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The Removal of Dioxins and the Formation of 2, 3, 7, 8-TeCDF in Drinking Water Treatment in Japan

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정수처리에서의 다이옥신 제거 및 2, 3, 7, 8-TeCDF 생성

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Abstract

To evaluate homologue patterns and removal efficiency before and after water treatment, the concentrations of dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and coplanar polychlorinated biphenyls (Co-PCBs) were determined in 122 samples from 42 drinking water treatment plants throughout Japan over a two year period. The mean concentrations and toxic equivalent (TEQ) values of dioxins in raw and treated waters were 60.24 pg/L (0.14 pg-WHO-TEQ/L) and 4.15 pg/L (0.016 pg-WHO-TEQ/L), respectively. The dioxins contribution ratio of drinking water in relation to dioxins tolerable daily intake (TDI, 4 pg-TEQ/kg/day) was 0.016%. The mean TEQ removal rate of dioxins by drinking water treatment was over 88%. However, the mean removal rate of 2, 3, 7, 8-TeCDF (tetrachlorodibenzofuran) by water treatment in the 122 samples was minus 17%. Therefore, to identify which process affected the level of 2, 3, 7, 8-TeCDF, the removal efficiencies at both the advanced and conventional water treatment plants were investigated. For the TEQ removal rate across the processes, the dioxin congeners, TeCDF and non-ortho-PCBs remarkably indicated minus values after chlorination in both the advanced and conventional water treatments plant. From this study, the level of 2, 3, 7, 8-TeCDF was found to be increased as a result of chlorination.

keywords : Chlorination, Drinking water treatment, Poly chlorinated dibenzo-p-dioxins (PCDDs), Poly chlorinated dibenzo furans (PCDFs), 2,3,7,8-TeCDF

1. Introduction

Dioxins, furans and dioxin like compounds are formed as unwanted byproducts of various chemical and combustion processes (Rappe and Buser, 1989), and enter aquatic environments from the atmosphere (Czuczwa and Hites, 1984), agricultural chemicals (Masunaga et al., 2001; Sakurai et al., 1998) and as direct discharges from industrial sources, sewage treatment plants and storm water drains (Wenning et al., 1992).

PCDDs (poly chlorinated dibenzo-p-dioxins) and PCDFs (poly chlorinated dibenzo furans) have low solubilities in water, with the most toxic isomer of the former, 2, 3, 7, 8-tetra-CDD, reportedly having a water solubility limits of 20 ng/L at 22°C for dissolution from a thin film (Marple et al., 1986). As a consequence of their low water solubility, PCDDs/DFs in aquatic environments are primarily found in sediments and soils. There are many difficulties in detecting low levels of dioxins in drinking water. Therefore, only a few papers have reported the level of dioxins in source water and their removal efficiencies by water treatment. However, it is necessary to identify the levels and characteristics of PCDDs/DFs and Co-PCBs (coplanar polychlorinated biphenyls) in source waters both before and after treatment. The World Health Organization's (WHO) TDI (tolerable daily intake) of 1~4 pg-TEQ/kg/day is intended to represent a TDI for life time exposure with no adverse health consequences (WHO, 2001). Thus, it is also necessary to assess the contribution of dioxins in drinking water as a TDI.

Fortunately, with the help of scientific analytical methods and instrumentation improvement, these compounds are able to be detected at lower concentrations, especially in drinking water. A large volume "in situ" pre-concentration system, newly developed for tap water, was used to sample source and tap waters (Magara et al., 1999). This system enabled us to study the removal efficiency, homo-

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logue patterns and the characteristic of dioxins in the source water before and after treatments, such as coagulation, sand-filtration, ozonation, biological activated carbon (BAC) and chlorination.

On the basis of the above, this study focused on the followings:

1. Identification of the levels of PCDDs/DFs and Co-PCBs, both before and after water treatment, at nationwide drinking water treatment plants and the dioxins contribution ratio of drinking water in relation to dioxins tolerable daily intake.
2. Comparison of the dioxins removal efficiency and homologue patterns between advanced and conventional water treatments.
3. Identification of the drinking water treatment process affecting the level of 2, 3, 7, 8-TeCDF.

2. Materials and methods

2.1. Large volume "in situ" pre-concentration system

The system was constructed of electrolyze-mirror polish stainless steel (SUS), and enclosed in an air removal chamber (ARC), with a glass fiber filter (GFF) holder, polyurethane foam (PUF) holders, valves and sensors, with an external computer controller. The computer controls the needle valve based on information sent from the sensors. After completion of sampling, shut down valves mounted at the entrance and exit of the line are closed to protect the samples from contamination. Using this large volume (m^3) in situ pre-concentration system, the dioxins in the water samples are concentrated, and then passed through the ARC to remove air bubbles to prevent air from reaching the water-bypass in the GFF or PUFs. After the removal of air bubbles, the sample was passed through the GFF (300 mm ID, 0.5 μm pore size), PUF (100 mm ID, 100 mm height) and back-up PUF (100 mm ID, 100 mm height). A flow rate sensor monitors the flow rate of sample, which was maintained at a constant rate of 1~2 L /min.

