# EFFECT OF WATER TREATMENT FOR THE MINIMIZATION OF DIOXINS AND ORIGIN OF DIOXINS IN DRINKING WATER

Hyun-koo Kim[1], Hiroshi Nakamura[1], Yoshie Seki[2], Tohru Matsumura[2], Koichi Ohno[1], Tasuku Kamei[1] and Yasumoto Magara[1]

[1]Department of Urban Environmental Engineering, Faculty of Engineering, Hokkaido University, Kita-13, Nishi-8, Kita-ku, Sapporo, Hokkaido, 060-8628, khk228@hotmail.com
[2]Environmental Research Center, Meteorological and Oceanographical Consultant Co.,Ltd. (METOCEAN), Riemon 1334-5, Ohigawa, Shieda, Shizuoka 421-0212, Japan

## Introduction

A national survey of dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and coplanar polychlorinated biphenyls (Co-PCBs) from the 42 drinking water treatment plants in 1999 and 2000 revealed that the 2,3,7,8-TeCDFs level from several drinking water treatment plants increased after drinking water treatment. Therefore, to identify why the level of 2,3,7,8-TeCDF increased after water treatment, reagents ( such as humics, KP lignin, SP lignin and chlorophenols) and environmental waters (such as secondary effluent for sewage treatment plant, peat water and pulp mill effluent) were chlorinated. From this study, it was identified that TeCDFs are formed from KP lignin and SP lignin and paper mill effluent via chlorophenols as a result of chlorination.

## Methods and Materials

Samples for the determination of dioxin levels before and after drinking water treatment: In 1999, the first year of this study, raw water (200L) and treated water samples (2000L) were collected both in July and November from 42 water plants using Automatic “in situ” pre-concentration system[1]. During the second year of this study (2000) 19 of the 42 water treatment plants were selected and samples collected following the same methods as the previous year.

Chemicals used for chlorination: Humics was purchased from Wako Pure Chemicals Industries Ltd and SP lignin and KP lignin were purchased from Aldrich Chemical Company, Inc. 4-monochlorophenol (99 %), 2,3-, 2,4-, 2,6-, 3,4-, 3,5-dichlorophenol (99 %), 2,5-dichlorophenol (98 %) 2,3,6-trichlorophenol (99 %), 2,4,6-trichlorophenol (98 %) and pentachlorophenol (99 %) were obtained from GL Sciences Inc. Reagents, secondary sewage effluent from treatment plant and pulp mill effluent were chlorinated to identify the formation level of dioxins and chlorophenols. The concentrations of reagents (humics, SP lignin and KP lignin) were 5mg/L as TOC and the residual free chlorine after 24 hours was 1mg/L. Chlorophenols (5mg/L) were also chlorinated to identify the dioxins formation mechanism based on the above chlorination condition.

Analysis: For detection of PCDDs/PCDFs and Co-PCBs, a high-resolution gas chromatograph (HRGC, Hewlett Packard6890), coupled to a high-resolution mass spectrometer (HRMS, Auto-Spec, Micromass) was used after soxhlet extraction and gel clean-up procedures. Chlorophenols were quantified by HPGC (6890)/HPMS (5973).

## Results and Discussion

*Dioxin levels and homologue patterns in water treatment process*

The average level of PCDDs, PCDFs and Co-PCBs in raw water were 43pg/L (0.06pg-TEQ/L), 4pg/L(0.057pg-TEQ/L) and 12pg/L (0.0087pg-TEQ/L), respectively.

**Table 1.** Average level of dioxins in 122 samples before and after water treatment

| | Raw water | | Water after treatment | |
|---|---|---|---|---|
| | pg/L | pg-TEQ/L | pg/L | pg-TEQ/L |
| TeCDDs | 11.52 | 0.0075 | 1.33 | 0.00078 |
| PeCDDs | 1.84 | 0.030 | 0.11 | 0.0016 |
| HxCDDs | 1.082 | 0.020 | 0.048 | 0.00061 |
| HpCDDs | 3.34 | 0.015 | 0.050 | 0.00022 |
| OCDD | 25.72 | 0.0026 | 0.13 | 1.3E-05 |
| Total PCDDs | 43.33 | 0.060 | 1.67 | 0.0030 |
| TeCDFs | 1.13 | 0.0071 | 0.39 | 0.0083 |
| PeCDFs | 0.73 | 0.022 | 0.066 | 0.0031 |
| HxCDFs | 0.78 | 0.023 | 0.025 | 0.00084 |
| HpCDFs | 0.93 | 0.0047 | 0.010 | 6.4E-05 |
| OCDF | 0.88 | 9.0E-05 | 0.0034 | 3.4E-07 |
| Total PCDFs | 4.30 | 0.057 | 0.49 | 0.012 |
| Non-*ortho* -PCBs | 1.02 | 0.0072 | 0.15 | 0.00083 |
| Mono-*ortho* -PCBs | 11.20 | 0.0015 | 1.84 | 0.00023 |
| Total Co-PCBs | 12.22 | 0.0087 | 1.99 | 0.0011 |
| Total dioxins | 59.84 | 0.13 | 4.14 | 0.016 |

For the ratio of PCDDs, PCDFs and Co-PCBs to total dioxins were 73%, 7% and 20%, respectively. After drinking water treatment, the average level of PCDDs, PCDFs and Co-PCBS in treated water were 1.66pg/L (0.0032pg-TEQ/L), 0.49pg/L (0.012pg-TEQ/L) and 1.99pg/L (0.0011pg-TEQ/L), respectively. The removal rate of total dioxins in terms of pg/L value by drinking water treatment was about 93% whereas 88% of total dioxins in terms of pg-TEQ/L value was removed. This result is in agreement with that of a previous result[2] and most dioxins and dioxin like compounds can be removed by drinking water treatment. However, the TEQ removal rate of 2,3,7,8-TeCDFs was approximately minus 17%.

