COMBUSTION-ORIGINATED DIOXINS TRANSFERRING FROM ATMOSPHERIC TO WATER ENVIRONMENT BY RAINWATER RUNOFF IN SAITAMA, JAPAN

Minomo K[1]*, Ohtsuka N[1], Nojiri K[1], Matsumoto R[1], Kohata K[1]

[1]Center for Environmental Science in Saitama, 914 Kamitanadare, Kazo, Saitama 347–0115, Japan

Introduction

The concentrations of dioxins (referred to as PCDDs, PCDFs and dioxin-like (DL) PCBs in this study) in the ambient air have achieved the environmental quality standard for atmosphere at all monitoring sites throughout Japan since 2006.[1] However, dioxin concentrations in some river waters have continuously exceeded the environmental standard of water quality (1.0 pg-toxic equivalency (TEQ)/L).[1] The TEQs in some of the river waters exceeded the environmental standard only by the contribution of combustion-originated dioxins.[2] It is presumed that such combustion-originated dioxins in river water were transferred from the atmosphere.

Most discharge of dioxins to the environment in Japan was evaluated as the release from waste incineration to the atmosphere.[3] In order to evaluate the contribution of the transferred combustion-originated dioxins in river waters, we estimated dioxin concentration in water from reported discharge and precipitation, assuming that all dioxins released to the atmosphere were captured by rainwater (Table 1). The estimated values were 0.24 pg-TEQ/L for all over Japan in 2011, and 2.1 pg-TEQ/L for Saitama prefecture in 2012: The latter was two times higher than the environmental quality standard. The rain water containing the air deposition might make a significant impact on the dioxin concentrations in the water environment. Therefore, in this study, we examined the transfer of combustion-originated dioxins from atmospheric to water environment by rainwater in Saitama prefecture.

Table 1 Dioxin TEQ in rainwater estimated by using dioxin inventory and precipitation

Year	Precipitation (m^3)[a]		Dioxin discharge to the atmosphere (g-TEQ)		Estimated dioxin concentration in rain water (pg-TEQ/L)	
	Saitama pref.	All over Japan	Saitama pref.[4]	All over Japan[3]	Saitama pref.	All over Japan
1997	4.11×10^9	5.24×10^{11}	338[b]	8122[b]	82	15
1998	6.84×10^9	6.43×10^{11}	288[b]	4139[b]	42	6.4
1999	5.59×10^9	5.73×10^{11}	199[b]	3196[b]	36	5.6
2000	6.06×10^9	5.52×10^{11}	118[b]	2518[b]	20	4.6
2001	4.94×10^9	5.22×10^{11}	50[b]	2009[b]	10	3.8
2002	4.29×10^9	5.08×10^{11}	26[b]	973[b]	6.1	1.9
2003	5.30×10^9	5.59×10^{11}	16[b]	398[b]	3.0	0.71
2004	5.57×10^9	6.11×10^{11}	14[b]	367[b]	2.6	0.60
2005	4.94×10^9	4.90×10^{11}	16[b]	352[b]	3.3	0.72
2006	6.42×10^9	5.91×10^{11}	13[b]	315[b]	1.9	0.53
2007	4.62×10^9	4.86×10^{11}	13[b]	303[b]	2.8	0.62
2008	5.80×10^9	4.91×10^{11}	11[c]	222[c]	1.8	0.45
2009	4.94×10^9	5.25×10^{11}	9.4[c]	156[c]	1.9	0.30
2010	5.04×10^9	6.29×10^{11}	9.0[c]	158[c]	1.8	0.25
2011	5.21×10^9	5.89×10^{11}	9.1[c]	142[c]	1.7	0.24
2012	4.43×10^9	5.79×10^{11}	9.2[c]	–	2.1	–

[a] Precipitation volume was estimated using AMeDAS data (mm, Ref. 5) and the land area (3,768 km^2 for Saitama prefecture and 377,950 km^2 for all over Japan). [b] Based of WHO-1998 toxic equivalency factor (TEF, Ref. 6). [c] Based on WHO-2006 TEF (Ref. 7).

