6. Dioxins in water sources and its risk assessment of drinking water

Presenter

Yasmoto Magara, Hokkaido University

Dioxins in water sources and its risk assessment of drinking water

Yasmoto Magara· Hyun-koo Kim, Tasuku Kameiand Kohich Ohno

Abstract

PCDDs/DFs and Co-PCBs were monitored in raw and treated water of public water supply system in throughout Japan. In 40 water treatment plants for surface water and 5 for ground water, the removal efficiency of dioxins and the influence of chlorination in the several types of treatment processes were studied. Location of water treatment plant significantly not only influenced the concentration level of dioxins but also resulted in homologue patterns of dioxins.

This study showed that most of dioxins are well removed by conventional rapid sand filtration (CRSF) system, though powdered activated carbon (PAC) is much more effective to remove dioxins in water treatment process. However, in some water treatment plants, the level of TeCDFs (pg-WHO-TEQ/L) increased as the result of chlorination.

Origin of dioxins in raw water was estimated by multivariate statistical methods. In raw water, it was estimated that the most of dioxins and dioxin like compounds originates from pesticide such as pentachlorophenol (PCP) and 1,3,5-trichloro-2- (4-nitrophenoxy) benzene (CNP) that had been restricted their uses because of carcinogenic effect at least some years ago.

Key words —dioxins, water treatment, drinking water, pesticides run off

1.Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs) and coplanar polychlorinated biphenyls (Co-PCBs) are distributed worldwide. Dioxins, furans and Co-PCBs are formed as unwanted byproducts in various chemical formulations and combustion process. These compounds enter the aquatic environment from the atmosphere and agricultural chemicals and as direct discharges from industrial sources, sewage treatment plants

Polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs) and Co-PCBs are two classes of compounds that contain some of the most toxic chemical substances that are known. Some of these compounds are also regarded as potential human carcinogens. In addition, these compounds may accumulate in the food chain. For these reasons their presence in the environment is of concern. 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. This enabled us to find that these compounds appear to be ubiquitous in the environment. However, the U.S. EPA has set a maximum allowable value for

----

Department of Urban Environmental Engineering, Graduate School of Engineering, Hokkaido University, Kita-13, Nishi-8, Kita-ku, Sapporo, Hokkaido, 060-8628, Japan

2,3,7,8-tetraCDD in drinking water as low as 0.13 to 0.0013pg/L based on estimated human cancer risks at 10^{-5} to 10^{-7}, respectively, the true risk of these contaminants is still not well understood.

Based on the above backgrounds, this study has focused on the followings.

To find out the levels of PCDDs/Fs and Co-PCBs before and after water treatment at water treatment plant.

To identify the contribution of particulates dioxin to total dioxin levels in raw water.

To identify the behavior of dioxins in four types of water treatment system such as chlorination (process only for ground water), CRSF, PAC adsorption followed by CRSF and CRSF followed by ozonation / biological activated carbon adsorption (O_3/BAC).

To identify the origin attribution of dioxins in raw water

2.Materials and Methods

2.1 Sample collection

As shown in Fig 1., raw and treated water samples were collected at 45 water treatment plants in Japan. Water sources for 40 water treatment plants and five water treatment plants were surface water and ground waters, respectively. Each water plant was sampled twice, July and November in 1999. 200L for raw water and 2000L for treated water were collected, respectively.
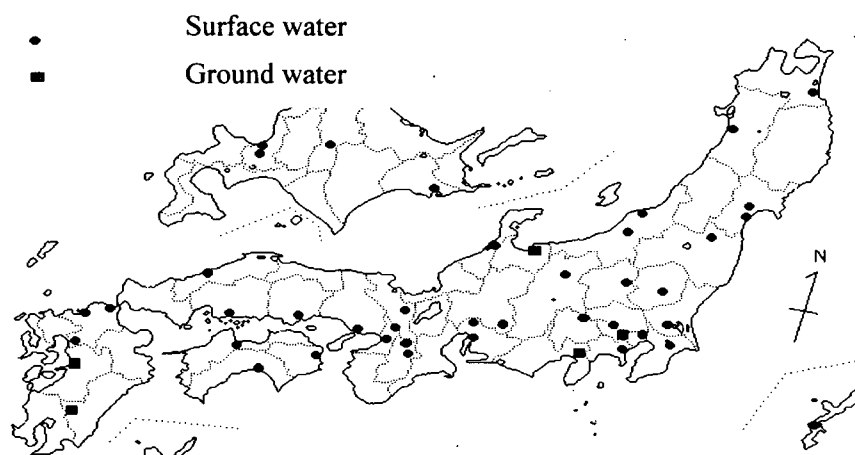

