

JES

JOURNAL OF
ENVIRONMENTAL
SCIENCES

ISSN 1001-0742
CN 11-2629/X

March 1, 2013 Volume 25 Number 3
www.jesc.ac.cn

PM_{2.5}

PM₁₀

OC

EC

PM_{2.1}



Sponsored by
Research Center for Eco-Environmental Sciences
Chinese Academy of Sciences

CONTENTS

Aquatic environment

Applicable models for multi-component adsorption of dyes: A review Babak Noroozi, George A. Sorial	419
Effects of sludge dredging on the prevention and control of algae-caused black bloom in Taihu Lake, China Wei He, Jingge Shang, Xin Lu, Chengxin Fan	430
Distribution characteristics and source identification of polychlorinated dibenzo- <i>p</i> -dioxin and dibenzofurans, and dioxin-like polychlorinated biphenyls in the waters from River Kanzaki, running through Osaka urban area, Japan Masao Kishida	441
Pre-oxidation with KMnO ₄ changes extra-cellular organic matter's secretion characteristics to improve algal removal by coagulation with a low dosage of polyaluminium chloride Lei Wang (female), Junlian Qiao, Yinghui Hu, Lei Wang (male), Long Zhang, Qiaoli Zhou, Naiyun Gao	452
Identification of causative compounds and microorganisms for musty odor occurrence in the Huangpu River, China Daolin Sun, Jianwei Yu, Wei An, Min Yang, Guoguang Chen, Shujun Zhang	460
Influences of perfluorooctanoic acid on the aggregation of multi-walled carbon nanotubes Chengliang Li, Andreas Schäffer, Harry Vereecken, Marc Heggen, Rong Ji, Erwin Klumpp	466
Rapid degradation of hexachlorobenzene by micron Ag/Fe bimetal particles Xiaoqin Nie, Jianguo Liu, Xianwei Zeng, Dongbei Yue	473
Removal of Pb(II) from aqueous solution by hydrous manganese dioxide: Adsorption behavior and mechanism Meng Xu, Hongjie Wang, Di Lei, Dan Qu, Yujia Zhai, Yili Wang	479
Cr(VI) reduction capability of humic acid extracted from the organic component of municipal solid waste Barbara Scaglia, Fulvia Tambone, Fabrizio Adani	487
Off-flavor compounds from decaying cyanobacterial blooms of Lake Taihu Zhimei Ma, Yuan Niu, Ping Xie, Jun Chen, Min Tao, Xuwei Deng	495
Pollutant concentrations and pollution loads in stormwater runoff from different land uses in Chongqing Shumin Wang, Qiang He, Hainan Ai, Zhentao Wang, Qianqian Zhang	502

Atmospheric environment

Influence of fuel mass load, oxygen supply and burning rate on emission factor and size distribution of carbonaceous particulate matter from indoor corn straw burning (Cover story) Guofeng Shen, Miao Xue, Siye Wei, Yuanchen Chen, Bin Wang, Rong Wang, Huizhong Shen, Wei Li, Yanyan Zhang, Ye Huang, Han Chen, Wen Wei, Quyu Zhao, Bin Li, Haisu Wu, Shu Tao	511
Synergistic impacts of anthropogenic and biogenic emissions on summer surface O ₃ in East Asia Yu Qu, Junling An, Jian Li	520
Effect of central ventilation and air conditioner system on the concentration and health risk from airborne polycyclic aromatic hydrocarbons Jinze Lv, Lizhong Zhu	531
Emission inventory evaluation using observations of regional atmospheric background stations of China Xingqin An, Zhaobin Sun, Weili Lin, Min Jin, Nan Li	537
An improved GC-ECD method for measuring atmospheric N ₂ O Yuan Yuan Zhang, Yujing Mu, Shuangxi Fang, Junfeng Liu	547
Adsorption of carbon dioxide on amine-modified TiO ₂ nanotubes Fujiao Song, Yunxia Zhao, Qin Zhong	554

Terrestrial environment

Factors influencing the contents of metals and As in soils around the watershed of Guanting Reservoir, China Li Xu, Tiejue Wang, Wei Luo, Kun Ni, Shijie Liu, Lin Wang, Qiushuang Li, Yonglong Lu	561
Photolysis of polycyclic aromatic hydrocarbons on soil surfaces under UV irradiation Chengbin Xu, Dianbo Dong, Xuelian Meng, Xin Su, Xu Zheng, Yaoyao Li	569
Sorption and transport studies of cetyl trimethylammonium bromide (CTAB) and Triton X-100 in clayey soil Sivaram Harendra, Kumaraswamy Vipulanandan	576

Environmental biology

Effects of soil water and nitrogen availability on photosynthesis and water use efficiency of <i>Robinia pseudoacacia</i> seedlings Xiping Liu, Yangyang Fan, Junxia Long, Ruifeng Wei, Roger Kjellgren, Chunmei Gong, Jun Zhao	585
Phytoremediation potential of charophytes: Bioaccumulation and toxicity studies of cadmium, lead and zinc Najjapak Sooksawat, Metha Meetam, Maleeya Kruatrachue, Prayad Pokethitiyook, Koravid Nathalang	596
Sulfur speciation and bioaccumulation in camphor tree leaves as atmospheric sulfur indicator analyzed by synchrotron radiation XRF and XANES Jianrong Zeng, Guilin Zhang, Liangman Bao, Shilei Long, Mingguang Tan, Yan Li, Chenyan Ma, Yidong Zhao	605
Hydrocarbon biodegradation and dynamic laser speckle for detecting chemotactic responses at low bacterial concentration Melina Nisenbaum, Gonzalo Hernán Sendra, Gastón Alfredo Cerdá Gilbert, Marcelo Scagliola, Jorge Froilán González, Silvia Elena Murialdo	613

Environmental health and toxicology

Biogeochemical reductive release of soil embedded arsenate around a crater area (Guandu) in northern Taiwan using X-ray absorption near-edge spectroscopy Kai-Ying Chiang, Tsan-Yao Chen, Chih-Hao Lee, Tsang-Lang Lin, Ming-Kuang Wang, Ling-Yun Jang, Jyh-Fu Lee	626
---	-----



Distribution characteristics and source identification of polychlorinated dibenzo-*p*-dioxin and dibenzofurans, and dioxin-like polychlorinated biphenyls in the waters from River Kanzaki, running through Osaka urban area, Japan

Masao Kishida^{1,2}

1. Research Institute of Environment, Agriculture, and Fisheries, Osaka Prefecture, 1-3-62 Nakamichi, Higashinari-ku, Osaka 537-0025, Japan.

