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Influence of combustion-originated dioxins in atmospheric deposition on water quality of an urban river in Japan

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ABSTRACT

Bulk (wet and dry) deposition samples were collected in Saitama Prefecture, Japan throughout a year (February 8, 2012 to February 7, 2013) to estimate the influence of dioxins emitting from waste incinerators on river water quality. The annual deposition flux of dioxins was 3.3 ng-toxic equivalent (TEQ)/m^2/year. Source identification using indicative congeners estimated that 82% of dioxin TEQ in the bulk deposition (2.7 ng-TEQ/m^2/year) was combustion-originated, indicating that most of the dioxins in the deposition were derived from waste incinerators. In Saitama prefecture the annual flux of combustion-originated dioxins in depositions was apparently consistent with that of dioxin emission into the air from waste incinerators. The TEQ of combustion-originated dioxins in the deposition per rainfall was 2.4 pg-TEQ/L on annual average, exceeding the environmental quality standard (EQS) for water in Japan of 1 pg-TEQ/L. This suggests there is a possibility that dioxins in atmospheric deposition have a significant influence on the water quality of urban rivers which rainwater directly flows into because of many paved areas in the basins. The influence of combustion-originated dioxin in the deposition on the water quality of Ayase River, an urban river heavily polluted with dioxins, was estimated at 0.29 pg-TEQ/L on annual average in 2015. It seems that dioxins in atmospheric deposition from waste incinerators have a significant influence on water quality of some urban rivers *via* rainwater though the dioxins in the ambient air have achieved the EQS for atmosphere at all monitoring sites in Japan.

Introduction

In the 1990s, environmental pollution by polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DL-PCBs) (these compounds are referred to as dioxins in this study) emitted from waste incinerators was a serious problem in Japan. To reduce the dioxin emission, the Law Concerning Special Measures against Dioxins (Environment Agency of Japan, 1999) enacted in 1999 and went into effect in 2000. The dioxin emission had been drastically reduced after the Law (MOE, 2016b). The concentrations of dioxins in the ambient air have achieved the environmental quality standard (EQS) for air of 0.6 pg-toxic equivalent (TEQ)/m^3 at all monitoring sites throughout Japan since 2006; however, dioxin concentrations in some river waters have continuously exceeded the EQS for water of 1 pg-TEQ/L (MOE, 2001, 2002, 2003, 2004, 2005, 2006, 2007, 2008, 2009, 2010, 2012, 2013, 2014, 2015, 2016a). Ayase River, which is an urban river flowing from the eastern part of Saitama prefecture to Tokyo Bay *via* Tokyo metropolitan, is one of such rivers. Dioxins in the water of Ayase River have been largely accounted for by herbicide-originated dioxins

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followed by combustion-originated ones (Minomo et al., 2011b). A large amount of pentachlorophenol (PCP) and Chlornitrofen (CNP, 4-nitrophenyl-2,4,6-trichlorophenyl ether) formulations was widely used as herbicides for the paddy fields in Japan, and the herbicides contained dioxins as impurities (Masunaga et al., 2001; Seike et al., 2003). The herbicide-originated dioxins still remain in the soil of paddy fields (Seike et al., 2003; Kiguchi et al., 2007), and the dioxins flow from paddy fields into the surrounding catchments (Seike et al., 2007). The herbicide-originated dioxins in the water of Ayase River are also derived from runoff water from paddy fields (Minomo et al., 2011b). On the other hand, it is presumed that combustion-originated dioxins in the river water are transferred from waste incinerators through the atmosphere. However, it is not well understood how much dioxins derived from waste incinerators affect water quality in these days when the dioxin emission from incinerators is controlled.

Most of the dioxin discharge to the environment in Japan has been evaluated as the emission from waste incinerators into the air (MOE, 2016b). Assuming that all dioxins emitted to the air were captured by rainwater, we estimated dioxin concentration in rainwater in Saitama Prefecture by using the data of dioxin discharge (Saitama Prefectural Government, 2017) and rainfall (JMA web site) (Table 1). The estimated values have been higher than the EQS for water, implying there is a possibility that combustion-originated dioxins in atmospheric deposition have a significant influence on the water quality of smaller rivers which rainwater directly flows into. Thus, in this study, we measured the dioxins in the atmospheric deposition and estimated the influence of the combustion-originated dioxins *via* runoff rainwater on water quality of an urban river.