Fig. 1. Sites for the collection of water samples in Japan

Automatic "in situ" pre-concentration system was used for sampling 200L for raw water and 2000L for treated water, respectively (Magara et al. 1999). This system is fabricated by 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.

2.2 Analysis

For analysis and 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. The TEF value established by WHO in 1997 was applied to the above compounds for TEQ value.

GFF and PUFP were dried in a desiccator. After spiking with internal standard ^{13}C compounds, PCDDs/PCDFs and Co-PCBs were extracted by methylene chloride for 24hrs, GFF

using toluene for 24hrs with a soxhlet extractor. Multi layer silica gel and activated carbon column chromatographies were employed for sample clean up. Concentration of PCDDs/PCDFs and Co-PCBs was determined by use of isotope dilution HRGC (6890, Hewlett Packard, US)/HRMS (Auto-Spec, Micromass, UK). Seventeen native and ^{13}C 2,3,7,8-substituted dioxin/furan isomers (Wellington Laboratories, Canada) and twelve native (IUPAC #77, #81, #126, #169, #105, #114, #118, #123, #156, #157, #167 and #189; AccuStandard, USA) and ^{13}C (Wellington Laboratories, Canada) Co-PCBs were used as internal and isotope spike standards.

Organic solvents used for analysis were purified by non-boiling distillations. Glassware, GFF and SUS were heated to 300°C after applying an organic solvent wash. PUFPs were pre-washed by soxhlet reflux with methylene chloride for longer than 24hrs after a purified water and acetone wash. All procedures were carried out in a clean room (class <10,000).

BPX-5 (60m length, 0.25mm ID, 0.25μm film thickness, SGE, Australia) for TeCDDs-OCDD, TeCDFs-OCDF, Co-PCBs and BPX-50 (60m length, 0.25mm ID, 0.25μm film thickness, SGE, Australia) for PeCDFs, HxCDFs are equipped for HRGC to reduce the chemical background from liquid phase. Residual blanks were analyzed to check for interference or contamination arising from solvents or glassware.

3.Results and Discussion

3.1 Dioxins level before water treatment at water treatment plant

Histograms of measured concentration (pg/L) and toxic equivalent (pg-TEQ/L) for 90 raw water samples are shown in Fig. 2 and Fig.3. The survey found that 76 samples had concentrations below 100pg/L and 12 samples had values 100~300pg/L. The highest concentration found in one sample was 540pg/L. In terms of TEQ shown in Figure 3, level of TEQ at 11 sampling sites were below 0.01 pg-TEQ/L, level of TEQ of 46 sampling sites ranged from 0.01 to 0.1pg-TEQ/L. At 29 sampling sites and 4sampling sites, concentration ranged from 0.1~0.5pg-TEQ/L and 0.5~1.0pg-TEQ/L, respectively.

