Tokyo Bay and Kasumigaura Lake

The total amount of dioxins in Tokyo Bay and Kasumigaura Lake sediment will be calculated in this section. The sediment samples analyzed in this project were collected until 5 to 10 cm from the bottom surface using an Ekman Birge or an Smith McIntyre grab sampler. It has been reported that sediment mixing occurs down to 5 to 10 cm deep from the bottom surface in Tokyo Bay (Matsumoto, 1986). For Kasumigaura Lake, this value was down to 20 cm deep and this corresponded to about 40 years of sedimentation (Tanaka *et al.* 1991). Therefore, the sediment samples here were considered to be a mixture from the past ten years to a couple of decades of sedimentation. This means that the concentrations obtained here represent the majority of the period after the start of production of the chloroaromatic compounds listed in Table 2. The rate of sediment deposition measured in Tokyo Bay was in the range of 0.15 - 0.60

g/cm²/y (Matsumoto, 1983). The average rate for the entire bay was approximately 0.2 g/cm²/y. The rate of sediment deposition in Kasumigaura Lake was reported to be 5 - 15 mm/y and the volume of sediment was 4 - 10 ml/g dry sediment (Kasumigaura Lake Research Group, 1977). This corresponds to the average rate of 0.14 (0.05 - 0.38) g/cm²/y. The sedimentation masses for the past 35 years were calculated to be 70,000 and 49,000 ton/km² for Tokyo Bay and Kasumigaura Lake, respectively. These values, the dioxin concentration at each site, the representative area of each site and the contribution ratio of each dioxin source in Table 3 are used to calculate the total amount of dioxins accumulated in the bottom sediment during the past 35 years (Table 4).

Table 4 Dioxins in the sediment of Tokyo Bay and Kasumigaura Lake accumulated over the past 35 years

Sampling Site	Area km ²	Amount of Sediment 10 ⁶ ton	ΣPCDD/Fs Conc. pg/g dry sed.	Amount of ΣPCDD/Fs (kg)				
				Atmos. Dep. ¹⁾	CNP	PCP	Unknown	Total
TB#1	58	4.1	9,540	4.8	4.1	17.9	12.0	39
TB#2	194	13.6	20,300	16.1	28.0	158.2	72.9	275
TB#4	93	6.5	10,400	7.6	5.0	31.9	23.1	68
TB#5	155	10.8	18,200	13.5	14.4	116.6	52.9	197
TB#6	155	10.8	5,010	6.4	3.8	20.1	24.0	54
TB#7	116	8.1	8,470	5.1	4.7	33.8	25.2	69
TB#8	209	14.6	3,160	5.3	3.1	17.6	20.3	46
Tokyo Bay	980	68.6	10,912	58.8	63.2	396.3	230.3	749
LC	110	5.4	7,100	3.3	2.7	3.5	28.8	38.3
TK	27.5	1.3	15,800	1.1	1.2	3.2	15.8	21.3
TT	55	2.7	5,550	1.7	1.2	1.3	10.8	15.0
TZ	27.5	1.3	1,270	0.2	0.4	0.2	0.8	1.7
Kasumi. L.²⁾	220	10.8	7,071	6.3	5.6	8.2	56.2	76.2

1) Atmospheric deposition. 2) Kasumigaura Lake

3.6 Dioxin load to Tokyo Bay and Kasumigaura Lake basin

The dioxin loads in Japan from CNP and PCP are shown in Table 2. Their contributions to the two basins can be estimated by the ratio of paddy-field areas in the basin to that of the whole nation. The dioxin load from atmospheric deposition can be calculated using the monitoring data obtained in the Kanto region (Ogura, 1998) based on the assumption that the deposition rate has remained stable over the past 35 years. These estimations are shown in Table 5 together with the amounts of dioxins accumulated in the sediment.

As the degradation rates of dioxins are considered to be very small and almost all the dioxins are present as particulate fractions in water, it is reasonable to assume that most of the dioxins that entered into the two water bodies were conserved in the bottom sediment. Thus, the comparison of the amount entering the basin and the amount accumulated in the sediment is

noteworthy. For the both basins, the direct entries to the water bodies due to atmospheric deposition is comparable to the amount accumulated in the sediment. This indicates that most of dioxins deposited to terrestrial land are not transported to the water bodies. The run-off ratios of dioxin originating from CNP were around 1%. If this run-off ratio could be applicable to the terrestrial dioxin load from atmospheric deposition, the load to the water bodies and the amount accumulated in the sediment are well balanced for atmospheric deposition. As for the dioxins due to PCP in Tokyo Bay basin, the run-off ratio was unexpectedly large. A possible explanation for this could be the use of PCP other than herbicides. There are timber-ponds in the head of the bay and a direct dioxin entry to water from PCP used as wood preservative could have occurred.