Table 1 – Dioxin emission flux in Saitama, Japan.

Year	Dioxin inventory (g-TEQ/year) [a]	Rainfall (mm) [b]	Emission flux (ng-TEQ/m^2/year) [c]	Emission flux per rainfall (pg-TEQ/L)
1997	338.2	1085	90	83
1998	287.7	1841	76	41
1999	199.2	1553	53	34
2000	118.2	1404	31	22
2001	49.8	1551	13	8.5
2002	26.3	1448	7.0	4.8
2003	16.1	1389	4.3	3.1
2004	14.4	1490	3.8	2.6
2005	16.2	1310	4.3	3.3
2006	12.5	1525	3.3	2.2
2007	12.8	1299	3.4	2.6
2008	10.7	1519	2.8	1.9
2009	9.4	1248	2.5	2.0
2010	9.0	1485	2.4	1.6
2011	9.1	1534	2.4	1.6
2012	9.2	1328	2.4	1.8
2013	6.8	1305	1.8	1.4
2014	8.4	1571	2.2	1.4
2015	7.5	1389	2.0	1.4

TEQ: toxic equivalent.
[a] Emission into the air; data were cited from Saitama Prefectural Government (2017); TEQ values from 1997 to 2007 were based on WHO-1998 TEF (Van den Berg et al., 1998) and those from 2008 to 2015 were based on WHO-2006 TEF (Van den Berg et al., 2006).
[b] Rainfall data were openly available on the web (JMA web site). Values are the average of 14 AMeDAS rainfall stations in Saitama (Fig. 1).
[c] Calculated by the land area of Saitama prefecture (3768 km^2).

1. Materials and methods

1.1. Sample collection

The locations where atmospheric deposition samples were collected, Kazo-city, Saitama-city and Yorii-town in Saitama prefecture, are shown in Fig. 1. The Kazo-city (latitude: 36.0848° north, longitude: 139.5609° east), located in the eastern part of the prefecture and surrounded by paddy fields, is the main sampling site where sample collections were performed throughout a year from February 8, 2012 to February 7, 2013. In addition to the Kazo-city site, other sample collections were also carried out in parallel at Saitama-city site (latitude: 35.8689° north, longitude: 139.6136° east; urban area) and Yorii-town site (latitude: 36.0973° north, longitude: 139.2191° east; hilly area) four times during the period (May 16–23, July 23–August 7, October 19–24, and January 15–February 7).

Bulk (wet and dry) depositions were collected as water samples by using three stainless-steel vessels (40 cm in height and 30 cm in diameter) in accordance with the previous studies (Seike et al., 1998; Moon et al., 2005). It is assumed that dioxins from waste incinerators fall to the surface of the ground, then flow into rivers with rainwater. Thus, each sample collection was performed from the end of a rainfall event to the end of the next rainfall event. The rainfall was monitored at Kazo-city site.

1.2. Dioxin analysis

The analysis of dioxins in the deposition (water) samples was performed in accordance with the official method for water quality designated by JSA (2005). Prior to the dioxin extraction, acetone (Kanto Chemical, Japan) solution of $^{13}C_{12}$-labeled dioxin cleanup spikes (17 2,3,7,8-chlorine-substituted PCDDs/PCDFs and 12 DL-PCBs; Wellington Laboratories, Canada) were added to the water sample. The water was filtrated by glass fiber filters (GFFs; GC-50H 142 mm, ADVANTEC, Japan). The filtrate was passed through 2 pieces of polyurethane foam plugs (PUFs; 90 mm in diameter, 50 mm in tall; SIBATA, Japan) which are usually used for the collection of dioxins in the air. In addition to octadecyl group-modified extraction disc, the official method (JSA, 2005) approves PUF using for the solid phase extraction. Because PUF is easy to handle, we used it for solid phase extraction. The emptied stainless-steel vessels were rinsed with acetone, and the GFFs and the PUFs were Soxhlet extracted with toluene (Kanto Chemical) for 24 hr. The vessel rinsed solution and the GFF/PUF extract were combined and subjected to the cleanup procedure.