E-mail: kishida82477@iris.eonet.ne.jp

2. Commerce and Industry Promotion Office, Department of Commerce, Industry and Labor, Osaka Prefectural Government, Sakishima Building, 1-14-16 Nankohkita, Suminoe-ku, Osaka 559-8555, Japan

Received 25 June 2012; revised 05 October 2012; accepted 11 October 2012

Abstract

This is the first to elucidate the distribution and sources of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDFs), and dioxin-like polychlorinated biphenyls in the waters from Kanzaki River, which is one of the most heavily polluted rivers in Japan. The World Health Organization (WHO)-toxic equivalent quantities (TEQs) in waters from the mainstream exceeded the Japanese environmental standard (1.0 pg-TEQ/L). The PCDD/PCDFs were dominated by highly chlorinated DFs, which predominantly contributed to the WHO-TEQs, suggesting that the main causes would be the incineration-related wastes. To find the sources, the dioxin congener concentrations in water and sediment samples from its tributary small waterways were determined. Abnormally high WHO-TEQs were detected in a water (50 pg-TEQ/L) and a sediment sample (41,000 ng-TEQ/kg dry weight) near the industrial solid waste incinerators (ISWIs). The PCDD/PCDF characteristics agreed well with those of the incinerator-related wastes as seen in the mainstream. These facts indicate that the dioxin pollution in the mainstream could be largely related to the industrial wastes from the ISWIs. Here, a TEQ apportionment method was used to understand the contribution of the pyrogenic sources to the WHO-TEQs. The average contribution ratios of the pyrogenic sources to WHO-TEQs were more than 80% for river waters from the mainstream, indicating that the elevated WHO-TEQs in the mainstream had been largely caused by the ISWIs.

Key words: incinerator-related wastes; Kanzaki River Basin; river water; sediment; source identification

DOI: 10.1016/S1001-0742(12)60091-6

Introduction

The United Nations Environment Programme (UNEP, 1999) reported that large amounts of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDFs) had been emitted into the environment in Japan until the early 2000s. The main sources have been identified as herbicides (e.g., pentachlorophenol (PCP) and chloronitrofen (CNP)) (Masunaga et al., 2001a) and the incineration of solid wastes (Yasuhara et al., 1987). In the latter case, most solid wastes are mainly disposed of at the municipal solid waste incinerators (MSWIs). In the 1990s, an abnormally high World Health Organization (WHO)-toxic equivalent quantity (TEQ) value was detected in the soil around an MSWI in Nose, north of Osaka (8500 ng-TEQ/kg dry weight (dw)) (Ministry of the Environment (MOE), 2012). This accident triggered the enactment of 'Law Concerning Special Measures against Dioxins' by Government

of Japan in 1999. Since then, local governments have started monitoring the levels of the PCDD/PCDFs and dioxin-like polychlorinated biphenyls (DL-PCBs), which are the so-called 'dioxins' in waters, sediments, soils, and atmosphere. This monitoring showed that the WHO-TEQ values often exceeded the Japanese environmental standards for dioxins in sediments and waters (150 ng-TEQ/kg dw and 1.0 pg-TEQ/L, respectively), especially in urban and industrial areas such as Tokyo and Osaka (MOE, 2012).

Advanced studies aimed at understanding the characteristics of PCDD/PCDF and DL-PCB pollution in sediments were undertaken in many areas in Japan (Kiguchi et al., 2007; Kim et al., 2008; Masunaga et al., 2001b; Sakai et al., 2008). In contrast, there were limited studies focusing on the dioxin pollution in waters in Japan (Minomo et al., 2011) as well as in the other countries, such as Sweden (Broman et al., 1991), Germany (Götz et al., 1994), China

(Liu et al., 2008) and the USA (Lohmann et al., 2000; Suarez et al., 2006). Moreover, Minomo et al. (2011) targeted the rivers flowed from agricultural areas, and showed that the herbicides would be one of the main contributors to the elevated WHO-TEQs. In brief, few studies have focused on the dioxin pollution in waters at Japanese urban areas such as Tokyo and Osaka.

Osaka is the largest city in West Japan with a population of 8,860,000 in approximately 1800 km². Until now, this urban area has been seriously polluted by hazardous chemicals such as polycyclic aromatic hydrocarbons (Kishida et al., 2011), perfluorinated compounds (Saito et al., 2004), decabromobiphenyl ether (Watanabe et al., 1986), heavy metals (Sugimae, 1980) and nitrogen oxides (Osaka Prefectural Government, 2012a) for the last several decades. Regarding dioxin pollution, MOE (2012) reported that the Kanzaki River, running ca. 21 km through the northern part of Osaka urban area with its basin extending over an area of 627 km², is one of the most heavily polluted Japanese rivers like the Ayase River (Minomo et al., 2011). Since there are many incineration facilities in close proximity to this basin, the dioxin pollution is likely to be related to pyrogenic sources, as in Nose. Until now, Osaka Prefectural Government (2012a) has collected many sediment and water samples since 2001, apart from continuing with regular monitoring, in order to find the emission sources. However, only Kishida et al. (2010a) have effectively utilized part of the sedimentary data to advance the understanding of the dioxin pollution. Hazardous materials, such as dioxin congeners in water samples could significantly affect aquatic organisms (Kakimoto et al., 2006). Therefore, it has become critical to study the characteristics of the abundance and behavior of dioxin congeners in river waters as well as in sediments.

In the present study, the PCDD/PCDFs and DL-PCBs in river waters and sediments from the Kanzaki River Basin have been analyzed with the aim of elucidating their distribution and sources in greater detail. This study is aimed at understanding: (1) the dissolved and suspended concentrations of the dioxin congeners in river waters from the mainstream, (2) their distribution in river waters and sediments from its tributary small waterways to find the possible sources, and (3) the impact of incinerator-related wastes from industrial solid waste incinerators (ISWIs), which are located along one of the tributaries by using a TEQ apportionment method newly established by Minomo et al. (2010).