2.2. Sampling

2.2.1. 42 water treatment plants throughout the nation

During the first year of this study, 2000, raw (200 L) and chlorine treated waters (2000 L) were collected on two occasions, in July and November, from each of the 42 water treatment plants. In the second year of study, 2001, 19 out of the 42 water treatment plants were selected, with samples collected utilizing the same methods as previously employed. The sampling sites have been described in a previous report (Kim et al., 2002).

2.2.2. Advanced water treatment plant (Tamagwa pilot-plant process)

Raw (500 L), coagulated and sedimented (1200 L), sand-filtered (4000 L), ozonated (4000 L), BAC-filtered (4000 L) and chlorine treated waters (4000 L) were sampled from the Tamagawa water treatment pilot-plant, which has a capacity of 500 m^3 per day. The sampling was performed during December 2000. The Tamagawa water treatment pilot-plant is located along the main stream of the Tamagaea River, which flows through Tokyo, Japan.

2.2.3. Conventional water treatment plant (AY water plant)

Samples of raw (500 L), coagulated and sedimented (1200 L) and chlorine treated waters after sand filtration (4000 L) were collected, during April 2001, from the AY water treatment plant, located on the northern part of Japan.

2.3. Analysis

Analyses of the PCDDs/DFs and Co-PCBs generally followed the previously described method (Kim et al., 2002). Briefly, for the analyses of dioxins, after soxhlet extraction and gel clean-up procedures, high resolution gas chromatograph (HRGC, Hewlett Packard6890), coupled to a high resolution mass spectrometer (HRMS, Auto-Spec, Micromass), was used. BPX-5 (60 m length, 0.25 mm ID, 0.25 μm film thickness, SGE, Australia) and BPX-50 (60 m length, 0.25 mm ID, 0.25 μm film thickness, SGE, Australia) were used for TeCDDs-OCDD (tetrachloro & octachloro dibenzo-p-dioxins), TeCDFs-OCDF (tetrachloro & octachloro dibenzofurans) and Co-PCBs and for PeCDFs (pentachloro dibenzofurans) and HxCDFs (hexachloro dibenzofurans), respectively. Residual blanks were analyzed to check for interference or contamination arising from the solvents or glassware. The TEF (toxic equivalent factor) value established by WHO in 1998 was applied to the above compounds to find the TEQ value.

3. Results and discussion

3.1. Dioxin levels and homologue patterns before water treatment

3.1.1. In 122 sampling sites of 42 water treatment plants throughout the nation

The average dioxins concentrations are shown in Table 1. The average levels of PCDDs, PCDFs and Co-PCBs in raw water were 43.50 (0.076 pg-TEQ/L), 4.45 (0.057 pg-TEQ/L) and 12.29 pg/L (0.0089 pg-TEQ/L), respectively. This survey found that the highest and lowest concentrations of total dioxins were 540 (0.99 pg-TEQ/L) and 0.60 pg/L (4.5×10^{-5} pg-TEQ/L), respectively, in the raw

water. The average level of total dioxins was 60.24 pg/L (0.14 pg-TEQ/L) in raw water (Table 2). PCDDs/DFs and Co-PCBs were detected in 99 samples at levels less than 100 pg/L, and in 21 samples at levels between 100 and 300 pg/L. 2 samples were between 300 and 540 pg/L. In terms of TEQ representation, the levels of TEQ at 12 sampling sites were below 0.01 pg-TEQ/L, while the levels of TEQ at 58 sampling sites ranged between 0.01 and 0.1 pg-TEQ/L. At 48 sampling sites the concentrations ranged between 0.1 and 0.5 pg-TEQ/L, and at 4 between 0.5 and 1.0 pg-TEQ/L.

With respect to the distribution of dioxins, as shown in Table 1, the total PCDDs to total dioxins were 72 (43.50 pg/L) and 54% (0.076 pg-TEQ/L). The isomer distributions for PCDDs in descending order were: OCDD (43%, 25.72 pg/L), 1, 3, 6, 8-TeCDD (14%, 8.26 pg/L) and 1, 3, 7, 9-TeCDD (4%, 2.59 pg/L). However, the isomer distribution in terms of pg-TEQ/L changed sharply, as follows: 1, 2,

Table 1. Mean concentration levels of dioxins before and after water treatment in 122 samples from 42 water treatment plants