The cleanup procedure and dioxin detection were performed according to the way in the previous study (Minomo et al., 2011b). In brief, the extract was treated with concentrated sulfuric acid (Wako Pure Chemical Industries, Japan)

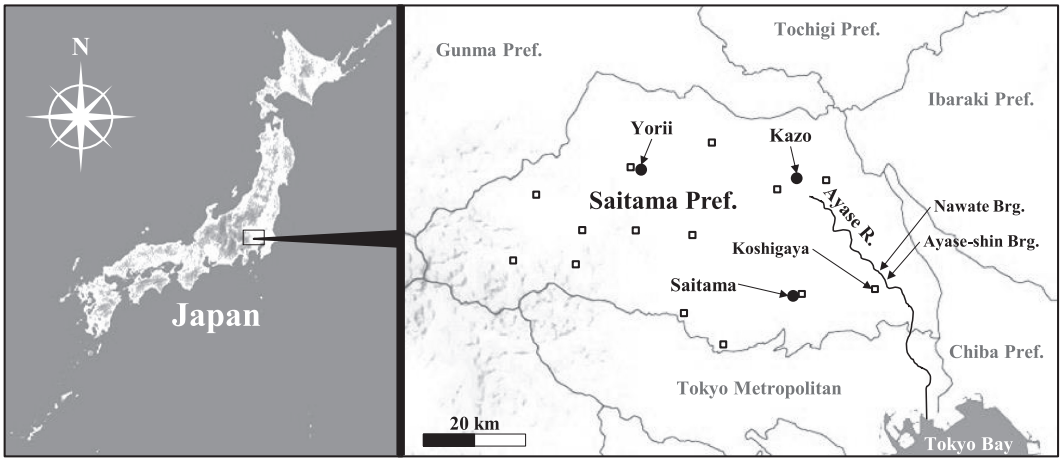

Fig. 1 – Sampling location. Filled circle: sampling site; open square: rainfall monitoring station (JMA web site).

followed by 44% sulfuric acid-impregnated silica gel (Wako Pure Chemical Industries). Then column chromatography was performed by 10% silver-nitrate impregnated silica gel (Wako Pure Chemical Industries) followed by an active-carbon dispersed silica gel column (Kanto Chemical). The treated solution was concentrated, and syringe spikes (8 $^{13}C_{12}$-labeled dioxins, Wellington Laboratories) were added to the concentrated solution. All the reagents used in this study were dioxin analysis grade except concentrated sulfuric acid (super special grade).

Instrumental analysis was performed by a high-resolution gas chromatograph/mass spectrometer (Agilent 7890 (Agilent Technologies, USA) + JMS-800D (JEOL, Japan)). Congeners from tetra- to hexa-chlorinated PCDDs/PCDFs were separated by a chromatographic column CP-Sil88 for Dioxins (Agilent Technologies) and those from hepta- to octa-chlorinated PCDDs/PCDFs and DL-PCBs were separated by a chromatographic column DB-5 ms (Agilent Technologies).

1.3. Quality assurance and quality control

Dioxins in the operational blank samples were negligible levels. The TEQ was calculated on the basis of toxicity equivalency factor (TEF) established by the World Health Organization (WHO) in 2006 (WHO-2006 TEF; Van den Berg et al., 2006). The detection limits were estimated depending on the sampling span. The concentrations less than the detection limits were considered to be zero. The recovery of the cleanup spikes was satisfactory and the recovery rates ranged within 50%–120% (PCDDs: 58%–102%, PCDFs: 51%–108%, and DL-PCBs: 51%–105%) which is required by the official method (JSA, 2005).

1.4. Dioxin-source identification

A method for dioxin-source identification developed by Minomo et al. (2010) was applied to the deposition samples to estimate the TEQ contributions of the four major dioxin sources in Japan (PCP formulations, CNP formulations, PCB products, and combustion by-products). This method gives the apportionment of WHO-2006 TEQ of dioxins in environmental samples by using only the concentrations of five indicative congeners (2,3,4,7,8-pentachlorodibenzofuran, 1,2,3,7,8-pentachlorodibenzo-*p*-dioxin, 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin, and International Union of Pure and Applied Chemistry Nos. #126- and #105-PCBs). The method has achieved some positive results in dioxin-source identification in Japan (Kishida, 2013; Kubo and Tabira, 2013; Minomo et al., 2011a, 2011b, 2011c; Ohtsuka et al., 2011).