1 Materials and methods

1.1 Sampling

The sampling locations are shown in **Fig. 1**. Approximately 25 L of each water sample was collected using a stainless steel bucket, and then, it was replaced in brown

glass bottles, and transferred to a laboratory in Osaka. The water samples were stored at 4°C until their analyses. Two sediment samples from mainstream Kanzaki River were collected at more than three points near each sampling site using an Eckmann Dredge Sampling Apparatus, whereas 16 sediment samples from a tributary small waterway (Sangamaki Waterway) were collected at more than ten points near each sampling site using a steam shovel. The sediment samples were placed in glass vessels, transported to the laboratory, and then, dried under room temperature in the laboratory. The dried sediments were passed through a 2 × 2 mm stainless steel sieve and fully homogenized.

1.2 Analysis of water samples

The levels of PCDD/PCDFs and DL-PCBs in the river waters were determined using the method provided by the MOE (1998). Approximately 25 L of each sample from mainstream Kanzaki River was first filtrated with two glass-fiber filters (GFFs: Advantec Toyo Ltd., Japan) to collect the dioxin congeners in the suspended phase (SP): former filter: GA-100 (diameter 150 mm, pore size 1.0 μm) and latter filter: GC-50 (diameter 150 mm, pore size 0.45 μm). Each water sample from its tributary small waterways was filtrated with only the GA-100. Subsequently, the filtrate was passed through an Empore Extraction Disk (EED: diameter 90 mm, C18-FF, 3M, USA) to collect the dioxin congeners in the dissolved phase (DP). The GFFs and EEDs were dried under room temperature, and stored at 4°C until extraction. The GFFs and EEDs of the mainstream were separately extracted with toluene for 16 hr using a Soxhlet extraction, while those of its tributaries were simultaneously extracted as in the case of the mainstream. After extraction, 18 ¹³C₁₂-labeled PCDD/PCDFs and 12 ¹³C₁₂-labeled DL-PCBs used as internal standards were added to the extract to check the recovery of the dioxin congeners throughout the clean-up procedure. The extract was concentrated to ca. 1 mL with solvent change to hexane, and shocked with concentrated sulfuric acid. Subsequently, it was purified with silica by gel column chromatography, shacked with reduced copper to remove sulfur, and then, fractionated using activated charcoal/silica by gel column chromatography. After the addition of three injection internal standards (¹³C₁₂-1,3,6,8-tetraCDF, ¹³C₁₂-1,2,3,4,6,8,9-heptaCDF, and ¹³C₁₂-2,3',4',5-tetraCB), each fraction was concentrated to 20 μL under a gentle stream of pure nitrogen gas. All native and ¹³C₁₂-substituted PCDD/PCDFs and DL-PCBs were purchased from Wellington Laboratories Inc. (Canada). The solvents and reagents were of the dioxin-free analytical grade except for sulfuric acid (heavy metal analytical grade), as obtained from Wako Pure Chemical Industries Ltd. (Japan) and Kanto Chemical Co., Inc. (Japan).

All samples were analyzed using high-resolution gas chromatography (GC)/high-resolution mass spectrometry