As expected, the portion of ground water to total average concentration was slight; 3.48pg/L (6.2% to total dioxins) whereas the concentration of surface water was much higher; 63.07pg/L. The average concentration of ground water is about 4 times lower than that of 25 sampling sites in Japan. The average concentration of surface water is similar to the results by the Japanese Environment Agency (Japanese Environmental Agency, 1998) and lower than that in Germany and England (Gotz et al., 1994; Rose et al., 1994).
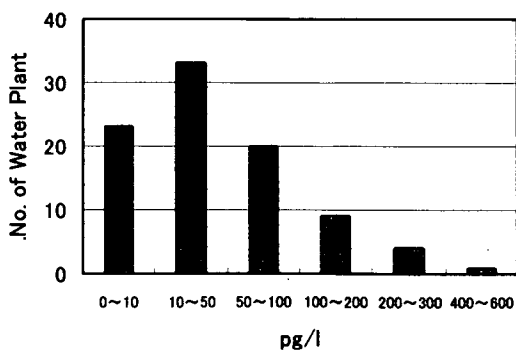

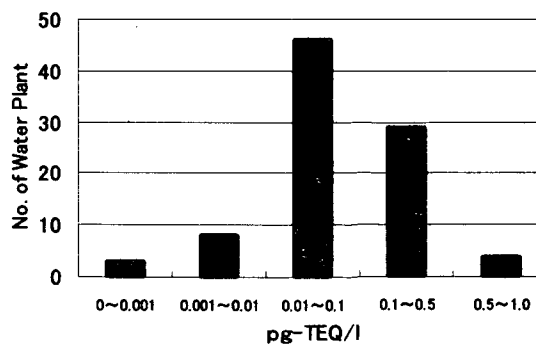
Fig. 2. Distribution dioxins in of raw water
as pg/l

Fig. 3. Distribution of dioxins in raw water
as pg-TEQ/L

As for the congener distribution of the total concentration of surface and ground water, total PCDDs were 45.33pg/L (70.0%) and 0.0076pg-TEQ/L (51.2%). Total PCDFs was

4.23pg/L (7.5%) and 0.0063pg-TEQ/L (42.4%). Total Co-PCBs was 12.71pg/L (22.5%) and 0.0094pg-TEQ/L (6.4%). The contribution of distribution varies depending on the types of "unit" used (pg/L or pg-TEQ/L). In terms of pg/L total PCDFs account for 7.5% of the total dioxins, whereas in terms of pg-TEQ/L account for 42.4% of total dioxins. OCDD (42.1%) and mono-ortho PCBs (20.9%) were predominant in terms of pg/L however, in terms of pg-TEQ/L the ratio of these homologues to total dioxins reduced from 42.1% to 1.6% for OCDD and 20.9% to 1.1% for mono-ortho PCBs.

In ground water, as the substituted number of chlorine increases from tetra to octa the concentrations of congeners decreased except OCDD. This result clearly indicates the relationship between the amount of chlorine in dioxins and the solubility of congeners in water. That is, the solubility of TeCDDs/DFs is 1,000 ~10,000 times higher than that of OCDD/DF. As regards the isomeric patterns, 1,3,6,8-TeCDD, 1,3,7,9-TeCDD, 2,4,6,8-TeCDF, 1,2,4,6,8,9-HxCDF, 1,2,3,4,6,7,9-HpCDD, OCDD and OCDF were the specific isomers in raw water. These isomers are present in herbicides such as CNP and PCP, which are ubiquitous in agricultural areas (Hagenmaier H. et al., 1987; Masunaga S., 1999).

3.2 Dioxins level after water treatment at water treatment plant

As we discussed in Fig. 2 and Fig. 3, concentration of total dioxins in treated water was one tenth as low as that of the raw water in pg/L value (Fig. 4). Dioxins levels for most of treated waters were below 0.1pg-TEQ/L (Fig. 5). However, dioxins were detected in two surface waters with concentrations ranging from 0.5 to 1.0 pg-TEQ/L. This concentration level is almost equal to the current maximum allowable dioxins level of 1 pg-TEQ/L (Japanese Environmental Agency, 1999).
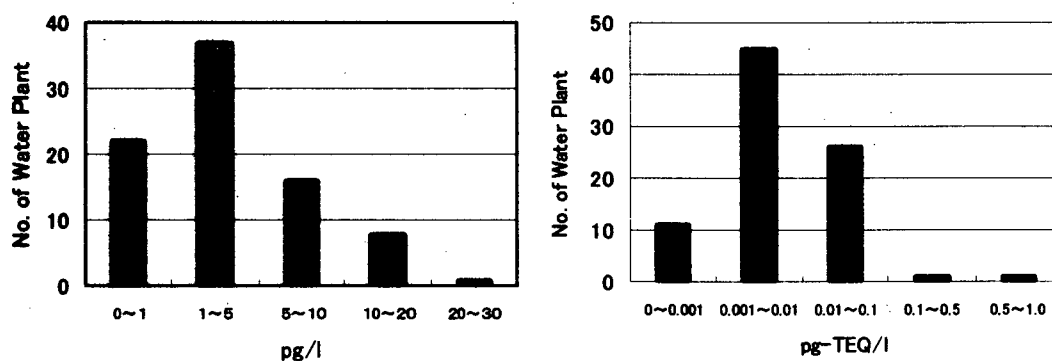

