DIOXIN CONCENTRATION IN LIQUID CHLORINE USED FOR WATER PURIFICATION

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Introduction

The authors have reported on dioxin concentrations[1,2] and formation mechanisms[3] for Japanese tap water. Reported results indicate that PCDF's are an important factor in characterizing tap water (in Japan, almost tap water is supplied after chlorination). In the present report, PCDDs/PCDFs concentrations in water after chlorination were measured.

Methods and Materials

A schematic for the experiment is shown in *Figure-1*. Chlorine gas was injected into water samples pumped from a 200L water tank. The Chlorine Injector and Controller adjusted the final concentration of chlorine in sampling bottles to 0.3%. 10L samples of two types of water, Tap Water and Pure Water, were prepared for dioxin analysis.

Analysis

Detection of PCDDs/PCDFs was carried out by HRGC/HRMS method after soxhlet extraction and gel clean-up procedures. Water samples were filtered by glass fiber filters (GFF) and C_{18} filters. After the filtration, GFF and C_{18} filters were dried in a desiccator. After spiking with internal standards (^{13}C 2,3,7,8-substituted PCDDs/PCDFs compounds) GFF and C_{18} filters were extracted with toluene for 20hrs, using a soxhlet extractor. Multi layer silica gel and activated carbon column chromatographies were employed for sample clean up. Concentration of PCDDs/PCDFs were determined by HRGC (6890, Hewlett Packard, US)/HRMS (AutoSpec-Ultima, Micromass, UK). Seventeen native (Wellington Laboratories, Canada) and ^{13}C 2,3,7,8-substituted PCDDs/PCDFs congeners (Wellington Laboratories, Canada) were used as standards and isotope spikes. To detect low pg/L concentrations of PCDDs/PCDFs, organic solvents used for analysis were purified by sub-boiling distillations. Glassware, GFF and silica gel were heated to 400-450ºC after an organic solvent wash. C_{18} filters were pre-washed by Soxhlet (toluene, >24hrs). All procedures were carried out in a chemical hazard clean room (class<10000). HRGC was equipped with BPX-DXN (SGE, Australia) and RH-12ms (Inventx, USA) to separate all 2,3,7,8-substituted congeners[4]. Analyses were performed in accordance with ISO/IEC 17025(JCLA4).

Results and Discussion

Obtained results are shown in Table 1, together with the data of a full operation blank. Homologue/ 2,3,7,8-substituted isomer distributions are shown in Figure-2. Regarding PCDDs, concentrations of each congener were within the operation blank levels for Tap Water and Pure Water. However, almost all PCDF congeners were detected at levels of interest. Characteristic PCDF's distributions were, (A) 2,3,7,8-substituted isomers in the ratio of each homologue were high, (B) There was a close resemblance between the isomer distributions of each homologue in Tap Water and Pure Water, (C) Homologue distribution of Tap Water was different from that of Pure Water's. HexaCDF was the dominant homologue for the two samples, but the fraction ratio of other homologues is different, (D) Distributions were different from that of all other ambient media.

As the concentrations of PCDFs in Pure Water were in the same range as Tap Water, it is quite conceivable that original liquid chlorine contained PCDF's contaminants. The difference between concentration/homologue distributions of Tap Water and Pure Water could be caused by (A) PCDFs compositions in supplied chlorine gas were inconsistent, and/or (B) difference of contents between Tap Water and Pure Water involved some undetermined process of synthesis/decomposition in water samples during/after chlorination.

References

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4. Matsumura,T., Masuzaki,Y., Seki,Y., Shamoto,H., Morita,M. and Ito,H. (2002) *submitted to Dioxin 2002*