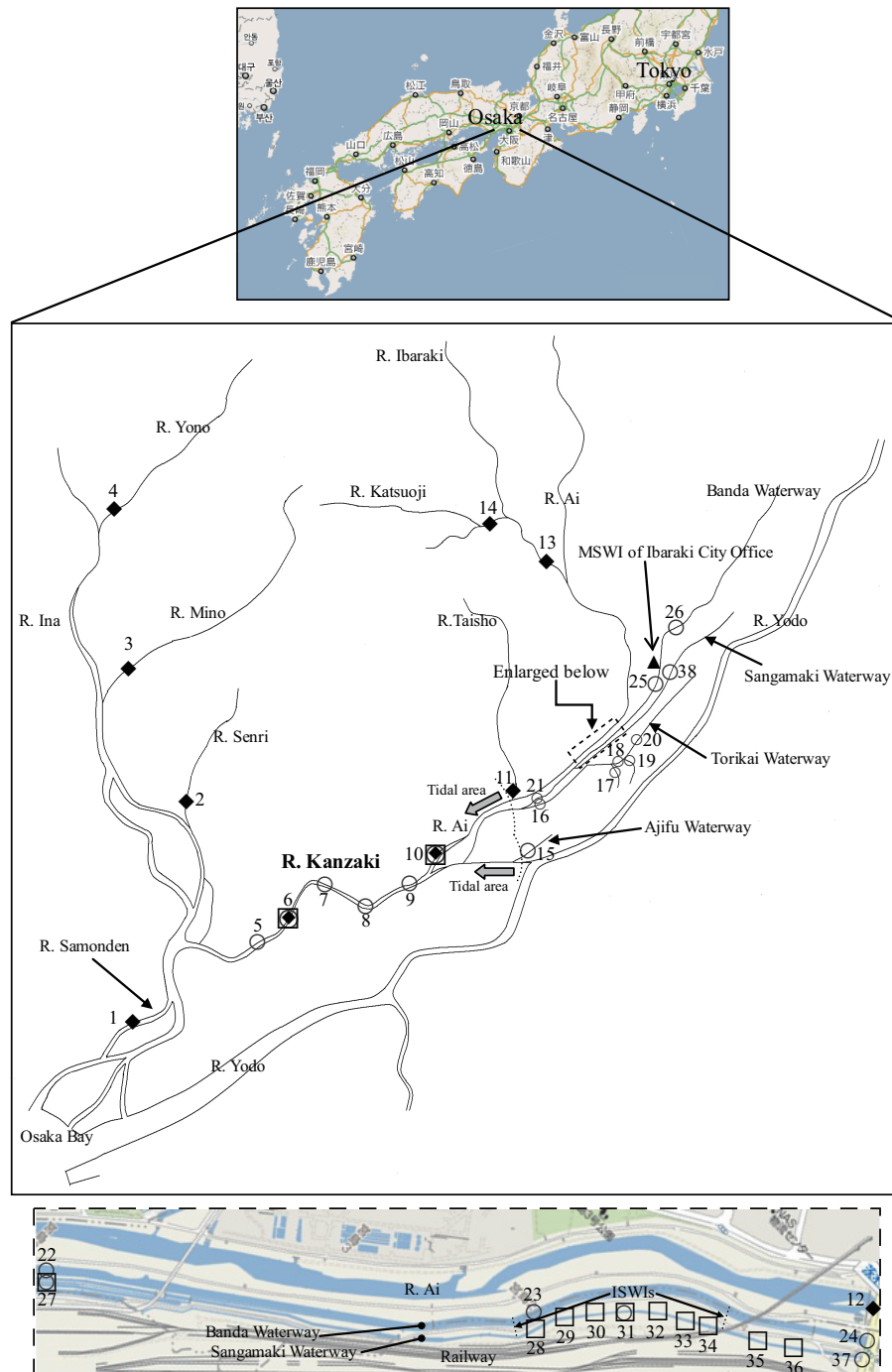


Fig. 1 A map of Kanzaki River Basin showing the sites monitored by Osaka Prefectural Government (closed diamonds) and the sampling sites for river waters (open circles) and sediments (open squares).

(MS) (HP5890, Agilent, USA; JMS-700D, JEOL, Japan) (Kishida et al., 2010a, 2010b). Chromatographic separations were carried out using an SP2331 (Supelco, USA) for tetra–hexaCDD/CDFs except for 1,2,3,7,8,9-hexaCDF, a DB-17MS (Agilent Technology, USA) for hepta–octaCDD/CDFs and 1,2,3,7,8,9-hexaCDF, and an HT-8PCB (Kanto Chem. Co., Inc.) for DL-PCBs. The

recovery of each $^{13}\text{C}_{12}$ -labeled internal standard was consistent with the guideline (50%–120%) provided by the MOE (1998). The laboratory blanks were analyzed for every batch. Blank values were subtracted from the measured levels for each batch. Method detection limits (MDLs) of the dioxin congeners in water samples were 0.02–0.07 pg/L for tetra–heptaCDD/CDFs, 0.08–0.1 pg/L

Table 1 Concentrations of PCDD/PCDF and DL-PCB congeners and WHO-TEQ values associated with dissolved and suspended phases in river waters and sediments from mainstream Kanzaki River

Congeners	Conc. in river waters ^a (pg/L)												Conc. in sediments ^c (ng/kg)	
	No.5-DP	No.5-SP	No.6-DP	No.6-SP	No.7-DP	No.7-SP	No.8-DP	No.8-SP	No.9-DP	No.9-SP	No.10-DP	No.10-SP	No.6	No.10
PCDD congeners														
1,3,6,8-TeCDD	1.9	9.4	1.8	9.1	1.2	8.1	1.3	8.7	1.5	7.5	0.72	4.8	590	75
1,3,7,9-TeCDD	0.52	3.5	0.52	3.8	0.37	3.2	0.37	3.5	0.45	2.9	0.19	1.9	240	29
2,3,7,8-TeCDD	0.03	0.23	0.03	0.18	N.D.	0.14	N.D.	0.17	N.D.	0.06	N.D.	0.04	12	0.84
TeCDDs	3.8	19	3.6	18	2.9	18	3.1	19	4.3	17	3.3	16	1000	140
1,2,3,7,8-PeCDD	0.04	0.19	N.D.	0.23	N.D.	0.18	N.D.	0.15	0.04	0.21	N.D.	0.11	18	6.3
PeCDDs	0.53	5.6	0.60	6.7	0.42	5.3	0.33	5.1	0.56	5.2	0.31	2.8	480	85
1,2,3,4,7,8-HxCDD	N.D. ^d	0.52	0.08	0.55	N.D.	0.38	N.D.	0.42	N.D.	0.48	N.D.	0.19	36	6.4
1,2,3,6,7,8-HxCDD	0.09	0.86	0.09	1.2	N.D.	0.57	N.D.	0.73	N.D.	0.87	N.D.	0.35	46	9.4
1,2,3,7,8,9-HxCDD	0.07	0.68	0.07	0.82	N.D.	0.53	0.08	0.52	0.05	0.62	N.D.	0.36	66	8.1
HxCDDs	0.54	13	1.0	15	0.43	10	0.59	11	0.55	13	N.D.	5.6	960	120
1,2,3,4,6,7,8-HpCDD	0.31	7.2	0.67	8.7	0.41	6.3	0.43	6.3	0.39	8.2	0.15	4.1	650	58
HpCDDs	0.71	15	1.2	17	0.82	12	0.80	12	0.83	16	0.29	8.2	1300	110
OCDD	2.5	64	4.5	76	3.0	62	2.7	61	3.0	61	1.5	49	4400	470
Total PCDDs	8.0	120	11	130	7.6	110	7.5	110	9.2	110	5.4	82	8200	930
PCDF congeners														
2,3,7,8-TeCDF	0.06	0.29	0.04	0.25	0.03	0.22	0.02	0.23	0.05	0.17	N.D.	0.11	2.0	2.5
TeCDFs	1.6	7.6	1.7	8.2	1.0	6.4	1.1	5.9	1.3	5.3	0.68	3.0	540	76
1,2,3,7,8-PeCDF	0.04	0.47	0.06	0.64	N.D.	0.43	0.04	0.08	0.05	0.47	N.D.	0.19	2.6	8.4
2,3,4,7,8-PeCDF	0.07	0.73	0.09	0.91	0.06	0.66	0.05	0.65	0.06	0.69	0.06	0.40	34	11
PeCDFs	0.88	10	1.1	12	0.67	8.2	0.57	7.8	0.84	9.0	0.38	3.6	840	130
1,2,3,4,7,8-HxCDF	0.09	1.7	0.19	2.2	0.11	1.5	0.08	1.3	0.11	1.7	N.D.	0.47	170	18
1,2,3,6,7,8-HxCDF	0.11	1.8	0.19	2.1	0.08	1.5	0.10	1.5	0.12	1.8	N.D.	0.48	160	18
1,2,3,7,8,9-HxCDF	N.D.	0.30	N.D.	0.57	N.D.	0.27	N.D.	0.22	N.D.	0.36	N.D.	0.14	24	1.6
2,3,4,6,7,8-HxCDF	0.25	3.5	0.34	4.8	0.15	3.0	0.19	3.0	0.19	3.3	0.11	1.6	350	25
HxCDFs	1.2	22	2.2	28	1.1	18	1.0	18	1.2	21	0.35	6.9	1900	180
1,2,3,4,6,7,8-HpCDF	0.31	7.9	0.75	9.6	0.36	6.2	0.18	5.7	0.41	8.0	0.07	2.0	790	46
1,2,3,4,7,8,9-HpCDF	N.D.	1.3	0.12	1.7	0.06	1.2	N.D.	1.1	0.07	1.5	N.D.	0.40	150	7.5
HpCDFs	0.60	14	1.4	18	0.62	12	0.58	11	0.73	15	0.14	4.0	1600	84
OCDF	0.44	13	1.0	14	0.36	9.7	0.32	8.5	0.45	11	0.15	3.4	1400	53
Total PCDFs	4.7	66	7.4	81	3.7	54	3.6	51	4.5	61	1.7	21	6300	530
DL-PCB congeners^a														
3,3',4,4'-TeCB (#77)	15	30	9.9	26	7.3	23	5.0	15	4.1	10	2.1	5.6	64	80
3,4,4',5-TeCB (#81)	0.49	0.86	0.25	0.80	0.22	0.64	0.22	0.49	0.18	0.35	0.09	0.27	1.0	3.1
2,3,3',4,4'-PeCB (#105)	17	51	14	60	12	57	7.7	37	7.2	28	4.9	19	4600	220
2,3,4,4',5-PeCB (#114)	0.98	3.2	1.1	4.5	0.91	4.0	0.50	2.0	0.54	1.2	0.29	1.4	350	15
2,3',4,4',5-PeCB (#118)	56	200	46	180	38	200	22	100	17	60	9.9	37	13000	460
2',3,4,4',5-PeCB (#123)	0.68	2.2	0.79	2.4	0.42	3.0	0.49	1.5	0.26	1.0	0.25	0.58	400	9.9
3,3',4,4',5-PeCB (#126)	0.23	0.96	0.13	0.96	0.11	0.88	0.06	0.66	0.09	0.57	N.D.	0.40	60	5.3
2,3,3',4,4',5-HxCB (#156)	2.9	23	2.9	26	3.1	28	1.4	13	1.4	8.8	0.86	5.8	1900	62
2,3,3',4,4',5'-HxCB (#157)	0.69	5.5	0.68	5.8	0.73	6.2	0.32	3.2	0.31	2.3	0.21	1.6	460	16
2,3',4,4',5,5'-HxCB (#167)	1.1	8.9	1.1	9.2	1.1	10	0.61	5.1	0.55	3.4	0.31	2.1	750	24
3,3',4,4',5,5'-HxCB (#169)	0.07	0.15	N.D.	0.22	N.D.	0.18	N.D.	0.16	N.D.	0.17	N.D.	0.09	17	2.0
2,3,3',4,4',5,5'-HpCB (#189)	0.14	1.4	0.14	1.6	0.12	1.6	0.11	0.84	N.D.	0.70	N.D.	0.40	140	5.1
WHO-TEQ ₂₀₀₆ ^b	0.20	1.9	0.21	2.3	0.11	1.6	0.10	1.5	0.15	1.7	0.08	0.77	150	21