2. Results and discussion

2.1. Dioxin fluxes

Fig. 2 shows the deposition fluxes for dioxin TEQ at Kazo-city site; the detailed congener information and rainfall are shown in Table S1. Sixty-one samples were obtained during the period. Each sampling span and rainfall ranged from 0.9 to 23 days and from 2.0 to 146 mm (total: 1116 mm), respectively. The dioxin fluxes at Kazo-city site had a range and annual total of 370–7000 pg/m^2/day and 560 ng/m^2/year, respectively. The TEQ flux ranged from 1.8 to 35 pg-TEQ/m^2/day, and the annual flux was 3.3 ng-TEQ/m^2/year. In Table 2, the annual TEQ flux was compared with the literature data of other regions. As shown, the flux of this study was higher than that measured in the Lagoon of Venice, Italy (Guerzoni et al., 2004), and was comparable to that measured in Porto Marghera, Italy (Rossini et al., 2005), in Busan, Korea (Moon et al., 2005), in Wushan, China (Ren et al., 2007), in Matsuyama, Japan (Seike et al., 1998), and in Kanazawa, Japan (Oka et al., 2006). The annual TEQ flux in Tokyo, an adjacent prefecture of Saitama, in 1996–1998 (Ogura et al., 2001) was much higher than the flux of this study; it is considered the decrease of dioxin discharge in the last 15 years (MOE, 2016a) was reflected. In this study, the dioxin TEQ per rainfall ranged from 0.36 to 36 pg-TEQ/L: the TEQs of 54 of 61 samples exceeded the EQS for water (1 pg-TEQ/L). The annual deposition flux of TEQ per rainfall was 2.9 pg-TEQ/L.

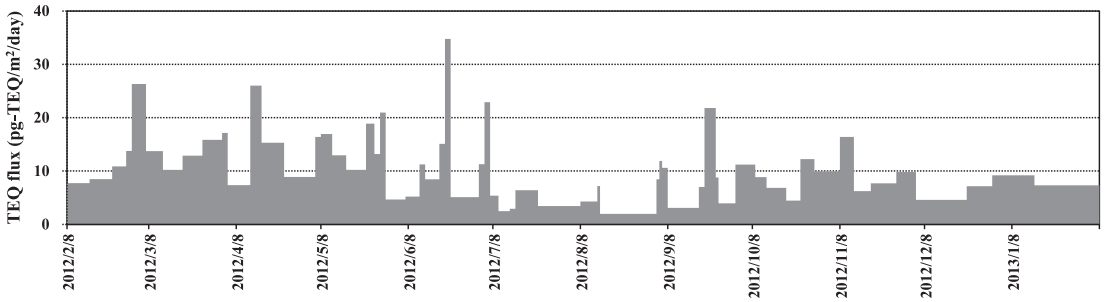

Fig. 2 – Dioxin deposition flux in the bulk deposition collected at Kazo-city site.

Table 2 – Comparison of atmospheric deposition fluxes of dioxin TEQs (ng-TEQ/m^2/year) in other regions.

Location	Sampling period	TEQ fluxes [a]	TEF [b]	References
Lagoon of Venice, Italy	1998–1999	0.47–0.73*	1998	Guerzoni et al. (2004)
Porto Marghera, Italy	2003–2004	0.77–4.4*	1998	Rossini et al. (2005)
Busan, Korea	2002	1.7–2.1*	I	Moon et al. (2005)
Wushan, China	2004–2005	7.3*	1998	Ren et al. (2007)
Matsuyama, Japan	1995–1996	3.2*	I	Seike et al. (1998)
Tokyo, Japan	1996–1998	17*	I	Ogura et al. (2001)
Kanazawa, Japan	2003–2004	2.8*	1998	Oka et al. (2006)
Saitama, Japan	2012–2013	3.3	2006	This study

TEQ: toxic equivalent; TEF: toxicity equivalency factor.
[a] *: DL-PCBs are not included.
[b] I: International-TEF (NATO/CCMS, 1988); 1998: WHO-1998 TEF (Van den Berg et al., 1998); 2006: WHO-2006 TEF (Van den Berg et al., 2006).