Materials and methods

Sample collection

Bulk (wet and dry) deposition samples were collected using three stainless-steel pots (40 cm in height and 30 cm in diameter) in Kazo-city, Saitama Prefecture throughout a year from February 8, 2012 to February 7, 2013. Each sampling was performed from the end of a rainfall event to the end of the next rainfall event. The Kazo-

city site is located in the eastern part of the prefecture and surrounded by paddy fields. Other sample collections were also carried out in parallel in Saitama-city (the southern part of the prefecture, urban area) and Yorii-town (the northern part of the prefecture, hilly area) four times during the period (May 16–23, July 23–August 7, October 19–24, and January 15–February 7).

Sample analysis

Prior to the extraction, $^{13}C_{12}$-labeled dioxin cleanup spikes were added to the water sample. The extraction, cleanup and dioxin detection were performed according to the way in the previous study[2] with some modification. The TEQ was calculated on the basis of WHO-2006 TEF.[7]

Results and discussion

Deposition flux and water concentration of dioxins

We obtained 61 water samples during a year (Fig. 1). The TEQ flux ranged from 2.0 to 35 pg-TEQ/m^2/d, and the total annual flux was 3.3 ng-TEQ/m^2/yr. This annual flux was much higher than that measured in Lagoon of Venice, Italy in 1998–1999 (0.47–0.73 ng WHO-1998-TEQ/m^2/yr; without DL-PCBs),[8] and was comparable to that measured in Matsuyama, Japan in 1995–1996 (3.2 ng I-TEQ/m^2/yr; without DL-PCBs),[9] in Daeyeon-dong and Gijang-gun, Korea in 2002 (2.1 and 1.7 ng I-TEQ/m^2/yr, respectively; without DL-PCBs)[10] and in Wushan, China in 2004–2005 (6.8–7.2 ng WHO-1998-TEQ/m^2/yr; without DL-PCBs).[11] The annual TEQ flux in Tokyo, an adjacent prefecture of Saitama, in 1996–1998 (17 ng I-TEQ/m^2/yr; without DL-PCBs)[12] was much higher than the value of this study; it is considered the decrease of dioxin discharge in the last 15 years (Table 1) was reflected. The dioxin concentrations of bulk deposition in rainwater ranged from 0.36 to 36 pg-TEQ/L; dioxin concentrations in 54 of 61 samples exceeded the environmental standard of the quality of the water. The annual average of TEQ in the rainwater including bulk deposition was 2.9 pg-TEQ/L.

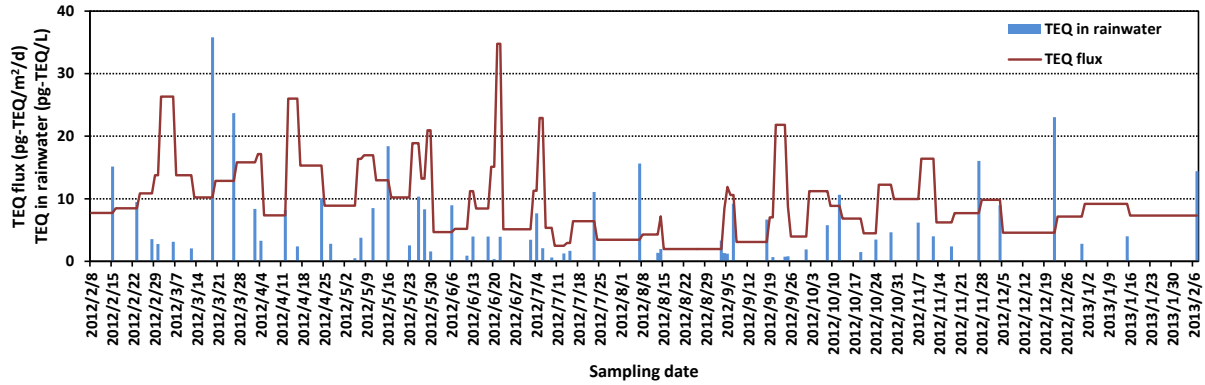

Fig. 1 TEQ of bulk deposition flux and TEQ in rainwater including bulk deposition in Kazo, Saitama.