	Method detection limit		Water before treatment (raw water)		Water after treatment (treated water)	
	Raw water pg/L	Treated water pg/L	pg/L	pg-TEQ/L	pg/L	pg-TEQ/L
1,3,6,8,-TeCDD	0.002	0.0002	8.260	-	1.020	-
1,3,7,9-TeCDD	0.002	0.0002	2.590	-	0.240	-
2,3,7,8-TeCDD	0.002	0.0002	0.008	0.008	0.0008	0.0008
TeCDDs	-	-	11.520	0.008	1.330	0.0008
1,2,3,7,8-PeCDD	0.003	0.0003	0.030	0.030	0.0016	0.0016
PeCDDs	-	-	1.840	0.030	0.1055	0.0016
1,2,3,4,7,8-HxCDD	0.003	0.0003	0.040	0.004	0.0014	0.00014
1,2,3,6,7,8-HxCDD	0.003	0.0003	0.081	0.0081	0.0028	0.00028
1,2,3,7,8,9-HxCDD	0.003	0.0003	0.074	0.0074	0.0019	0.00019
HxCDDs	-	-	1.082	0.020	0.048	0.00061
1,2,3,4,6,7,8-HpCDD	0.004	0.0004	1.520	0.015	0.022	0.00022
HpCDDs	-	-	3.340	0.015	0.050	0.00022
OCDD	0.003	0.0003	25.72	0.0026	0.130	1.3E-05
Total PCDDs	-	-	43.502	0.076	1.664	0.0032
1,2,7,8-TeCDF	0.002	0.0002	0.075	-	0.075	-
2,3,7,8-TeCDF	0.002	0.0002	0.071	0.0071	0.083	0.0083
TeCDFs	-	-	1.130	0.0071	0.390	0.0083
1,2,3,7,8-PeCDF	0.004	0.0004	0.030	0.0015	0.0061	0.00031
2,3,4,7,8-PeCDF	0.004	0.0004	0.041	0.020	0.0056	0.0028
PeCDFs	-	-	0.730	0.022	0.066	0.0031
1,2,3,4,7,8-HxCDF	0.003	0.0003	0.066	0.0066	0.003	0.0003
1,2,3,6,7,8-HxCDF	0.003	0.0003	0.057	0.0057	0.0019	0.00019
1,2,3,7,8,9-HxCDF	0.003	0.0003	0.011	0.0011	0.0006	6.3E-05
2,3,4,6,7,8-HxCDF	0.003	0.0003	0.096	0.0096	0.0029	0.00029
HxCDFs	-	-	0.780	0.023	0.025	0.00084
1,2,3,4,6,7,8-HpCDF	0.004	0.0004	0.400	0.004	0.0055	5.5-05
1,2,3,4,7,8,9-HpCDF	0.004	0.0006	0.070	0.0007	0.0009	9.0E-06
HpCDFs	-	-	0.930	0.0047	0.010	6.4E-05
OCDF	0.005	0.0005	0.880	9.0E-05	0.0034	3.4E-07
Total PCDFs	-	-	4.450	0.057	0.494	0.012

Total PCDDs (resp. total PCDFs) are the sum of tetra to octa CDD (resp. sum of tetra to octa CDF)

Table 2. Levels of dioxins before and after water treatment in 122 samples from 42 water treatment plants

	Measured value (pg/L)		TEQ value (pg-TEQ/L)	
	Raw water	Treated water	Raw water	Treated water
Maximum value	540.00	25.52	0.99	0.54
Minimum value	0.60	0.097	4.5×10-5	4.9×10-6
Average value	60.24	4.14	0.14	0.016
Removal rate	93%		88%	

3, 7, 8-PeCDD (21%, 0.030 pg-TEQ/L), 1, 2, 3, 6, 7, 8-HxCDD (6%, 0.0081 pg-TEQ/L) and OCDD (2%, 0.0026 pg-TEQ/L). The most toxic isomers, 2, 3, 7, 8-TeCDD and 1, 2, 3, 7, 8-PeCDD, were present at levels of 5 (0.008 pg-TEQ/L) and 21% (0.030 pg-TEQ/L), respectively. The reason 1, 2, 3, 7, 8-PeCDD contained a high portion of dioxins is because the 1998 WHO TEF value (1.0 for 1,2,3,7,8-PeCDD) was adopted. As the concentration of PCDDs changed in TEQ value, the TEQ contribution of PCDFs increased sharply from 7 (4.45 pg/L) to 41% (0.057 pg-TEQ/L). 2, 3, 4, 7, 8-PeCDF (14%, 0.020 pg-TEQ/L) was most predominant. The total Co-PCBs were 20 (12.29 pg/L) and 6% (0.0089 pg-TEQ/L).

3.1.2. In advanced water treatment plant (T pilot-plant process)

As shown in Tables 3 and 4, the dioxin levels at each treatment step were 18.86 pg/L (0.045 pg-TEQ/L) in raw, 11.27 pg/L (0.025 pg-TEQ/L) in coagulated, 3.29 pg/L (0.0036 pg-TEQ/L) in sand-filtered, 1.34 pg/L (0.0020 pg-TEQ/L) in ozonated, 0.10 pg/L (0.00010 pg-TEQ/L) in BAC treated and 0.12 pg/L (0.00013 pg-TEQ/L) in chlorine treated water. In raw water treatment step, the ratio of mono-ortho-PCBs concentration was 58%, with those of TeCDDs and OCDD being 12 and 11%, respectively. The levels of PCDFs I the raw water were much lower than those of PCDDs and Co-PCBs. Coagulated water showed the same homologue patterns to those shown in the raw water at the 60% level. Most dioxins were removed after coagulation and sand-filtration, with those remaining almost totally removed by ozonation and BAC adsorption. Conversely, the concentration of dioxins after chlorination was slightly increased.