2.2. Source identification

The above-mentioned method for source identification (Minomo et al., 2010) was applied to the deposition samples. The result of the application was satisfactory because the estimated total TEQs were almost equal to the measured total TEQs: the average in the ratio of the estimated total TEQ to the measured total TEQ was 1.06 ± 0.12. Fig. 3 shows the TEQ contribution of the four major dioxin sources in the deposition samples collected at Kazo-city site. The annual averages in the TEQ contribution of each source were 82%, 13%, 4.8% and 0.4% for combustion by-products, PCP formulations, CNP formulations and PCB products, respectively. The combustion-originated TEQ contributed significantly to the TEQ of the samples, indicating that most of the dioxins in the bulk deposition were derived from combustion processes such as waste incineration. The herbicide (PCP and CNP) originated TEQ was found in some samples. Possible causes of the influence of herbicides are rice-straw burning in the paddy fields (Minomo et al., 2011a) and a rise of paddy-field soil by the wind. The contribution of dioxins originated from commercial PCBs to the TEQ was minimal. The annual flux of the combustion-originated TEQ in the deposition samples was 2.7 ng-TEQ/m^2/year; this value was

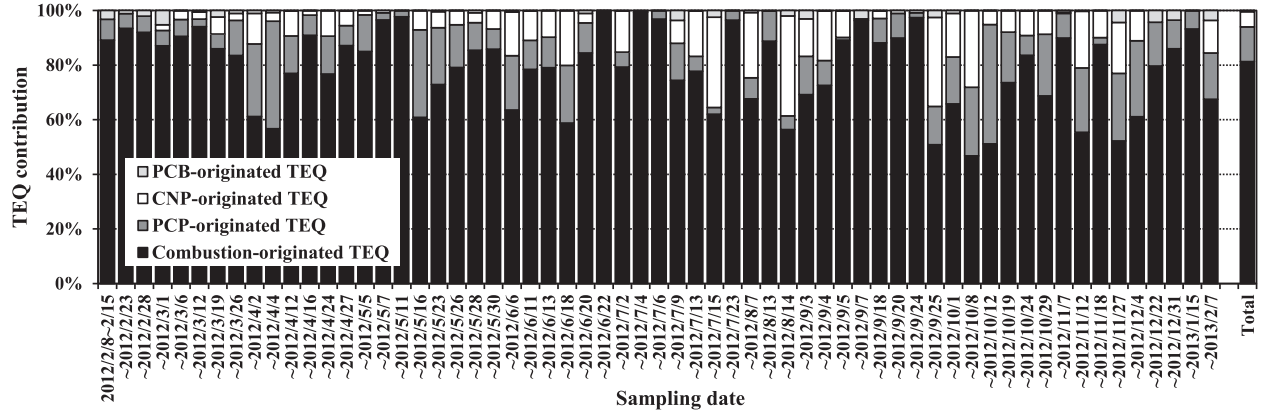

Fig. 3 – Contributions of the four major dioxin sources to TEQ of deposition samples collected at Kazo-city site. TEQ: toxic equivalent.

consistent with the value estimated from dioxin discharge into the air in Saitama in 2012 (2.4 ng-TEQ/m^2/year; Table 1). The TEQs in the depositions per rainfall ranged from 0.30 to 31 pg-TEQ/L; the TEQ per rainfall was roughly proportional to the sampling span and inversely proportional to the rainfall. The annual TEQ in the depositions per rainfall was 2.4 pg-TEQ/L (the value is 2.0 pg-TEQ/L if it uses the average rainfall in Saitama of 1328 mm). This was comparable to the estimated concentration in 2012 (1.8 pg-TEQ/L; Table 1). Therefore, there is a possibility that combustion-originated dioxins in atmospheric deposition have a significant influence on the water quality of small rivers which rainwater directly flows into.

Regarding the results of parallel sample collection performed four times at three sites in the prefecture, the combustion-originated TEQ fluxes at Saitama-city site, Yorii-town site and Kazo-city site were 2.1–7.2 (average: 4.7), 1.2–4.4 (average: 2.6) and 2.3–7.5 (average: 4.6) pg-TEQ/m^2/day, respectively (Table S2). The combustion-originated TEQ fluxes at three sites were comparable, suggesting the levels of waste incinerator-derived dioxins in the atmospheric deposition were roughly equal at any site within the prefecture. Therefore, in Saitama prefecture, the annual deposition flux of waste incinerator-derived dioxins in atmospheric deposition is apparently same as the annual emission flux of dioxins discharged into the air. There must be transportations of the atmospheric dioxins from or to the adjacent prefectures of Saitama such as Tokyo, Chiba and Gunma (Fig. 1); however, the amount of those dioxins is probably negligible.