Fig. 4. Distribution of treated water PCDDs/DFs   Fig. 5. Distribution of treated water CDDs/DFs
and Co-PCBs concentration as pg/L   and Co-PCBs concentration as pg-TEQ/L

The concentrations of PCDDs/DFs and Co-PCBs of ground water after treatment was approximately 1/10 of the level determined for the surface water after treatment. This is close to the TEQ concentration levels found earlier in Japan (Miyata H., et al., 1993) but approximately 1/4 of the level determined for the sample in Canada (Birmingham M. et al., 1989).

The percentage of OCDD (42.1% as pg/L) to total dioxins in raw water decreased to 3.7% after water treatment On the other hand, the percentage (pg/L base) of mono-ortho PCBs (20.9%), TeCDDs (17.4%). and TeCDFs (2.0%) in raw water increased drastically to 47.1%, 28.0% and 10.7% after water treatment. In addition, the ratio of PCDFs (pg-TEQ/L to pg/L) in raw water has been only increased from 7.5% (pg/L) to 42.4% (pg-TEQ/L). However, the ratio of PCDFs (pg-TEQ/L to pg/L) in treated water has been drastically increased from 13.3% (pg/L) to 83.8% (pg-TEQ/L). This result shows that the chlorination in water treatment has influenced the formation of dioxins.

3.3 Effect of water treatment on the removal of dioxins

Figure 6 shows the removal rate of total PCDDs/DFs and Co-PCBs by drinking water treatment. The average removal rate of total dioxins in terms of pg/L value was about 93% whereas 87% of total dioxins in terms of pg-TEQ/L value were removed. This result means that most of dioxins and dioxin like compounds can be removed by drinking water treatment such as coagulation, sedimentation and filtration.

Figure 6 also shows that as the substituted number of chlorine increases, the removal rate also increases. This result is also in agreement with the report as the substituted number of chlorine increases it becomes harder to be dissolved in the water. Because of its characteristic, one can assume that it can be easily removed as its particulate state.