As for congeners within the pg/L range in raw water, TeCDDs and TeCDFs accounted for the greatest proportion

Table 3. Concentrations of PCDD/DFs (pg/L) in advanced drinking water treatment processes

	Raw water	Coagulated water	Sand-filtered water	Ozonated water	BAC treated water	Chlorinated water
1,3,6,8-TeCDD	0.410	0.350	0.092	0.022	0.0072	0.0074
1,3,7,9-TeCDD	0.140	0.120	0.025	0.006	0.0027	0.0029
2,3,7,8-TeCDD	N.D.	N.D.	N.D.	0.0002	N.D.	N.D.
TeCDDs	2.200	1.600	0.540	0.081	0.016	0.017
1,2,3,7,8-PeCDD	0.008	0.006	0.0007	0.0004	N.D.	N.D.
PeCDDs	0.300	0.220	0.040	0.016	0.0040	0.0043
1,2,3,4,7,8-HxCDD	0.010	0.004	N.D.	N.D.	N.D.	N.D.
1,2,3,6,7,8-HxCDD	0.015	0.008	N.D.	N.D.	N.D.	N.D.
1,2,3,7,8,9-HxCDD	0.012	0.005	N.D.	N.D.	N.D.	N.D.
HxCDDs	0.240	0.130	0.009	0.005	0.0011	0.0012
1,2,3,4,6,7,8-HpCDD	0.200	0.079	0.003	0.002	0.0009	0.0010
HpCDDs	0.410	0.170	0.006	0.006	0.0024	0.0022
OCDD	2.100	0.720	0.021	0.023	0.0073	0.0067
Total PCDDs	5.250	2.840	0.616	0.131	0.031	0.031
1,2,7,8-TeCDF	0.024	0.015	0.003	0.001	0.0003	0.0004
2,3,7,8-TeCDF	0.019	0.012	0.004	0.0015	0.0003	0.0004
TeCDFs	0.600	0.400	0.150	0.063	0.0045	0.0051
1,2,3,7,8-PeCDF	0.013	0.008	0.0009	0.0005	N.D.	N.D.
2,3,4,7,8-PeCDF	0.020	0.010	0.0018	0.0008	N.D.	N.D.
PeCDFs	0.400	0.220	0.041	0.037	0.0033	0.0035
1,2,3,4,7,8-HxCDF	0.021	0.011	0.0008	0.0004	N.D.	N.D.
1,2,3,6,7,8-HxCDF	0.022	0.012	0.0008	0.0005	N.D.	N.D.
1,2,3,7,8,9-HxCDF	0.0037	0.0008	N.D.	N.D.	N.D.	N.D.
2,3,4,6,7,8-HxCDF	0.042	0.020	0.0014	0.0013	0.0002	0.0003
HxCDFs	0.300	0.140	0.010	0.0086	0.0009	0.0020
1,2,3,4,6,7,8-HpCDF	0.110	0.050	0.0015	0.0013	N.D.	N.D.
1,2,3,4,7,8,9-HpCDF	0.019	0.009	N.D.	N.D.	N.D.	N.D.
HpCDFs	0.220	0.093	0.003	0.0024	0.00060	0.0005
OCDF	0.140	0.053	N.D.	N.D.	N.D.	N.D.
Total PCDFs	1.660	0.906	0.204	0.111	0.009	0.011

Total PCDDs (resp. total PCDFs) are the sum of tetra to octa CDD (resp. sum of tetra to octa CDF)
N.D.: Not Detected

Table 4. TEQ Concentrations of PCDD/DFs (pg-TEQ/L) in advanced drinking water treatment processes