2.3. Estimation of the influence of combustion-originated TEQ in atmospheric deposition on river water quality

Most of dioxins in water environment exist in suspended solid (SS) (Kobayashi et al., 2003; Minomo et al., 2011b). Therefore, in an unpaved area such as farmlands and forests, the bulk deposition dioxins must make little influence on the water quality of a river, because the rainwater soaks into the ground and the SS is filtered by the soil and removed from the water. On the other hand, in a river that has much paved ground in the basin, much of rainwater including SS directly flows into the river, and the bulk deposition dioxins influence the water quality. We estimated the influence of combustion-originated dioxins in bulk deposition on the water quality of Ayase River — one of the rivers heavily polluted with dioxins in Japan (MOE, 2001, 2002, 2003, 2004, 2005, 2006, 2007, 2008, 2009, 2010, 2012, 2013, 2014, 2015, 2016a). There are many paved areas around the middle to lower part of the river basin, and the rainwater in the basin directly flows into the river. In a previous study, we have analyzed the river water every month for a year (April 2004–March 2005) at Ayase-shin Bridge (Fig. 1) and revealed the level of dioxins and TEQ contributions of the four major sources (Minomo et al., 2011b). On the basis of the TEQ contributions (Minomo et al., 2011b) and monthly water quantity of the river at Nawate Bridge (the nearest water quantity monitoring station to Ayase-shin Bridge; Fig. 1) (MLIT web site), the annual average of combustion-originated TEQ in the river water from April 2004 to March 2005 was calculated at 0.70 pg-TEQ/L: the monthly combustion-originated TEQ and the river water quantity were shown in Table S3.

It is difficult to accurately estimate the amount of deposition flowing into a river at each rain event because there are many factors to be considered such as rain quantity, rainfall intensity, land inclination, and so on. Smaller amount of rainwater contains the deposition at higher concentration, but it is hard to flow out from the surface of the ground; on the other hand, larger amount of rainwater contains the deposition at lower concentration, but it is easy to flow out. In the long run, it is assumed the deposition should be washed from the surface of the ground. Therefore, in order to grasp the general overview of the influence of combustion-derived dioxins on the water quality, we examined a simple model assuming runoff rainwater contains the estimated concentration of dioxins (Table 1) throughout a year. The water quantity of Ayase River from April 2004 to March 2005 was illustrated in Fig. 4a. The water quantity of the river sharply increased at the time of rainfall; these sharp increases were caused by runoff rainwater. The annual quantity of the river water from April 2004 to March 2005 was 1.3×10^8 m^3/year, and the annual quantity of the runoff rainwater in the same period was estimated at 3.3×10^7 m^3/year (Fig. 4a). If it is assumed that the runoff rainwater contained 2.6–3.3 pg-TEQ/L — the estimated dioxin TEQ in rainwater in 2004–2005 (Table 1), the annual average of combustion-originated TEQ in the river water was 0.64–0.81 pg-TEQ/L (Fig. 4b). This estimated annual

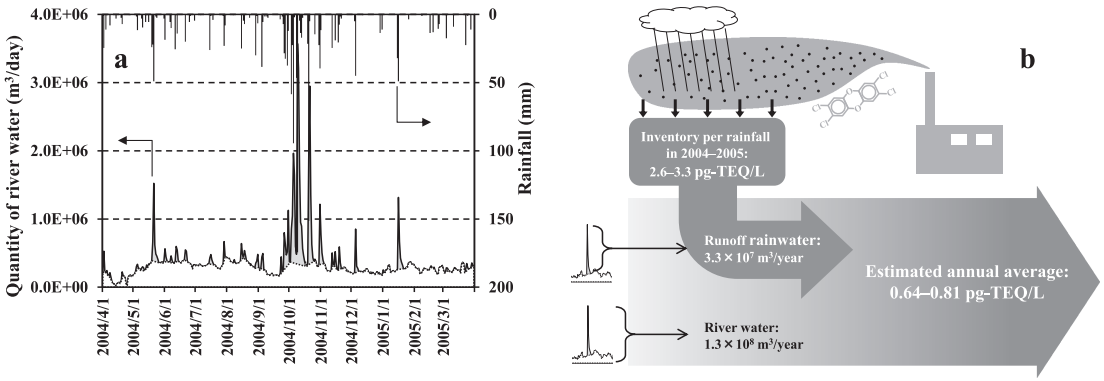

Fig. 4 – Influence of combustion-originated TEQ on the water quality of Ayase River in 2004–2005. (a) River water quantity at Nawate Bridge (MLIT web site) and rainfall at Koshigaya (JMA web site), (b) estimation of the influence. TEQ: toxic equivalent.

