

ENVIRONMENTAL LEVELS II -POSTER

DIOXINS IN DRINKING WATER TREATMENT PROCESS

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Introduction

Few papers related to the level of dioxins in source water and removal efficiency of dioxins by water treatment have been reported. The reason is the level of dioxins is very low. However, it is necessary to identify the level of PCDDs/Fs and Co-PCBs and the characteristic of those in the source water before and after treatment and to assess the health risk to humans. Fortunately, with the help of scientific analytical methods and instrumentation improvement, we were able to detect these compounds 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 water and tap water. This system enabled us to study removal efficiency, homologue patterns and the characteristic of dioxins in the drinking water before and after treatment such as coagulation, sand-filtration, ozonation, Biological Activated Carbon (BAC), and chlorination.

Methods and Materials

Raw water(500L), coagulated and sedimented water(1200L), sand-filtered water(4000L), ozonated water(4000L), BAC-filtered water(4000L) and chlorine treated water(4000L) were sampled, respectively in the Tamagawa water treatment pilot-plant of which capacity is 500ton per day. Automatic "in situ" pre-concentration system was used for sampling¹. This system is constructed of electrolyze-mirror polish treated stainless steal, air removal chamber, a glass fiber filter (GFF, 300mm ID, 0.5um pore size) holder, polyurethane form plug (PUFP, 100mm ID, 100mm height) holders, valves and sensors with an external computer controller system.

Detection of PCDD/Fs and Co-PCBs was carried out by isotope dilution HRGC/HRMS (AutoSpec-Ultima, Micromass, UK) method after soxhlet extraction and gel clean up process. All procedure were carried out in a clean room(class<10,000, US, FS209E). BPX5 and BPX50(60m length, 0.25mm ID, 0.25µm film thickness, SGE, Australia) are designed for HRGC to obtain high sensitivity and reduce chemical background from the liquid phase.

ENVIRONMENTAL LEVELS II -POSTER

Results and Discussion

Dioxin Levels and Homologue Patterns in Water Treatment Process

As shown in Table 1, dioxin levels of each step were 19.00pg/L for raw, 11.21pg/L for coagulated, 3.32pg/L for sand-filtered, 1.34pg/L for ozonated, 0.10pg/L for BAC treated and 0.12pg/L for chlorine treated water (Table 1 and Fig 1). In the step of raw water, the ratio of mono-ortho-PCBs concentration was 58% and 12%&11% for TeCDDs and OCDD, respectively. It was indicated that the level of PCDFs was much lower than those of PCDDs and Co-PCBs in raw water. Coagulated water showed the same homologue patterns in the 60% level of raw water concentration. Most of dioxins were removed in the step of coagulation and sand-filtration. The rest of dioxins after coagulation were removed by ozonation and BAC adsorption. On the other hand, the concentration of dioxins after chlorination was slightly increased. This increase may be attributable to the reaction of chlorine with the precursors of dioxins such as trichlorophenol or pentachlorophenol in raw water².

As shown in Fig. 2, relative abundance of Co-PCBs increased with the increment of process except BAC process and chlorination process.

Table 1 Concentration of PCDD/DFs and Co-PCBs (pg/L) in Drinking Water Treatment Process

	Raw	Coagulated	Sand-filtered	Ozonated	BAC	Chlorine treated
TeCDDs	2.20	1.60	0.54	0.081	0.016	0.017
PeCDDs	0.30	0.22	0.040	0.016	0.0040	0.0043
HxCDDs	0.24	0.13	0.0091	0.0049	0.0011	0.0012
HpCDDs	0.41	0.17	0.0059	0.0055	0.0024	0.0022
OCDD	2.10	0.72	0.021	0.023	0.0073	0.0067
Total PCDDs	5.30	2.80	0.62	0.13	0.031	0.031
TeCDFs	0.60	0.40	0.15	0.063	0.0045	0.0051
PeCDFs	0.40	0.22	0.041	0.037	0.0033	0.0035
HxCDFs	0.30	0.14	0.010	0.0086	0.0009	0.0020
HpCDFs	0.22	0.093	0.0027	0.0024	0.0006	0.0005
OCDF	0.14	0.053	0.0011	0.0014	0.00	0.00
Total PCDFs	1.70	0.91	0.20	0.11	0.0093	0.011
non- <i>o</i> - PCBs	0.95	0.62	0.27	0.11	0.014	0.027
mono- <i>o</i> - PCBs	11.00	6.90	2.20	0.99	0.047	0.046
Total Co-PCBs	12.00	7.50	2.50	1.10	0.060	0.073
Total Dioxins	19.00	11.21	3.32	1.34	0.10	0.12

In toxic equivalents, dioxin concentrations of each step were 0.044pg-TEQ/L for raw, 0.025pg-TEQ/L for coagulated, 0.0038pg-TEQ/L for sand-filtered, 0.0020pg-TEQ/L for ozonated, 0.00021pg-TEQ/L for BAC treated and 0.0018pg-TEQ/L for chlorine treated water (Fig. 3).