TECDDs, PeCDDS HxCDDS,HpCDDs,OCDD,TeCDFs,PeCDFS,HxCDFS,OCDF,nPCBs,mPCBs
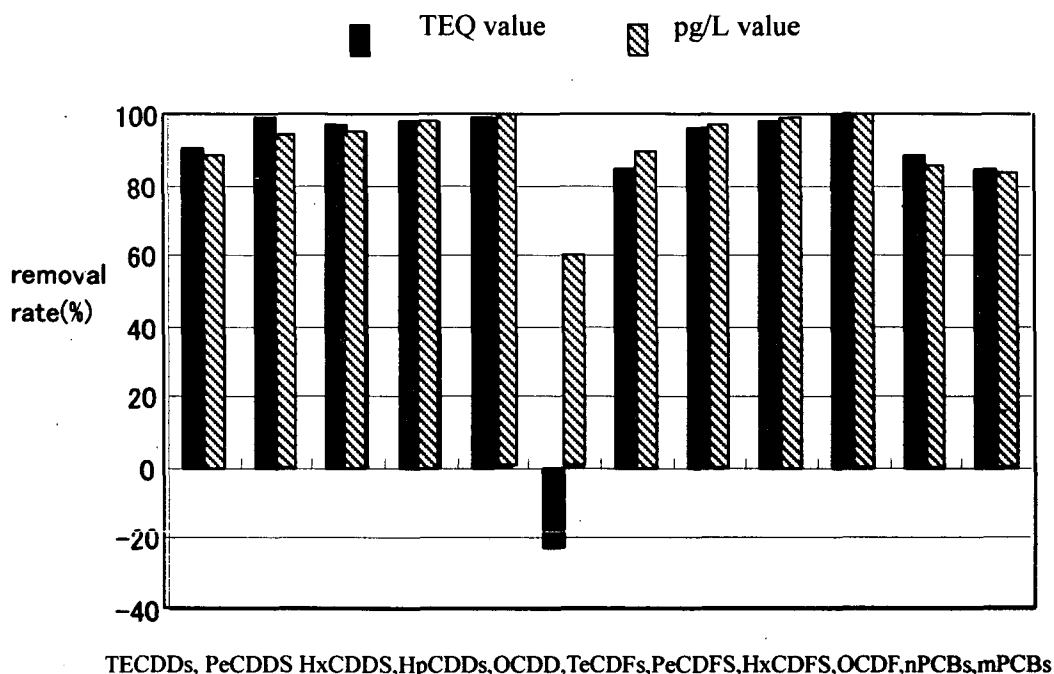
Fig. 6.   Removal rate of total dioxins concentration in the drinking
water treatment process: mean values of 42 water plants (84 samples)

As indicated in Figure 6, particularly in terms of pg-TEQ/L, removal rate of   TeCDFs was minus around 22%. The removal rate of TeCDFs in pg/L value was much lower than average. This reason is the removal rate of 1,2,7,8-TeCDF and 2,3,7,8-TeCDF were minus 14% and minus 22%, respectively. Out of 84 sampling site, the concentration of 1,2,7,8-TeCDF and 2,3,7,9-TeCDF increased in 9 sampling sites and 17 sampling site, respectively. This increase may be attributable to the reaction of chlorine with the precursors of dioxins such as dichlorophenol, trichlorophenol in the process of water treatment.

3.4 Contribution of particulates dioxins to total dioxins levels in raw water

The relationship between turbidity and total concentration (pg/L basis) of PCDDs/DFs and Co-PCBs is shown in Figure 7. It shows as turbidity (kaolin unit) increases, the total concentration of dioxins also increases in the raw water. This result is in agreement with the report that most of dioxins and dioxin like compounds is attached to particulates in raw water (Gotz et al., 1994).

To identify this result more clearly, as shown in table 1, both particulate dioxins

(separated by glass fiber filter) and soluble dioxins (separated by poly urethane foam) were determined and found out that the concentration ratio of particulate dioxins to total dioxins was 96.9% in one water plant and 91.5% in another water treatment plant. This result indicates that wise management of coagulation and sand filtration is necessary to improve the removal efficiency of particulate dioxins in drinking water treatment.
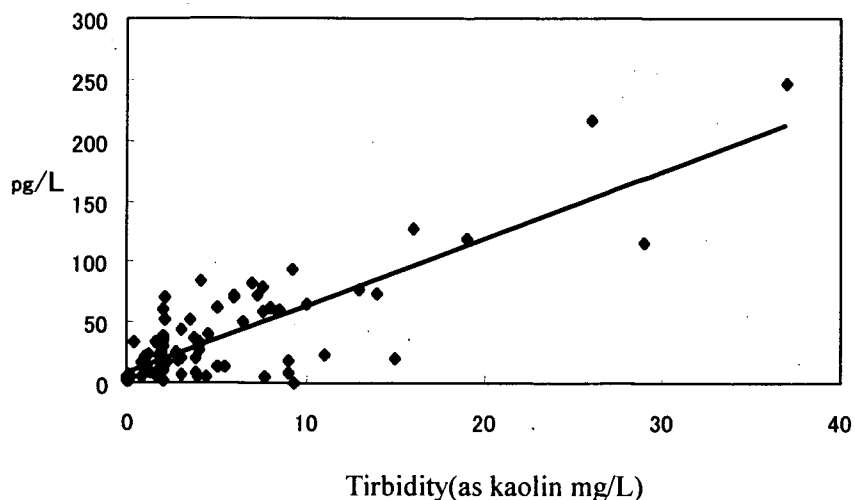