Table 5. Dioxin load to Tokyo Bay and Kasumigaura Lake basin during the past 35 years

Source	Basic data (deposition rate / national load)	Directly to water body (kg)	To terrestrial basin (kg)	Accumulation in sediment (kg)	Run-off ratio (%)
Tokyo Bay basin : Percentage of national paddy field = 3.6%					
Atmos. Dep. ¹⁾	2 - 6 ng/m ² /d	25 - 75	155 - 466	59	
CNP	140,300 kg (17,200 - 202,000) kg	-	5100 (620 - 7300)	63	1.2 (0.87 - 10)
PCP	87,850 kg (880 - 176,000) kg	-	3200 (32 - 6300)	396	12% (6.3 - 1200)
Unknown				230	
Kasumigaura Lake basin : Percentage of national paddy field = 2.1%					
Atmos. Dep. ¹⁾	2 - 6 ng/m ² /d	5.6 - 16.8	50 - 149	6.3	
CNP	140,300 kg (17,200 - 202,000)kg	-	2900 (360 - 4200)	5.6	0.19 (0.13 - 1.6)
PCP	87,850 kg (880 - 176,000) kg	-	1800 (18 - 3700)	8.2	0.46 (0.22 - 46)
Unknown				56.2	

1) Atmospheric deposition.

3.7 Verification based on the monitoring data of source compounds

The PCB levels in Tokyo Bay were reported to be about 50ng/g-dry sediment in the central part of the bay and between 50 and 400 ng/g for most sections of the canals on the west side of the bay (Ogura *et al.*, 1997). As PCBs are considered to be as persistent as dioxins, the concentration of dioxins corresponding to the PCB levels can be estimated at 0.07~15pg/g dry sediment, which is less than 1% of the total dioxin level in Tokyo Bay sediment. This result confirmed that PCB was not the major source of dioxin pollution in Tokyo Bay.

Ono & Nakanishi (1987) reported the total CNP levels in Kasumigaura Lake sediment including transformation intermediate of amino derivatives to be between 27 and 210 ppb (average of about 40 ppb excluding the high values near the mouth of the river). The corresponding

dioxin concentration was calculated to be 5.6 - 514 (average of 68) pg/g, which is lower than the obtained dioxin concentration of 330 - 900 pg/g due to CNP. This is most likely because CNP has a faster degradation rate than dioxins. The half life of CNP in sediment was reported to be about 3 years (Ono & Nakanishi, 1987).

These two examinations do not contradict the dioxin mass balance calculations shown above.

4. Conclusions

The above examination of dioxin mass balances in the two basins can be summarized as shown in Figure 2. This is based on the assumption that the dioxin load from combustion processes has been at a similar level to now throughout the past 35 years. Compared to the amount of dioxin input from atmospheric deposition i.e. from incineration processes, a much larger amount of dioxins has been formed as pesticide impurities. Also, as pesticides are used in the open environment, almost all has been introduced into the terrestrial environment. It is reasonably assumed that most are still present in the agricultural soil. The percentage currently deposited in water bodies is less than a few percent but these chemicals will continue to flow into water bodies in the future. Another conclusion is that direct water input from atmospheric deposition is conserved in sediment and most of terrestrial input from the same is still in the soil.

The contribution of dioxins from unknown sources was fairly large especially in Kasumigaura Lake. This must be clarified before the whole picture of dioxin pollution can be obtained. In spite of this obscurity, the results of the present analysis showed that dioxins present in the aquatic environment are still largely influenced by past pesticide use. It is true that control of dioxin emission from incineration processes will reduce the dioxin exposure near these sources, but the reduction of exposure through the aquatic food chain may be far off.

It is worth noting that the present analysis was performed on the total amount of dioxin, not

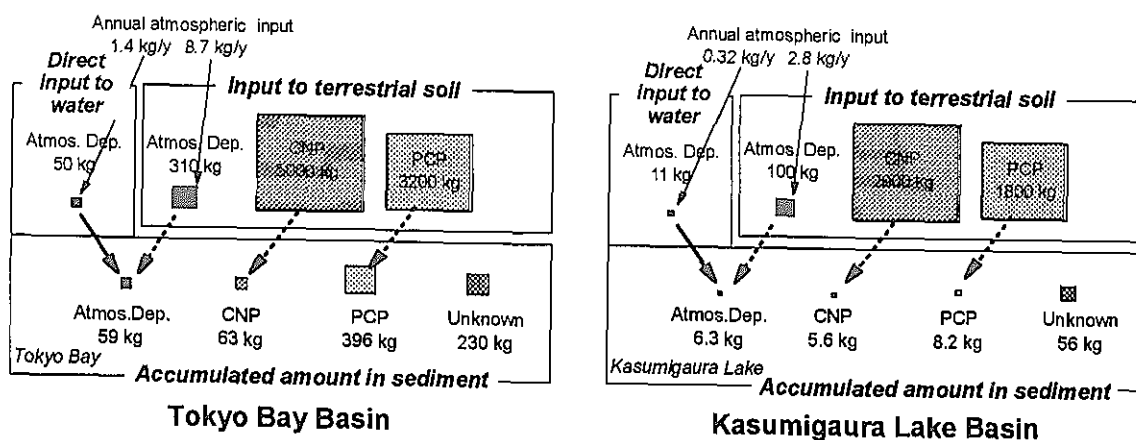


Figure 2 Dioxin mass balance in Tokyo Bay and Kasumigaura Lake basins, accumulated over the past 35 years

the TEQ amount. As CNP contains almost no 2,3,7,8-congeners and PCP contains mostly highly chlorinated congeners, a similar analysis based on TEQ may give quite a different picture.

The present results are based on insufficient data. If more reliable data, particularly on the dioxin impurity in chloroaromatics had been obtained and dated sediment had been analyzed, a more complete indication of the dioxin balance in Japan could have been obtained.

5. Acknowledgment

This work was supported by Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Corporation.

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