	Raw water	Coagulated water	Sand-filtered water	Ozonated water	BAC treated water	Chlorinated water
2,3,7,8-TeCDD	N.D.	N.D.	N.D.	0.0002	N.D.	N.D.
TeCDDs	N.D.	N.D.	N.D.	0.0002	N.D.	N.D.
1,2,3,7,8-PeCDD	0.0080	0.0060	0.0007	0.0004	N.D.	N.D.
PeCDDs	0.0080	0.0060	0.0007	0.0004	N.D.	N.D.
1,2,3,4,7,8-HxCDD	0.0010	0.0004	N.D.	N.D.	N.D.	N.D.
1,2,3,6,7,8-HxCDD	0.0015	0.0008	N.D.	N.D.	N.D.	N.D.
1,2,3,7,8,9-HxCDD	0.0012	0.0005	N.D.	N.D.	N.D.	N.D.
HxCDDs	0.0037	0.0017	N.D.	N.D.	N.D.	N.D.
1,2,3,4,6,7,8-HpCDD	0.0021	0.00079	N.D.	2.3E-05	9.0E-06	1.0E-05
HpCDDs	0.0021	0.00079	2.5E-5	2.3E-05	9.0E-06	1.0E-05
OCDD	0.00021	0.000072	2.1E-06	2.3E-06	7.3E-07	6.7E-07
Total PCDDs	0.0140	0.0086	0.00073	0.00063	9.7E-06	1.1E-05
2,3,7,8-TeCDF	0.0019	0.0012	0.0004	0.00015	3.0E-05	4.0E-05
TeCDFs	0.0019	0.0012	0.0004	0.00015	3.0E-05	4.0E-05
1,2,3,7,8-PeCDF	0.00065	0.00039	4.5E-05	2.5E-05	N.D.	N.D.
2,3,4,7,8-PeCDF	0.0103	0.0054	0.0009	0.00040	N.D.	N.D.
PeCDFs	0.0110	0.0058	0.00095	0.00043	N.D.	N.D.
1,2,3,4,7,8-HxCDF	0.0021	0.0011	8.0E-05	4.0E-05	N.D.	N.D.
1,2,3,6,7,8-HxCDF	0.0022	0.0012	8.0E-05	5.0E-05	N.D.	N.D.
1,2,3,7,8,9-HxCDF	0.00037	0.00008	N.D.	N.D.	N.D.	N.D.
2,3,4,6,7,8-HxCDF	0.0041	0.0020	0.00014	0.00013	2.0E-05	3.0E-05
HxCDFs	0.0088	0.0044	0.0003	0.00022	2.0E-05	3.0E-05
1,2,3,4,6,7,8-HpCDF	0.0011	0.0005	1.5E-05	1.3E-05	3.0E-06	3.0E-06
1,2,3,4,7,8,9-HpCDF	0.00019	0.00009	N.D.	N.D.	N.D.	N.D.
HpCDFs	0.0013	0.00059	1.5E-05	1.3E-05	3.0E-06	3.0E-06
OCDF	1.4E-05	5.3E-06	N.D.	N.D.	N.D.	N.D.
Total PCDFs	0.0230	0.0120	0.0017	0.00081	5.3E-05	7.3E-05

Total PCDDs (resp. total PCDFs) are the sum of tetra to octa CDD (resp. sum of tetra to octa CDF)
N.D.: Not Detected

of PCDDs/DFs, but the most toxic, 2, 3, 7, 8- TCDD, was not detected. The dominant fraction in raw water was Co-PCBs (63%), which was found in the pg/L range, but with respect to the TEQ value, the fraction was greatly changed; for example PCDFs (52%), which increased from 9 (measured value, pg/L) to 52% (TEQ value, pg-TEQ/L); with PCDDs (31%) and Co-PCBs (17%) also present. In addition, the PCDFs after BAC adsorption and chlorination accounted for 80 and 70% of the total dioxins, respectively.

3.1.3. In conventional water treatment plant (AY water plant)

As shown in Table 5, the dioxin levels at each step were 183.25 pg/L (0.28 pg-TEQ/L) in raw, 11.66 pg/L (0.019 pg-TEQ/L) in coagulated and 4.51 pg/L (0.0077 pg-TEQ/L) in chlorine treated water. The concentrations in raw water were found to be three times higher than the average concentration found at the 122 sampling sites of the 42 water plants. However, after chlorine treatment, the total dioxins levels were similar to the average concentrations found at the 122 sampling sites.

The isomer distributions to total dioxins in raw water were high; in the order: OCDD (71%, 130.00 pg/L), 1, 3, 6, 8-TeCDD (9%, 16.00 pg/L) and 1, 3, 7, 9-TeCDD (3%, 5.50 pg/L). These three isomers were dominant in all of the raw, coagulated and chlorinated waters. These specific isomers have been reported as the major by-products of herbicides, PCP and CNP (Masunaga et al., 2001). The AY area, located in Niigata, is a major agricultural area within Japan, and our results support the findings from previous studies.

3.2 Dioxin levels and homologue patterns after water treatment in 122 sampling sites of 42 water treatment plants throughout the nation

The average levels of PCDDs, PCDFs and Co-PCBS in treated water were 1.66 pg/L (0.0032 pg-TEQ/L), 0.49 pg/L (0.012 pg-TEQ/L) and 1.99pg/L (0.0011 pg-TEQ/L) (Table 1). The highest and lowest concentrations of total dioxins were 25.52 (0.54 pg-TEQ/L) and 0.097 pg/L (4.9×10^{-6} pg-TEQ/L), respectively. The average level of total dioxins was 4.15 pg/L (0.016 pg-TEQ/L) (Table 2).