TEQ apportionment

The method for apportionment of TEQs from the four major sources in Japan by using indicative congeners has been developed[13]—the four sources were combustion by-products, pentachlorophenol (PCP) formulations, chlornitrofen (CNP) formulations, and commercial PCBs. This method was applied to the water samples obtained in this work (Figure 2). The apportionment gave satisfactory solutions for all samples. The total TEQs estimated as the sum of the four sources were almost equal to the observed total TEQs: The average in the ratio of the estimated total TEQ to the measured total TEQ was 1.02 ± 0.08 SD. The combustion-originated TEQ contributed significantly (80% in annual average) to the TEQ of the water samples. This indicates that the most of the dioxins in the bulk deposition was derived from combustion process such as waste incineration. The annual average of the combustion-originated TEQ in the water samples was 2.3 pg-TEQ/L; this value was consistent with the value estimated from dioxin inventory in Saitama in recent years (1.7–2.1 pg-TEQ/L (2010–2012), Table 1). The combustion-originated TEQ fluxes at the Saitama-city site, the Yorii-town site and the Kazo-city site were 2.1–7.3 (average: 4.0) pg-TEQ/m^2/d, 1.6–4.5 (average: 2.6) pg-TEQ/m^2/d and 2.3–7.5 (average: 4.4) pg-TEQ/m^2/d, respectively. The fluxes at three sites were comparable, indicating the levels of

waste-incinerator-derived dioxins in the air were almost equal at any site within the prefecture. Therefore, it can be regarded that the most of the dioxins discharged to the air from waste incinerators in Saitama prefecture roughly transferred as bulk depositions to the land inside the prefecture. There must be transportations of the atmosphere from/to the adjacent prefectures such as Tokyo, Chiba and Gunma. However, it is assumed that the amount of dioxins from the adjacent prefectures to Saitama and that from Saitama to the adjacent prefectures were almost equal, and the influence of the atmosphere transportations was negligible. The most of dioxins in water exist in suspended solid (SS).[2] Therefore, the bulk-deposition dioxins make little influence on the water quality of a river in an unpaved area such as farmlands and forests, because the rainwater soaks into the ground and the SS is filtered by the soil and is removed from the water. On the other hand, in a river that has much paved ground in the basin, much of rainwater including SS might directly flow into the river, and the bulk-deposition dioxins influence on the water quality.

The herbicide (PCP and CNP) originated TEQ was found in some samples. Possible causes of the influence of herbicides were rice-straw burning on the paddy fields[14] and suspension of paddy-field soil in the air. The contribution of dioxins originated from commercial PCBs to the TEQ was negligible.

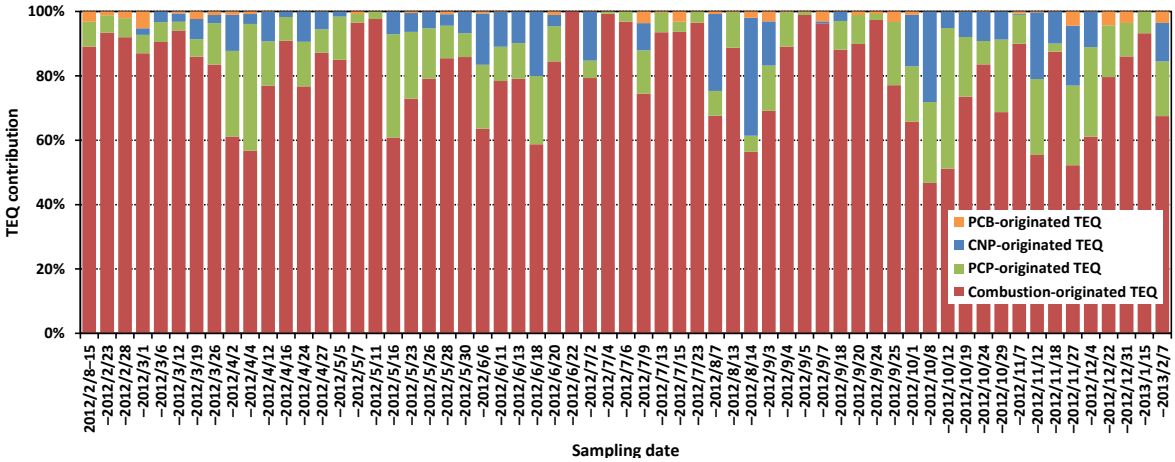

Fig. 2 TEQ contribution of the four major dioxin sources for the bulk deposition samples by using indicative congeners.[13]