ENVIRONMENTAL LEVELS II - POSTER

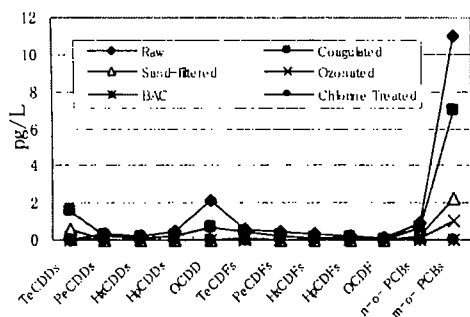


Fig.1 Homologue Profiles of Dioxins in Water Treatment Process

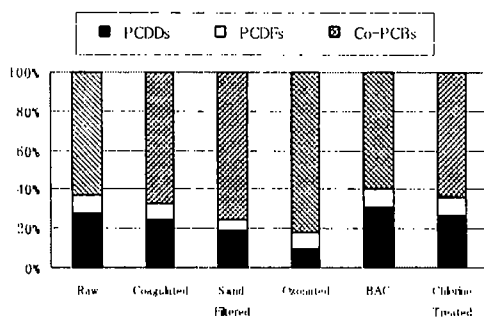


Fig.2 Relative Abundance of Dioxins Homologues at Each Water Treatment Process

In the measured (pg/L) value, the dominant fraction (about 63%) in raw water was Co-PCBs, but in TEQ value the fraction was changed greatly such as PCDFs(52%), PCDDs(32%) and Co-PCBs(16%)(Fig. 4). Especially, PCDFs was increased from 5% (measured value, pg/L) to 52% (TEQ value, pg-TEQ/L). Therefore, we have to put more focus on the PCDFs for the future studies in drinking water treatment.

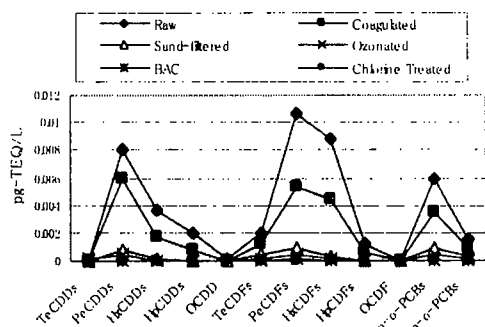


Fig. 3 Homologue Profiles of Dioxins in Water Treatment Process(TEQ Conc.)

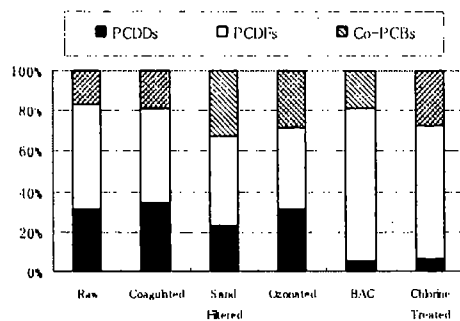


Fig.4 Relative Abundance of Dioxins Homologues at Each water Treatment Process (TEQ Conc.)

Dioxins Removal Rate in Contrast to Raw Water

Removal rates compared with raw water were 41% (after coagulation), 83% (after sand-filtration), 93% (after ozonation), 99.5% (after BAC filtration) and 99.4% (after chlorination). It was reported that the ratio of particulate dioxins to soluble dioxins was 96:4³. Therefore, the high removal rate of dioxins in the coagulation process would be expected but it was 41% which was lower than expected. This result indicates that wise management of sand filtration is necessary to improve the removal efficiency of particulate dioxins. Most of soluble dioxins were removed in the process of ozonation. In raw water, it can be also seen that the removal efficiency increased with increase of the number of substituted chlorine in dioxin (Fig. 5). The removal rates of

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ENVIRONMENTAL LEVELS II -POSTER

TeCDD/Fs after coagulation were 27~33% while those of OCDD/F were 62~66%. This result is also in agreement with the report that it becomes harder for dioxins to dissolve in water with the increase of substituted chlorine number in dioxin⁴.

Dioxins Removal Rate Across the Processes

Dioxins removal rates after various process were 41% (after coagulation), 70% (after sand-filtration), 60% (after ozonation), 93% (after BAC filtration) and minus 15% (after chlorination). Up to sand-filtration, removal rates of TeCDD/Fs were 63%~66% while that of OCDD/F was 97%. This result also shows that removal rate of dioxins is proportional to substituted number of chlorine in dioxin. However, this trend was reversed in the step of ozonation. As the number of substituted chlorine increases, removal rates of dioxins decreased (Fig. 6). This decrease indicates that 8 chlorine dioxin and furan are more resistant to oxidation because all the position of aromatic ring is already occupied by chlorine.

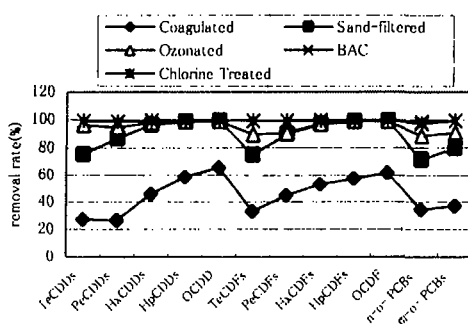


Fig. 5 Removal Rate of Dioxins in Contrast to Raw Water in pg/L Value

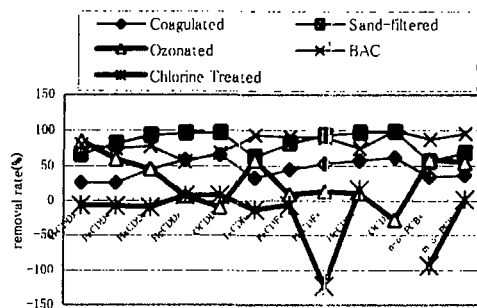


Fig. 6 Removal Rate of Dioxins Across the Processes in pg/L Value

Acknowledgement

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