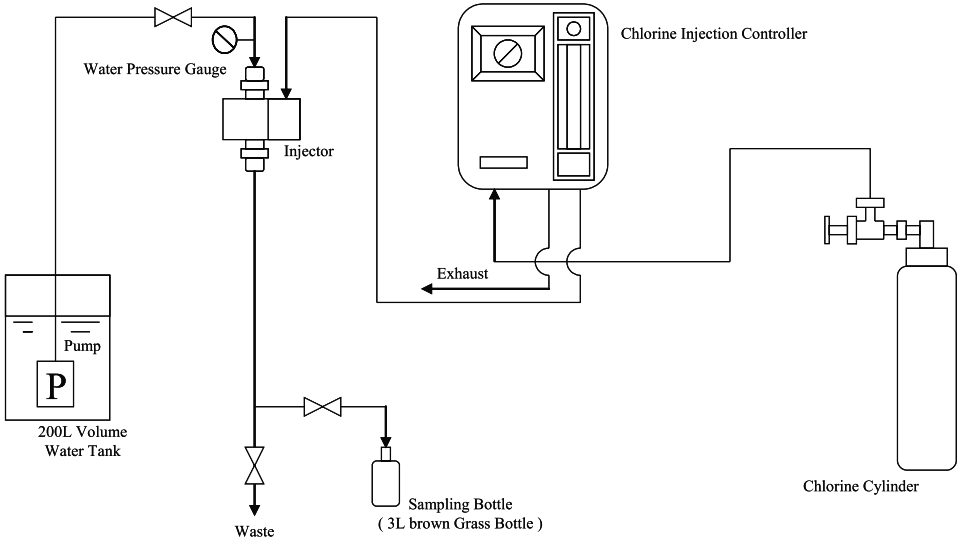

Figure 1. Schematic of chlorination experiment.

Table 1. Concentration of PCDDs/PCDFs in water sample after chlorination.

	Congeners	Tap Water		Pure Water		Full Operation Blank	
		Concentration (pg/L)	TEQ* (pg-TEQ/L)	Concentration (pg/L)	TEQ* (pg-TEQ/L)	Concentration (pg/L)	TEQ* (pg-TEQ/L)
	2,3,7,8-TeCDD	<0.1	0.050	<0.1	0.050	<0.1	0.050
	TeCDDs	-	-	-	-	-	-
	1,2,3,7,8-PeCDD	<0.1	0.050	<0.1	0.050	<0.1	0.050
P	PeCDDs	-	-	-	-	-	-
C	1,2,3,4,7,8-HxCDD	<0.2	0.010	<0.2	0.010	<0.2	0.010
D	1,2,3,6,7,8-HxCDD	<0.2	0.010	<0.2	0.010	<0.2	0.010
D	1,2,3,7,8,9-HxCDD	<0.2	0.010	<0.2	0.010	<0.2	0.010
s	HxCDDs	-	-	-	-	-	-
	1,2,3,4,6,7,8-HpCDD	<0.5	0.0025	<0.5	0.0025	<0.5	0.0025
	HpCDDs	-	-	-	-	-	-
	OCDD	<1	0.00005	<1	0.00005	<1	0.00005
	Total PCDDs	-	0.13	-	0.13	-	0.13
	2,3,7,8-TeCDF	0.3	0.030	3.2	0.32	<0.1	0.0050
	TeCDFs	1.1	-	11	-	-	-
	1,2,3,7,8-PeCDF	2.1	0.11	120	6.0	<0.1	0.0025
	2,3,4,7,8-PeCDF	0.50	0.25	23	12	<0.1	0.025
P	PeCDFs	12	-	330	-	-	-
C	1,2,3,4,7,8-HxCDF	170	17	600	60	<0.2	0.010
D	1,2,3,6,7,8-HxCDF	6.8	0.68	80	8.0	<0.2	0.010
F	1,2,3,7,8,9-HxCDF	0.8	0.080	38	3.8	<0.2	0.010
s	2,3,4,6,7,8-HxCDF	0.3	0.030	5.0	0.50	<0.2	0.010
	HxCDFs	280	-	1100	-	-	-
	1,2,3,4,6,7,8-HpCDF	31	0.31	24	0.24	<0.5	0.0025
	1,2,3,4,7,8,9-HpCDF	60	0.60	74	0.74	<0.5	0.0025
	HpCDFs	150	-	130	-	-	-
	OCDF	40	0.0040	4.3	0.00043	<1	0.00005
	Total PCDFs	480	19	1600	91	-	0.078
	Total (PCDDs+PCDFs)	480	19	1600	91	-	0.21

*: TEQ was calculated by WHO-1998's TEF. When measured concentration is less than LOD (Limited of Detection), TEQ was calculated by LOD/2 x TEF.