Table 5. Concentrations of PCDD/DFs (pg-TEQ/L) in conventional drinking water treatment processes

	Raw water		Coagulated water		Chlorine treated water	
	pg/L	pg-TEQ/L	pg/L	pg-TEQ/L	pg/L	pg-TEQ/L
1,3,6,8-TeCDD	16.00	-	2.000	-	1.900	-
1,3,7,9-TeCDD	5.50	-	0.520	-	0.440	-
2,3,7,8-TeCDD	0.013	0.013	0.0012	0.0012	0.0005	0.0005
TeCDDs	22.00	0.013	2.700	0.0012	2.400	0.0005
1,2,3,7,8-PeCDD	0.061	0.061	0.005	0.0048	0.0021	0.0021
PeCDDs	3.80	0.061	0.230	0.0048	0.160	0.0021
1,2,3,4,7,8-HxCDD	0.094	0.0094	0.006	0.0006	0.0016	0.00016
1,2,3,6,7,8-HxCDD	0.22	0.022	0.011	0.0011	0.0029	0.00029
1,2,3,7,8,9-HxCDD	0.22	0.022	0.011	0.0011	0.0020	0.00020
HxCDDs	2.20	0.053	0.120	0.0028	0.036	0.00065
1,2,3,4,6,7,8-HpCDD	5.90	0.059	0.270	0.0027	0.018	0.00018
HpCDDs	11.00	0.059	0.530	0.0027	0.036	0.00018
OCDD	130.00	0.013	6.300	0.00063	0.066	6.6E-06
Total PCDDs	169.00	0.199	9.880	0.012	2.698	0.0034
1,2,7,8-TeCDF	0.043	-	0.007	-	0.0060	-
2,3,7,8-TeCDF	0.029	0.0029	0.005	0.0005	0.0087	0.00087
TeCDFs	1.60	0.0029	0.300	0.0005	0.31	0.00087
1,2,3,7,8-PeCDF	0.035	0.0018	0.004	0.0002	0.002	9.0E-05
2,3,4,7,8-PeCDF	0.048	0.024	0.005	0.0025	0.003	0.0015
PeCDFs	1.20	0.026	0.14	0.0027	0.10	0.0015
1,2,3,4,7,8-HxCDF	0.10	0.010	0.006	0.0006	0.002	0.00020
1,2,3,6,7,8-HxCDF	0.085	0.0085	0.006	0.0006	0.002	0.00020
1,2,3,7,8,9-HxCDF	0.011	0.0011	N.D.	N.D.	N.D.	N.D.
2,3,4,6,7,8-HxCDF	0.12	0.012	0.008	0.0008	0.003	0.0003
HxCDFs	1.30	0.032	0.083	0.0020	0.028	0.00063
1,2,3,4,6,7,8-HpCDF	0.80	0.008	0.039	0.00039	0.005	5.0E-05
1,2,3,4,7,8,9-HpCDF	0.13	0.0013	0.008	8.0E-05	0.001	1.0E-05
HpCDFs	2.20	0.009	0.10	0.00047	0.011	5.9E-05
OCDF	2.50	0.0003	0.11	1.1E-05	0.003	3.0E-07
Total PCDFs	8.80	0.070	0.73	0.0057	0.45	0.0031

Total PCDDs (resp. total PCDFs) are the sum of tetra to octa CDD (resp. sum of tetra to octa CDF)
N.D.: Not Detected

The mean, lowest and highest contributions of dioxins, as TDI (4 pg-TEQ/kg/day) after water treatment, were the 0.016, 4.9×10^{-6} and 0.54%, respectively, under the condition that a 50 kg person drinks 2 L a day. The Ministry of Health and Welfare reported that the daily intake of dioxins from food and the environment in Japan was 2.60 pg-TEQ/kg/day (Japanese Ministry of Health and Welfare, 1997). The intake of dioxins through tap water accounts for 0.023% of the total daily intake.

As discussed previously, the concentration of total dioxins in treated water was one tenth that of raw water in both in terms of pg/L and the pg-TEQ/L value (Table. 1). Dioxins levels for most treated waters were below 0.1 pg-TEQ/L. For the congener distribution of dioxins, the total PCDDs to total dioxins was 40 (1.66 pg/L) and 20% (0.0032 pg-TEQ/L). The OCDD congener contribution decreased from 43% in raw water to 3% (0.13 pg/L) in treated water. The most toxic isomers, 2, 3, 7, 8-TeCDD and 1, 2, 3, 7, 8-PeCDD, were at levels of 5 (0.0008 pg-TEQ/L) and 10% (0.0016 pg-TEQ/L), respectively. With respect to the total PCDFs and Co-PCBs, the TEQ rate of PCDFs increased drastically, from 12 (0.49 pg/L) to 74% (0.012 pg-TEQ/L). 2, 3, 7, 8-TeCDF (51%, 0.0083 pg-TEQ/L) was most predominant. The ratio of total Co-PCBs to total dioxins was 48 (1.99 pg/L) and 6% (0.0011 pg-TEQ/L).