Tirbidity(as kaolin mg/L)

Fig. 7. Relationship between turbidity and total concentration of dioxins

Table 3. Ratio of particulates or soluble dioxins to total dioxins (unit: pg-TEQ/L)

Water plant	Type of dioxins	PCDDs/DFs	Co-PCBs	Total dioxins	Percentage (%)
A	Particulate	0.60	0.019	0.62	96.9
	Soluble	0.0087	0.018	0.020	3.1
B	Particulate	0.26	0.017	0.28	91.5
	Soluble	0.0023	0.0031	0.026	8.5

3.5 Effect of water treatment processes on the removal of total dioxins and homologues

The characteristic of congener on PCDDs/Fs and Co-PCBs was identified in 4 types of water treatment such as chlorination only for ground water (4 water plants, 8 samples), conventional rapid sand filtration (16 water plants, 32 samples), powered activated carbon adsorption with conventional rapid sand filtration (5 water plants, 10 samples) and ozonation followed by BAC (O_3/BAC) with conventional rapid sand filtration (5 water plants, 10 samples). Removal efficiency of total dioxins showed the lowest 87.3% in conventional rapid sand filtration, 89.3% in chlorination only for ground, 89.7% in O_3/BAC treatment and the highest 97% in powered activated carbon adsorption with conventional rapid sand filtration (Fig. 8). This result seems to indicate that powered activated carbon adsorption with conventional rapid sand filtration is more effective than O_3/BAC treatment with conventional rapid sand filtration to remove dioxins in water. In general, however, O_3 / GAC treatment are supposed to be more effective than powdered activated carbon to remove dioxins. Accordingly, it is more likely that BAC used for O_3/BAC treatment system was almost exhausted.

3.6 Origin attribution of dioxins in raw water

The major objective of principal components analysis (PCA) was to determine the PCDDs/DFs and Co-PCBs patterns in the raw water. The patterns were also compared with literature reports of patterns from known sources and from these comparisons; some preliminary observations could be made on potential sources for the PCDDs/DFs and Co-PCBs. Under the assumption that the largest sources of dioxin and dioxin like compounds, on a global scale, are pentachlorophenol (PCP) (S.J. Harrad et al., 1992), 1,3,5-trichloro-2- (4-nitrophenoxy) benzene (CNP) used as herbicide and various combustion sources (R.A. Hites, 1991), PCA was carried out using Stat Flex V5.0 software. The congener group concentrations of tetra- to octa-CDDs, tetra-to-octa-CDFs and non-ortho-, mono-ortho-PCBs as specific congeners were resulted from 37 isomers of PCDDs, 51 isomers of PCDFs and 14 isomers of Co-PCBs.

The results of PCA are shown in Table 4. The first PC is made up with HxCDDs, HpCDDs, OCDD, HxCDFs, HpCDFs, OCDF and its contribution is 64.9%. These specific congeners are representing the PCP due to high relation with five congeners, especially for 1,2,3,4,7,8,9-HpCDF, which were reported to the main constituents of PCDDs/DFs in PCP (Hagenmaier H. et al., 1987, Shigeki Masunaga, 1999). When we consider approximately 175,000 tons of PCP had been used in Japan in 1960s (Takeo Skurai et al., 1998), these specific congeners can be originated from PCP. The second PC is made up with TeCDDs, PeCDDs, TeCDFs, Co-PCBs representing CNP and its contribution is 16.4%. Specific isomers such as 1,3,6,8-TCDD, 1,3,7,9-TCDD and 2,4,6,8-TCDF resulting from herbicide chlorophenols, were reported as the main components of CNP, which had been used in Japan in 1970s (Yamagishi T. et al., 1981). In particular, non-and mono-ortho PCBs are the specific congeners but need to be further studied because the exact sources dioxin-like PCBs is still unknown. The third PC is made up with TeCDDs, PeCDDs, TeCDFs, HxCDFs and its contribution is 7.1%. These isomer patterns are similar to the results of airborne PCDDs/DFs reported in the United States (Eitzer B.D. and. Hites R.A., 1989). The cumulate rate of pesticide (PCP&CNP) was 81.3%. From this result, it can be thought most of Dioxins, Dibenzofurans and Co-PCBs are originated from pesticide not that atmosphere.