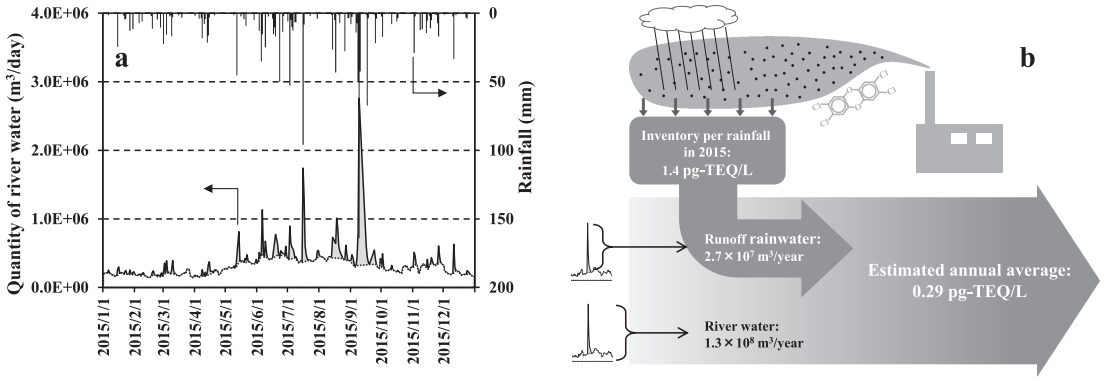

Fig. 5 – Influence of combustion-originated TEQ on the water quality of Ayase River in 2015. (a) River water quantity at Nawate Bridge (MLIT web site) and rainfall at Koshigaya (JMA web site), (b) estimation of the influence. TEQ: toxic equivalent.

concentration was consistent with the above-mentioned observed value of 0.70 pg-TEQ/L, suggesting the combustion-originated dioxins in the water of Ayase River mainly consist of the rainwater including bulk deposition. This simple model seems to be suitable for estimating the influence of dioxins in atmospheric deposition on the water quality of Ayase River.

In a manner similar to the above, current influence of combustion-originated dioxins in depositions to the river water quality was estimated. The annual quantity of the river water in 2015 was 1.3×10^8 m^3/year; and the quantity of the runoff rainwater was estimated at 2.7×10^7 m^3/year (Fig. 5a). By using the estimated TEQ in rainwater in 2015 (1.4 pg-TEQ/L; Table 1), the combustion-originated TEQ in the river water was calculated at 0.29 pg-TEQ/L (Fig. 5b). This value amounted to approximately 30% of the EQS for water and is unignorably level. It is suggested that dioxins emitted from waste incinerator to the air have considerably influenced water quality of urban rivers *via* atmospheric deposition though the dioxins in the ambient air have achieved the EQS for atmosphere at all monitoring sites in Japan.

3. Conclusions

In order to elucidate the influence of combustion-originated dioxins from waste incinerators on river water quality, we collected bulk deposition samples in Saitama Prefecture, Japan throughout a year (February 8, 2012 to February 7, 2013). The annual deposition flux of dioxins was 3.3 ng-TEQ/m^2/year. Source identification using indicative congeners estimated that 82% of dioxin TEQ in the bulk deposition (2.7 ng-TEQ/m^2/year) was combustion-originated, indicating that most of the dioxins in the deposition were derived from waste incinerators. The annual flux of combustion-originated dioxins in depositions was apparently consistent with that of dioxin discharge into the air from waste incinerators in Saitama prefecture. The TEQ of combustion-originated dioxins in the deposition per rainfall exceeded the EQS for water of 1 pg-TEQ/L. The influence of combustion-originated dioxin in the deposition on the water quality of Ayase River – an urban river heavily polluted with dioxins – was estimated at 0.29 pg-TEQ/L on annual average in 2015. It seems that dioxins from waste incinerators have a significant influence on water quality of some urban rivers *via* atmospheric deposition though the dioxins in the ambient air have achieved the EQS for atmosphere at all monitoring sites in Japan.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2017.06.027.

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