Figure 1 and Table 2 show the removal rates of total PCDDs/DFs and Co-PCBs by the treatment of drinking water. The average removal rate of total dioxins was about 93% (pg/L), whereas the TEQ removal rate of total dioxins was 88%. This result is in agreement with that of previous studies (Kim et al., 2002; Smirnov et al., 1996). Most of the dioxins and dioxin like compounds can be removed by drinking water treatment processes, such as coagulation, sedimentation and filtration. As indicated in Figure 1, particularly in terms of pg-TEQ/L, the removal

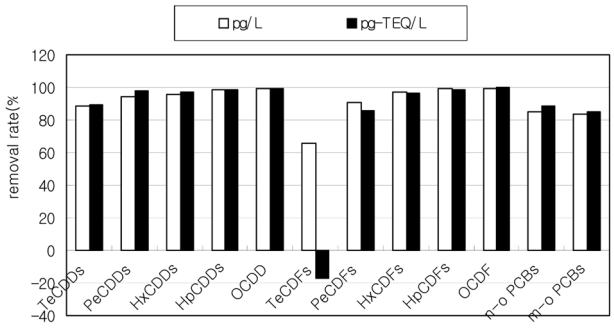

Fig. 1. Mean removal rates of the total dioxins concentration by the drinking water treatment process in 122 samples from 42 water treatment plants: 42 water treatment plants included 34 conventional water treatment plants, 4 advanced water treatment plants and 4 water treatment plants that utilized ground water.

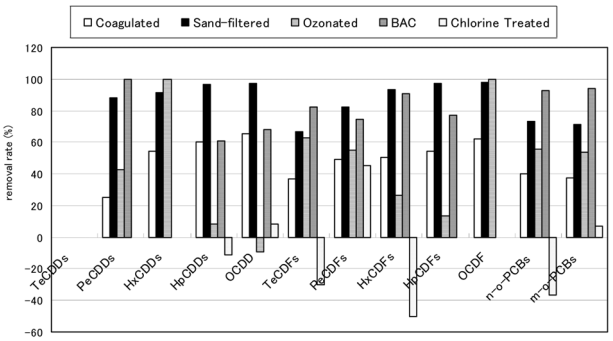

Fig. 2. TEQ removal rates of dioxins across the processes in the advanced water treatment plant: Coagulated (A); Coagulation and sedimentation, Sand-filtered (B); A + rapid sand-filtration, Ozonated (C); B + ozonation, BAC (D); C + BAC adsorption, Chlorine treated; D + chlorination.

rate of 2, 3, 7, 8-TeCDFs was around minus 17%. At 21 of the 122 sampling sites, the concentration of 2, 3, 7, 8-TeCDF increased. To more clearly identify the process with the greatest effect on the formation of 2, 3, 7, 8-TeCDF, advanced and conventional water treatment plants were selected for the sampling and analysis of dioxins. In the advanced water treatment process, the steps involved at the conventional treatment processes (coagulation, and sand-filtration) were followed by ozonation and BAC adsorption.

3.3. Dioxins removal effect across the processes

3.3.1. In advanced water treatment plant (T pilot-plant process)

The dioxins removal rates across the processes were 40 (after coagulation), 71 (after sand-filtration), 59 (after ozonation), 93 (after BAC filtration) and minus 15% (after chlorination), as measured in pg/L (Table 3). It has been reported that the ratio of particulate dioxins to soluble dioxins was 96:4 (Kim et al., 2002). However, contrary to our expectation, the TEQ removal rate of dioxins by the coagulation process was 44%. The TEQ removal rate increased to 92% after sand-filtration, indicating that wise management of sand filtration is necessary to improve the removal efficiency of particulate dioxins.

After the sand-filtration process, the removal rates of TeCDDs and TeCDFs were 66 and 63%, as pg/L (not detected and 67% as pg-TEQ/L), while those of OCDD and OCDF were 97 and 100%, respectively. These results also show that the removal rate of dioxins is proportional to the number of chlorine atoms substituted in the dioxins (Kim et al., in submission). However, this trend was reversed with ozonation. As the number of substituted chlorine atom increases, the removal rates of dioxins decrease (Fig. 2). This decrease indicates that dioxin and furan with eight substituted chlorine atoms are more resistant to oxidation, as all the available positions around the aromatic ring are already occupied by chlorine (Morrison and Boyd, 1983). Biological activate carbon (BAC) adsorption following ozonation gave the highest removal rate (93% as pg/L) of all the treatment processes tested. Conversely, after chlorination, the dioxin removal rate was minus 15%. In other words, the level of total dioxins increased from 0.10 to 0.115 pg/L as a result of chlorination. This increase may be attributable to the reaction of chlorine with the precursors of dioxins, such as trichlorophenol or pentachlorophenol, in raw water (Luthe and Berry, 1996).

In terms of the pg-TEQ/L value (Table 4), the total dioxins removal rates across the processes were 44 (after coagulation), 86 (after sand-filtration), 44 (after ozonation), 95 (after BAC filtration) and minus 30% (after chlorination). The TEQ removal patterns of the congeners were similar to those of the measured values, in pg/L. As shown in Figure 2, the congeners removal rates were remarkably reduced after chlorination; HxCDFs (minus 50%), non-ortho-PCBs (minus 36%) and 2, 3, 7, 8-TeCDFs (minus 11%), as the pg-TEQ/L value. These results indicate that chlorination was responsible for the increase in the 2, 3, 7, 8-TeCDF concentration.