Table 4. Origin attribution of dioxins in raw water by PCA

Principal Component	Contribution Rate (%)	Cumulate Rate (%)	Specific Congeners		Matter of Origin
PC 1	64.9	64.9	HxCDDs, OCDD, HpCDFs,	HpCDDs HxCDFs OCDF	PCP
PC 2	16.4	81.3	TeCDDs, TeCDFs,	PeCDDs Co-PCBs	CNP
PC 3	7.1	88.4	TeCDDs, TeCDFs,	PeCDDs HxCDFs	Atmosphere
PC 4	5.3	93.7	TeCDDs, OCDD	PeCDDs	Uncertainty

PCP and CNP were used as herbicides in paddy fields after the plantation of young rice until 1970th and 1994, respectively. However, because of their carcinogencity there are not used in Japan. Both of them are synthesized for 2,4,6-trichlorophenol, therefore, it is reported that they content dioxins, especially 1,3,6,8-TeCDD.

Because it has been resulted that the contribution ratio of PCP and CNP to dioxins are high in surface water by multivalent statistical analysis. The amounts of them used in each prefecture are collected by the annual report of pesticides consumption. PCP has summed up its consumption from 1962 to 1986, and CNP has summed up from 1965 to 1995. The amounts of them are calculated by the consumption of marketed herbicide and their contents in the marketed herbicides.
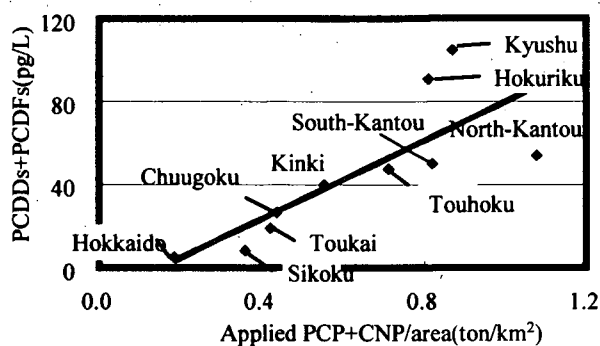

Figure 8 the relationship between Dioxins in raw water and applied herbicides in past

The amount of PCP and CNP in each prefecture was divided by the catchments area of each water source in order to assess the effect of them to dioxins in surface water. The relationship between PCP and CNP load to dioxins concentration is shown in Figure 8. The figure shows there is a clear relationship among them.

4. Conclusions

Raw and treated water samples were collected from 49-water treatment plants throughout Japan over three years. The water source for 44 of the water treatment plants is surface water and the remaining five water treatment plants are fed by ground water. The mean concentration of dioxins in raw water and treated water was 61pg/L (0.14pg-WHO-TEQ/L) and 4.0pg/L (0.015pg-WHO-TEQ/L), respectively. Location of water treatment plants not only significantly influenced the concentration level of dioxins but also resulted in different homologue patterns of dioxins. Levels of dioxins in ground water were much less than that of surface water in both raw and treated water.