^a The IUPAC No. of each DL-PCB congener is provided in parentheses; ^b the values were obtained using TEFs proposed by WHO in 2006; ^c DP and SP represent the dioxin congeners in dissolved and suspended phases, respectively, and sample collected on 7th August, 2002; ^d not detected.

for octaCDD/CDFs and 0.02–0.1 pg/L for DL-PCBs.

In this study, the WHO-TEQ value for each sample was obtained from the concentrations of 2,3,7,8-substituted PCDD/PCDFs and DL-PCBs using their toxic equivalent factors proposed by WHO in 2006. Concentrations of the not-detected congeners were assumed to be equal to half of the MDLs for the calculation of WHO-TEQ values.

1.3 Analysis of sediment samples

Approximately 2–30 g of each sediment sample was submitted to the analysis. Dioxin congeners in the sediments were determined according to the literature (Kishida et al., 2010a, 2010b). The recovery of each ¹³C₁₂-labeled internal standard was also consistent with the guideline (50%–120%) provided by the MOE (1998). Accuracy and precision of the dioxin analysis in sediment samples were reported previously (Kishida et al., 2010b).

2 Results and discussion

2.1 Aquatic pollution of PCDD/PCDFs and DL-PCBs in dissolved and suspended phases from mainstream Kanzaki River

2.1.1 PCDD/PCDF and DL-PCB concentrations and WHO-TEQ values

Previously, Uebori et al. (2002) reported that WHO-TEQ value at location 6 (1.7 pg-TEQ/L) exceeded the Japanese environmental standard of 1.0 pg-TEQ/L, while those at other locations (site numbers 1–4 and 11–14: 0.11–0.76 pg-TEQ/L) were lower than the standard. This indicates that the mainstream Kanzaki River could possibly be facing a critical situation with respect to dioxin pollution, but this could not be attributable solely to the tributaries.

Here, dioxin congener concentrations in DP and SP collected from the mainstream were investigated at locations

5–10 in order to understand their distribution characteristics in greater detail (Table 1). Average concentrations of total PCDD/PCDF congeners (Σ PCDD/PCDFs) of the six samples were 12 ± 3.7 pg/L in DP and 170 ± 36 pg/L in SP, while those of total DL-PCB congeners (Σ DL-PCBs) were 54 ± 29 pg/L in DP and 220 ± 120 pg/L in SP. The values of Σ PCDD/PCDFs and Σ DL-PCBs in SP were much higher than those in DP. In particular, approximately 95% of high-chlorinated compounds (e.g., hepta–octaCDDs/CDFs and heptaCBs) mainly occurred in SP due to their higher K_{ow} values (Lohmann et al., 2000). Similarly, an average WHO-TEQ value in SP from the six sites (1.6 ± 0.51 pg-TEQ/L) was found to be more than ten times higher than that in DP (0.14 ± 0.05 pg-TEQ/L). In particular, the WHO-TEQ values in SP from locations 5–9 (1.5 – 2.3 pg-TEQ/L) exceeded the Japanese environmental standard.