3.3.2. In conventional water treatment plant (AY water treatment plant)

The dioxins removal rates across the processes were 94%, as pg/L (93% as pg-TEQ/L), after coagulation and 61%, as pg/L (59% as pg-TEQ/L), after chlorination (Table 5). However, the removal rates of 2, 3, 7, 8-TeCDF, non-ortho-PCBs and mono-ortho-PCBs, as the pg-TEQ/L value, decreased to minus 64, minus 28 and minus 27%, respectively, as a result of chlorination, as shown in Figure 3 and Table 5. These results highlight a problem, as a trade-off needs to be established between the benefit of chlorination,

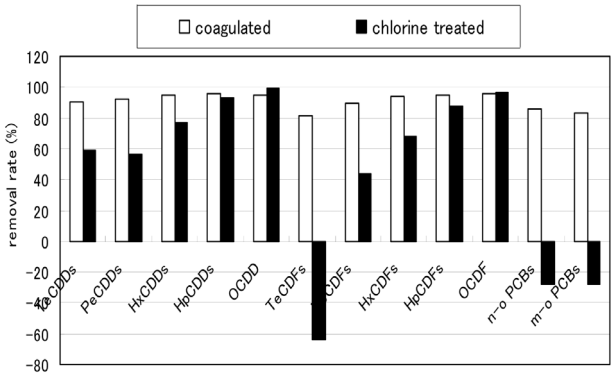

Fig. 3. TEQ removal rates of dioxins across the processes in the conventional water treatment plant: Coagulated (A); Coagulation and sedimentation, Chlorine treated; A + chlorination.

which is a reduction in most congeners, and the disadvantage of chlorination, which is the increased formation of 2, 3, 7, 8-TeCDF. Therefore, further investigations are necessary to identify the substances affecting the levels of 2, 3, 7, 8-TeCDF during chlorination.

4. Conclusion

The mean levels of dioxins before and after water treatment at the 122 sampling sites of the 42 water plants were 60.24 (0.14 pg-TEQ/L) and 4.15 pg/L (0.016 pg-TEQ/L), respectively. These mean concentrations were relatively low compared to previously reported literature values. However, the highest concentration of total dioxins after water treatment, 0.54 pg-TEQ/L, suggests that more periodic surveys are necessary. The concentration level found in this study was half that of the current maximum allowable dioxins level of 1 pg-TEQ/L (Japanese Environmental Agency, 1999). The contribution of dioxins after water treatment, as TDI (4 pg-TEQ/kg/day), based on the mean concentration, was 0.016%.

The average removal rate of dioxins after water treatment was over 88%, in terms of the pg-TEQ/L value, at the 122 sampling sites of the 42 water plants. This result shows that dioxins and dioxin like compounds can be effectively removed by the treatment of drinking water. However, the removal rate of 2, 3, 7, 8-TeCDF after water treatment was minus 17%.

The removal rates of the dioxin congeners were remarkably reduced after chlorination, i.e. those of 2, 3, 7, 8-TeCDFs and non-ortho-PCBs, in both the advanced and conventional water treatment plants. As a consequence, chlorination at drinking water treatment plants has both positive and negative impacts; removing most congeners, with the except of some isomers.

국문요약

먹는물 처리 전후 다이옥신류의 동족체 패턴 및 제거율을 평가하기 위해서 42개의 일본 정수처리장에서 2년간 122개의 시료를 채취해 dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) 및 coplanar polychlorinated biphenyls (Co-PCBs)를 분석하였다. 다이옥신류의 평균 농도와 독성등가값 (toxic equivalent, TEQ)은 원수와 처리수에서 각각 60.24 pg/L (0.14 pg-WHO-TEQ/L), 4.15 pg/L (0.016 pg-WHO-TEQ/L)였다. 먹는물의 다이옥신류 기여 농도는 일일섭취량 (tolerable daily intake (TDI), 4 pg-TEQ/kg/day)의 0.016%이었다. 정수처리에 의한 다이옥신류의 평균 TEQ 제거율은 88% 이상이었다. 그러나 112개의 샘플에서 2, 3, 7, 8-TeCDF (tetrachlorodibenzofuran)의 농도는 17% 증가하였다. 따라서, 2, 3, 7, 8-TeCDF의 농도에 영향을 미치는 공정을 파악하기 위하여 고도정수처리 및 일반정수처리에서의 제거율을 조사하였다. 다이옥신 동족체 (congener)인 TeCDF와 non-ortho-PCB는 고도처리 및 표준정수처리에서 염소소독처리 후 TEQ 농도가 증가함을 보여, 먹는물 중 2, 3, 7, 8-TeCDF 농도는 염소소독처리에 의해 상승한 것으로 밝혀졌다.

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