The mean TEQ removal rate of dioxins by drinking water treatment was over 89%. It is the reason that the most of PCDDs/DFs and Co-PCBs are associated with the particulates that is easily removed by conventional treatment. However, the mean removal rate of 2,3,7,8-TeCDF by water treatment in the 143 samples was minus 12%. Therefore, to identify which process affected the level of 2,3,7,8-TeCDF, removal efficiencies at both the advanced and the conventional water treatment plant were investigated. For the TEQ removal rate across the processes, the dioxin congeners reduced remarkably after chlorination, in both an advanced and a conventional water treatment plant, were TeCDF and non-ortho-PCBs. From this study, it was clearly identified that the level of 2,3,7,8-TeCDF increased as a reaction in a chlorination.

The multivalent statistical analysis of dioxins congeners shows that most part of dioxin's origin comes from pesticides such as PCP and CNP. Although those pesticides have been restricted their use about ten years or more ago, they remains in agricultural fields and run-off into the water environments. Nevertheless, it is anticipated the dioxins relating with pesticides is gradually decreased. However, the highest concentration of them in raw water is close to the target concentration of drinking water quality, therefore, it is necessary the monitoring activities

of dioxins in specific catchments area used a large amount of pesticides and an appropriate water treatment such as an application of powdered activated carbon.

Acknowledgement

References

Birmingham B., Gilman A., Grant D., Salminen J., Bodington M., Thorpe B., Wile I., Toft P. and Amstrong V. (1989) PCDD/PCDF multimrdia exposure analysis for the Canadian population : Detailed exposure sestimation. *Chemosphere* 19 : 637-642.

Czuczwa JM, Hites RA (1984) Environmental fate of combustion-generated polychlorinated dioxins and furans. *Environ Sci. Technol.* 18 : 444-450.

Fiedler H, Schramm KW (1990) QSAR generated octanol-water partition coefficients of selected mixed halogenated dibenzodioxins and dibenxofurans. *Chemosphere* 20: 1597-1602.

Gotz R., Enge P., Friesel P., Roch K., Kjeller L.O., Klup S.E. and Rappe C. (1994) Sampling and analysis of water and suspended particulate matter of the river Elber for polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans(PCDFs). *Chemosphere* 28 : 63-74.

Hagenmaier H. and Brunner H. (1987) Isomerspecific analysis of pentachlorophenol and sodium pentachlorophenate for 2,3,7,8-substituted PCDD and PCDF at sub-ppb levels. *Chemosphere* 16 : 1759-1764.

Japanese Environmental Agency (1998) Gesuishorijouni kakaru daiokisinrui chousakekkani tsuite, kannkouchou kougai senmon shiryou.

Japanese Environmental Agency (1999) Environmental Standard Regulation of atmosphere, water and land contamination by dioxins. Notification No. 68 of Japanese Environmental Agency.

Magara Yasumoto, Aizawa Takako, Ando Masanoro, Morita Masatoshi, Ito Hiroyasu, Seki Yoshie and Mastumura Tohru (1999) Determination of low dioxins and PCB's concentration in ambient water using large volume "in situ" pre-concentration system. 19th international Symposium Halogenated Environmental Organic Pollutants POPs 40 : 205-210.

Masunaga Shigeki (1999) Nihonno kankyouchuu daiokisinwa nanini urai siteiruka. Mizujouhou, 19(12) : 4-11.

Miyata H., Aozasa O., Ohta S., Chang T. and Yasuda Y. (1993) Estimated daily intakes of PCDDs, PCDFs and Non-ortho coplanar PCBs via drinking water in Japan. *Chemosphere* 26 : 1527-1536.

Sakurai Takeo, Suzuki Noriyuki, Masunaga Shigeki and Nakanishi Junko (1998) Origin attribution of polychlorinated dibenzo-p-dioxins and dibenzofurans in sediment and soil from a Japanese fresh water lake area through congener-specific data analysis. *Chemosphere* 37(9-12) : 2211-2224.

Yamagishi T., Miyazaki T., Akiyama K., Morita M., Nakagawa J., Horii S. and Kaneko S. (1981) Polychlorinated dibenzo-p-dioxins and dibenzofurans in commercial diphenyl ether

herbicides, and in freshwater fish collected from the application area. *Chemosphere* 10 : 1137-1144.