Compared to previous studies, the WHO-TEQ values in DP plus SP were similar to those in the polluted sites in Kahokugata Lagoon, Japan (Kakimoto et al., 2006), Ayase River (Minomo et al., 2011) and Elbe River, Germany (Götz et al., 1994), but the levels were much higher than those in the non-polluted sites in Kahokugata Lagoon (Kakimoto et al., 2006), Baltic Sea, Sweden (Broman et al., 1991), Xijiang River, China (Liu et al., 2008), Rartian Bay and Hudson River (Lohmann et al., 2000), and Houstone Ship Channel (Suarez et al., 2006), each in the USA.

2.1.2 Profiles of PCDD/PCDF and DL-PCB homologues and an estimation of their sources

The dominant homologues in DP from site numbers 5–9 were tetraCDDs (27%), octaCDD (23%), tetraCDFs (10%) and hexaCDFs (10%), whereas those in SP were octaCDD (37%), hexaCDFs (12%), tetraCDDs (10%), heptaCDDs (8%) and heptaCDFs (8%). The strong predominance of octaCDD in both phases was considered attributable to the PCP used to enhance the growth of rice crops or enhance the density of forests, or natural resources (Kishida et al., 2010a). Here, the PCDD/PCDF profiles bore no characteristics of PCP for treating timber and natural origins as seen in sediments from this basin (Kishida et al., 2010a). Hence, the octaCDD was attributable to PCP, which had been used for protecting the rice crops (Japan Plant Protection Association (JPPA), 2011). In terms of tetraCDDs, their main congeners in DP and SP were 1,3,6,8- and 1,3,7,9-tetraCDDs, and the average ratios of sum of the two congeners to total tetraCDD congeners at the 5–9 were (56 ± 8)% in DP and (66 ± 4)% in SP. This shows that the contribution of products could be considerable (JPPA, 2011; Masunaga et al., 2001a).

Another characteristic of the PCDD/PCDF homologues from sites 5–9 was significantly higher PCDF concentrations compared to those in the other areas (Broman et al., 1991; Götz et al., 1994; Kakimoto et al., 2006; Liu et al., 2008; Lohmann et al., 2000; Minomo et al., 2011; Suarez et al., 2006). The PCDFs in SP were characterized by high

levels of highly chlorinated DFs with six to eight chlorine atoms. This could be clearly attributed to incinerator-related materials e.g., ash and fly ash (Yasuhara et al., 1987). In terms of DP, the dominated homologues were low chlorinated compounds (e.g., tetraCDFs). This could be attributable to the fact that their K_{ow} values were lower than those of the high chlorinated compounds (Lohmann et al., 2000).

The dominant congeners of DL-PCBs in DP and SP from site numbers 5–9 are 3,3',4,4'-tetraCB (IUPAC No. 77), 2,3,3',4,4'-pentaCB (#105), and 2,3',4,4',5-pentaCB (#118), with the order of #118 (60%) > #105 (20%) > #77 (10%). The main source of DL-PCBs can be estimated using the ratio of sum of 3,3',4,4',5-pentaCB (#126) and 3,3',4,4',5,5'-hexaCB (#169) to sum of #77, #126 and #169 (Kishida et al., 2010a). The proportion of DL-PCBs in commercial PCBs was approximately 1%, whereas that from the combustion sources was approximately 50%. The average values of ($\#126 + \#169$)/($\#77 + \#126 + \#169$) were < 1% in both phases, corresponding to those for commercial PCBs. In Japan, the use and production of commercial PCBs such as Kanechlor has been prohibited by law since 1973. Therefore, commercial PCBs in water samples would be attributable to their past usage until the 1970s (Osaka Prefectural Government, 2004).

2.1.3 Dominant contributors to WHO-TEQs

As shown in Fig. 2, the dominant congeners contributing to WHO-TEQ values in DP plus SP from sites 5–9 were 2,3,4,6,7,8-hexaCDF (19%), 2,3,4,7,8-pentaCDF (12%), 1,2,3,7,8-pentaCDD (11%), 1,2,3,4,7,8-hexaCDF (9%) and 2,3,7,8-tetraCDD (9%). Notably, the ratios of total 2,3,7,8-substituted PCDFs in DP and SP were higher than those of total 2,3,7,8-substituted PCDDs and total

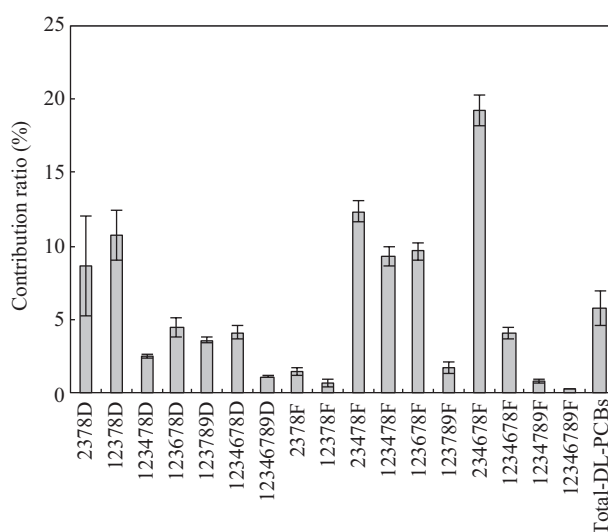


Fig. 2 Average contribution ratios of 2,3,7,8-substituted PCDD/PCDFs and total DL-PCBs to the WHO-TEQ values in water samples (dissolved plus suspended phases) from site numbers 5–9 in mainstream Kanzaki River. D and F in horizontal axis represent PCDDs and PCDFs, respectively. Error bars show SDs.

DL-PCBs. As reported previously, 2,3,4,7,8-pentaCDF and 2,3,7,8-substituted hexaCDFs could be related to the incinerator-related materials (Yasuhara et al., 1987). In contrast, high contribution of 1,2,3,7,8-pentaCDD was observed in CNP products (Masunaga et al., 2001a). Thus, the main contributor was likely to be the incineration of solid wastes, whose effect would largely exceed that of herbicides such as CNP.