*Dioxin levels after chlorination of reagents and environmental waters*

PCDD/Fs were produced from SP lignin, KP lignin and paper mill effluent (Fig. 1). However, no PCDFs was formed from commercial humics, peat water and sewage water. TeCDFs was the most abundant class derived from KP lignin, whereas TeCDFs and PeCDFs were the most abundant class in the paper mill effluent. By the cluster analysis, not shown on the graph, the isomer patterns of KP lignin, paper mill effluent and some drinking waters in which 2,3,7,8-TeCDF increased were very similar. This result shows chlorination of lignin compounds is responsible for increasing TeCDFs in drinking water.

To identify chlorophenols that are thought to be precursors of dioxins, reagents such as SP lignin, KP lignin and humics were also chlorinated. From the lignin and KP lignin, not shown on the graph, chlorophenols were produced but not detected from the humics. This is in strong agreement with the results of dioxin formation from SP lignin and KP lignin after chlorination. In other words, PCDFs was formed from lignin but not from commercial humics.

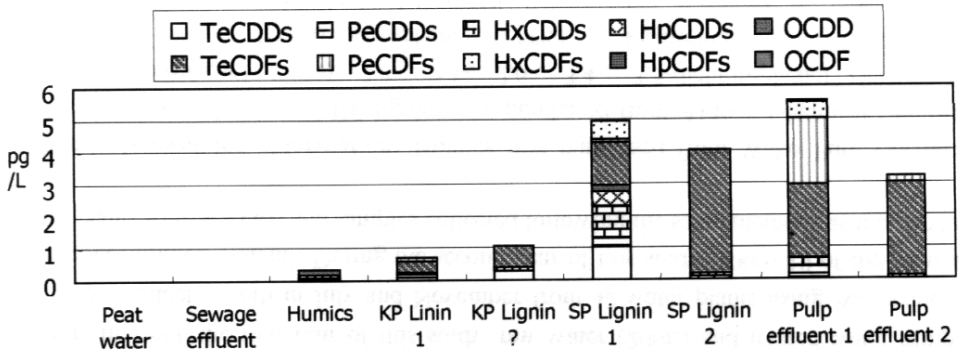


**Figure 1.** Increased homologues more than blank level after chlorination of commercial reagents (SP lignin, KP lignin and humics) and environmental waters (sewage effluent and pulp mill effluent)

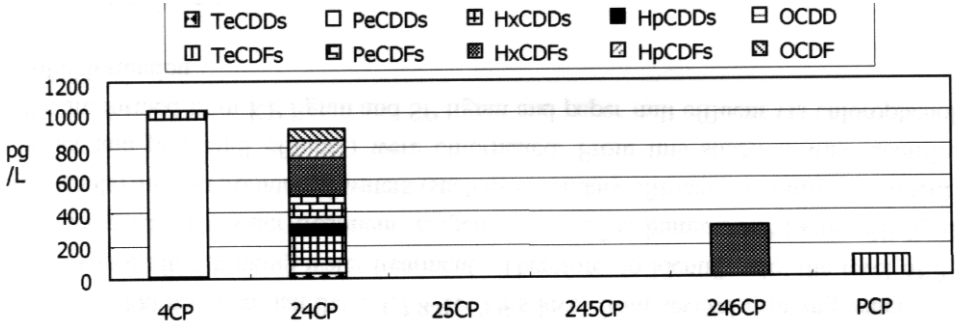


**Figure 2.** Increased homologues more than blank level after chlorination of chlorophenols

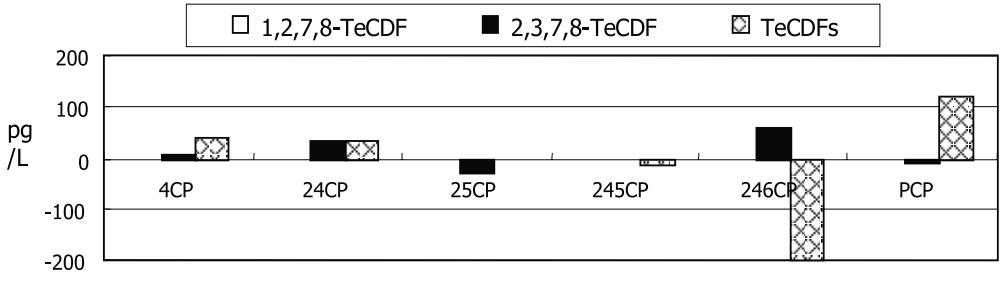


**Figure 3.** Formation of 2,3,7,8-TeCDF from chlorophenols as a result of chlorination

TeCDFs was formed from chlorophenols, after chlorination for 24 hours, such as 4-monochlorophenol, 2,4-dichlorophenol and pentachlorophenol (Fig. 2). The level of total TeCDFs formed from 2,4,6-trichlorophenol as a result of chlorination was lower than blank level. However, the 2,3,7,8-TeCDF increased in 2-monochlorophenol, 2,4-dichlorophenols and 2,4,6-trichorophenols after chlorination (Fig. 3). Consequently, when the lignin-contained samples were chlorinated, the 2,3,7,8-TeCDFs were formed via dioxin precursor chlorophenols.

**Acknowledgement**

This study is supported by the research grant of the Ministry of Health, Labor and Welfare, Japan.

**References**

1. Magara, Y., Aizawa, T., Andoh, M. and Matsumura, T. (1999) Oganohalogen Compounds, 40, 205-208
2. Smirnov A.D., Schecter A., Papke O., Beljak A.A.,(1996)Chemosphere,32,479-489