Estimation of the impact of combustion-originated TEQ on river water

The impact of combustion-originated dioxins from the air to the water of Ayase River—one of the most polluted rivers by dioxins in Japan—was estimated. The river starts its flow from the northeastern part of Saitama prefecture and flows to south and then reaches to Tokyo metropolitan: There is much paved ground around the mid to downstream area. In the river basin, there is no facility for discharging waste water that can influence on the dioxin concentration of the river water. In a previous study, we have analyzed the river water once per month for a year (April 2004–May 2005) and revealed the level of dioxins and their sources.[2] On the basis of the result in the previous paper[2] and water quantity data,[15] the annual average of combustion-originated TEQ in the river water in April 2004–May 2005 is calculated at 0.70 pg-TEQ/L.

The water quantity of Ayase River sharply increased at the time of rainfall; these increases were caused by runoff of rainwater. The annual quantity of the river water and that of runoff rainwater in April 2004–May 2005 was 1.34×10^8 m^3/yr; the quantity of the runoff rainwater was estimated at 2.99×10^7 m^3/yr. If it is assumed that the runoff rainwater contained 2.6–3.3 pg-TEQ/L, the estimated dioxin TEQ in rainwater in Saitama in 2003–2005 (Table 1), the annual average of combustion-originated TEQ in the river water was 0.58–0.74 pg-TEQ/L (Fig. 3a). The calculated values were consistent with the observed value of 0.70 pg-TEQ/L. This suggests that the combustion-originated dioxins in the water of Ayase River mainly consist of the rainwater including bulk deposition.

In a manner similar to the above, the annual quantity of the river water in 2012 was 1.16×10^8 m^3/yr; and the quantity of the runoff rainwater was estimated at 2.23×10^7 m^3/yr. By using the estimated TEQ in rainwater in 2010–2012 (1.7–2.1 pg-TEQ/L; Table 1), the combustion-originated TEQ in the river water were calculated at 0.33–0.40 pg-TEQ/L (Fig. 3b). The calculated TEQs amounted to 40% of the environmental standard of water quality.

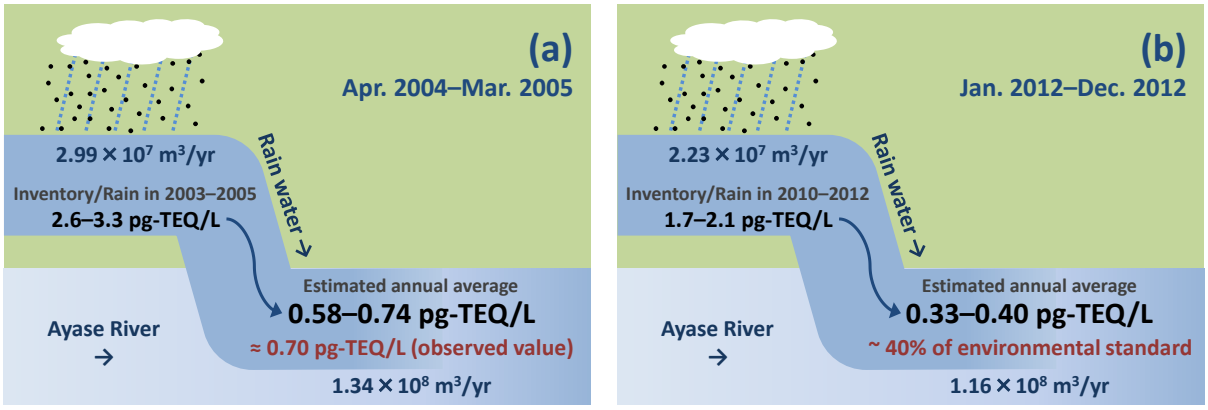

Fig. 3 Estimation of the impact of combustion-originated TEQ on the water of Ayase River.

Conclusions

Combustion-originated dioxin TEQ in rainwater including bulk deposition in Saitama, Japan was much higher than the environmental standard of water quality, whereas the environmental standard of the ambient air quality has been achieved. It is suggested the air deposition has a considerable influence upon the dioxin concentration of some river water.

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