2.1.4 Comparison of sedimentary PCDD/PCDFs and DL-PCBs with those in river waters

The author also analyzed two sediment samples collected at locations 6 and 10 (Table 1). The WHO-TEQ value at site 6 (150 ng-TEQ/kg dw) was as high as the Japanese environmental standard, and in synchronization with a previous study (Kishida et al., 2010a). In addition, the value was similar to that in the SP (190 ng-TEQ/kg dw), which was calculated using the corresponding suspended solid (SS) concentration (12 mg/L). Further, at the site, the PCDD/PCDF profile in the sediment was similar to that in the SP. These facts indicate that the dioxin pollution in SP from site 6 could have originated as a result of the dispersion of sediments. However, there are no significant sources of dioxin congeners along this mainstream. The main causes were speculated to be incinerator-related wastes dumped by MSWIs and/or ISWIs located along the tributaries of the Kanzaki River (Examination Committee for Environmental Dioxin Pollution (ECFEDP), 2007; Kishida et al., 2010a). However, greater detailed studies have never been performed on this issue until now.

At location No. 10, a WHO-TEQ value in sediment (21 ng-TEQ/kg dw) was lower than that in the SP (64 ng-TEQ/kg dw), which was also obtained using the corresponding SS concentration (12 mg/L). As shown in Table 1, the PCDD/PCDF homologue pattern in the sediment was not in agreement with that in the SP. However, the pattern in the sediment was similar to those in SP from downstream locations 5–9 (Table 1). Osaka Prefectural Government (2012b) announces on its website that the tidal area stretches from the estuary of the Kanzaki River to the area around sites 9–10 (Fig. 1). This shows that the dioxin congeners in the sediment from site No. 10 were thought to have been transferred from the downstream area at the time of high tide. In contrast, the PCDD/PCDF characteristics in the SP from location 10 were similar to those in waters collected from sites 11–14 (Uebori et al., 2002) because of the high content of octaCDD, tetraCDDs, and heptaCDDs. This was simply due to the fact that the water sample had been collected at the time of low tide.

2.2 Distribution of PCDD/PCDF and DL-PCB concentrations and WHO-TEQs in river waters from tributary small waterways

For the first time, the author analyzed PCDD/PCDF and the DL-PCB concentrations in the waters from tributary small waterways to identify the sources of dioxin con-

geners in the mainstream Kanzaki River (Table 2). The Σ PCDD/PCDF concentration at location 27 was 3800 pg/L, more than those in the other sites. The highest Σ DL-PCB concentration was observed at location No.15 (5200 pg/L). WHO-TEQ values at locations 15 (1.9 pg-TEQ/L), 16 (2.8–4.5 pg-TEQ/L), 21 (1.1–8.5 pg-TEQ/L), 27 (50 pg-TEQ/L), and 31 (4.7 pg-TEQ/L) exceeded the Japanese environmental standard. In particular, the value at location 27 was fifty times higher than the standard. There are two possible sources: an MSWI of Ibaraki City Office located along Banda Waterway and some ISWIs located between Banda Waterway and Sangamaki Waterway (Fig. 1). The high WHO-TEQ values at the five sites could not be attributable to the MSWI, because WHO-TEQs at downstream sites from the MSWI (e.g., sites 24 and 25) were lower than the environmental standard. In contrast, the site numbers 27 and 31 are located beside the ISWIs which had been dumping the incineration-related wastes of solid materials mainly into the Sangamaki Waterway (ECFEDP, 2007). In addition, the WHO-TEQ value at site No. 37, located several hundred meters upstream from the ISWIs, was much lower than those at the 27 and 31. Therefore, the ISWIs would be main causes of the elevated WHO-TEQ values at the tributaries and the mainstream.

The PCDD/PCDF profiles in the tributaries were characterized by the dominance of tetraCDDs, octaCDD, and/or highly chlorinated DFs (e.g., hexa–octaCDFs). A higher content of PCDFs was observed mainly at locations 16, 21, 27, and 31 (Table 2) as seen in the mainstream. At the four sites, dominant contributors to WHO-TEQ values were estimated as 2,3,4,6,7,8-hexaCDF (19%), 2,3,4,7,8-pentaCDF (16%), 1,2,3,7,8-pentaCDD (12%), 1,2,3,6,7,8-hexaCDF (10%), and 1,2,3,4,7,8-hexaCDF (9%) (Fig. 3). Further, sum of the contribution ratios of 2,3,4,7,8-pentaCDF and 2,3,7,8-substituted hexaCDFs attained 60% at sites 27 and 31. As mentioned above, these characteristics were strongly related to the incinerator-related wastes. Hence, the elevated WHO-TEQ values could be attributable to the incinerator-related wastes from the ISWIs.

2.3 Sedimentary pollution of PCDD/PCDFs and DL-PCBs in a tributary small waterway (Sangamaki Waterway) near the ISWIs

In order to elucidate the dioxin pollution caused by the ISWIs in more detail, sixteen sediment samples were collected from Sangamaki Waterway around the ISWIs (Table 3). An average Σ PCDD/PCDF concentration of the sixteen samples was $700,000 \pm 13,000$ ng/kg dw, while that of Σ DL-PCBs was $12,000 \pm 5300$ ng/kg dw, corresponding to an average WHO-TEQ value of $10,000 \pm 12,000$ ng-TEQ/kg dw. In particular, WHO-TEQs near the ISWIs (locations 27–34) restrictively exceeded the Japanese environmental standard, and were much higher than those at upstream sites from the ISWIs (numbers 35 and 36). Among the eight sites, an extremely high

Table 2 Concentrations of PCDD/PCDF and DL-PCB congeners and WHO-TEQ values in water samples from tributary small waterways