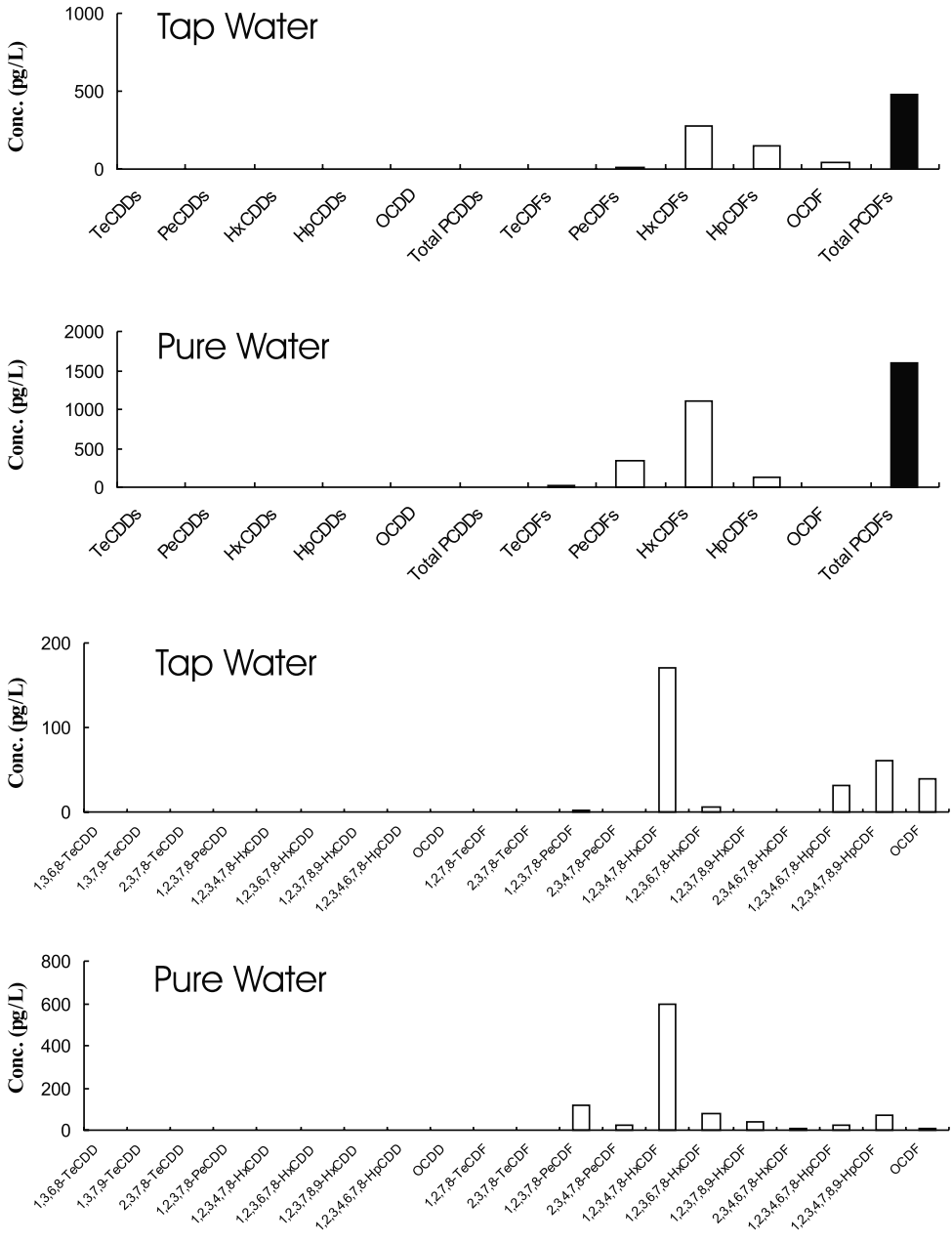

Figure 2. Homologue/isomer distributions of PCDDs/PCDFs for the Tap/Pure Water after chlorination.