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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)

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