Congeners	Concentration (pg/L)																	
	No.15 ^a	No.16 ^d	No.16 ^e	No.17 ^d	No.18 ^d	No.19 ^e	No.20 ^e	No.21 ^d	No.21 ^e	No.22 ^e	No.23 ^e	No.24 ^e	No.25 ^e	No.26 ^e	No.27 ^e	No.31 ^e	No.37 ^e	No.38 ^e
PCDD congeners																		
1,3,6,8-TeCDD	8.0	21	25	1.3	3.4	5.1	10	110	10	3.5	11	10	9.3	5.7	60	13	16	20
1,3,7,9-TeCDD	3.0	8.3	10	0.45	1.2	1.9	3.5	41	3.8	1.2	3.7	3.7	3.5	2.2	29	4.8	5.9	7.1
2,3,7,8-TeCDD	0.08	0.06	0.05	N.D. ^f	N.D.	N.D.	N.D.	0.18	N.D.	N.D.	N.D.	0.06	N.D.	N.D.	1.1	0.13	N.D.	N.D.
TeCDFs	15	34	37	2.2	5.8	8.7	18	160	18	5.3	20	20	19	13	130	23	27	31
1,2,3,7,8-PeCDD	0.23	0.50	0.32	N.D.	N.D.	N.D.	N.D.	1.6	0.16	N.D.	0.11	0.12	0.14	N.D.	5.0	0.33	0.11	0.11
PeCDDs	3.7	14	10	0.28	0.67	0.87	1.9	38	4.4	0.76	3.9	3.3	3.0	1.9	130	13	4.0	5.3
1,2,3,4,7,8-HxCDD	0.24	1.0	0.61	N.D.	N.D.	0.08	N.D.	2.1	0.26	N.D.	0.22	0.17	0.27	0.18	13	1.2	0.22	0.22
1,2,3,6,7,8-HxCDD	0.39	1.8	1.0	N.D.	0.09	0.10	0.11	3.4	0.54	N.D.	0.45	0.41	0.52	0.24	21	2.0	0.39	0.33
1,2,3,7,8,9-HxCDD	0.28	1.3	1.1	N.D.	0.08	0.06	0.07	2.8	0.38	0.07	0.36	0.43	0.30	0.23	15	1.4	0.22	0.30
HxCDDs	4.1	27	16	N.D.	1.3	0.90	1.5	48	6.2	0.68	5.0	4.3	4.4	2.8	330	29	3.9	4.8
1,2,3,4,6,7,8-HpCDD	2.8	18	14	0.40	0.94	0.83	1.8	31	10	0.70	7.0	7.5	6.6	3.3	190	20	5.1	7.1
HpCDDs	5.4	36	28	0.74	1.9	1.7	3.9	61	19	1.6	14	16	14	6.8	380	40	11	14
OCDD	21	88	78	2.1	11	7.7	18	230	94	9.5	97	110	97	70	400	53	78	120
Total PCDDs	50	200	170	5.3	20	20	44	540	140	9.5	140	150	140	95	1400	160	120	170
PCDF congeners																		
2,3,7,8-TeCDF	0.33	0.70	0.72	0.20	0.17	0.07	0.11	1.4	0.22	0.04	0.18	0.19	0.14	0.15	7.0	0.84	0.17	0.16
TeCDFs	11	17	11	2.0	2.5	2.5	4.3	42	4.4	1.1	3.8	3.6	3.5	2.7	200	22	6.3	5.3
1,2,3,7,8-PeCDF	0.65	1.8	1.4	0.15	0.17	0.09	0.13	3.2	0.35	0.05	0.27	0.26	0.25	0.19	16	1.8	0.24	0.31
2,3,4,7,8-PeCDF	0.29	2.7	1.5	N.D.	0.16	0.09	0.11	5.0	0.45	0.09	0.30	0.24	0.27	0.14	29	2.4	0.26	0.27
PeCDFs	6.1	29	17	0.59	2.1	1.6	2.2	57	6.2	0.70	4.3	3.6	3.7	2.6	320	33	4.8	4.9
1,2,3,4,7,8-HxCDF	0.55	4.4	2.8	0.13	0.22	0.09	0.18	6.3	0.92	0.09	0.53	0.40	0.36	0.28	52	5.0	0.50	0.53
1,2,3,6,7,8-HxCDF	0.47	4.5	2.5	0.09	0.15	0.08	0.13	6.0	1.3	N.D.	0.46	0.36	0.26	0.20	52	4.8	0.30	0.43
1,2,3,7,8,9-HxCDF	N.D.	0.35	0.32	N.D.	N.D.	N.D.	N.D.	0.67	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	4.8	0.41	N.D.	N.D.
2,3,4,6,7,8-HxCDF	0.52	9.4	5.0	0.08	0.26	0.12	0.20	13	1.6	0.24	0.58	0.43	0.27	0.06	110	11	0.25	0.4
HxCDFs	5.5	47	27	0.78	1.9	0.60	1.4	66	9.3	0.68	5.2	3.7	3.5	1.7	540	55	4.1	5.1
1,2,3,4,6,7,8-HpCDF	3.0	30	14	0.37	0.87	0.37	0.66	41	5.7	0.34	3.0	2.2	2.0	1.3	320	34	1.9	3.0
1,2,3,4,7,8,9-HpCDF	0.32	5.3	3.2	0.09	0.19	N.D.	0.12	6.9	1.0	N.D.	0.34	0.28	0.33	0.42	74	8.3	0.21	0.56
HpCDFs	5.0	60	30	1.1	1.9	0.69	1.4	81	14	0.75	5.9	4.7	4.2	3.1	720	72	4.0	6.7
OCDF	7.4	39	22	0.57	1.1	0.48	0.97	48	7.3	0.68	3.1	3.1	2.8	1.5	550	48	3.1	4.1
Total PCDFs	35	190	110	5.0	10	5.9	10	290	41	0.68	22	19	18	12	2300	230	22	26
DL-PCB congeners^a																		
3,3',4,4'-TeCB (#77)	770	24	27	4.0	5.7	5.2	14	26	25	2.8	28	28	28	22	20	10	10	10
3,4,4',5'-TeCB (#81)	26	1.0	0.86	0.21	0.32	0.18	0.66	1.5	1.2	0.16	1.2	1.3	1.3	1.1	1.2	0.55	0.56	0.45
2,3,3',4,4'-PeCB (#105)	1400	37	59	7.8	7.4	13	31	65	49	6.4	62	55	56	42	54	27	30	31
2,3,4,4',5'-PeCB (#114)	72	2.9	3.9	0.55	0.76	1.0	2.2	3.4	3.6	0.38	4.5	3.3	4.0	2.9	4.3	1.8	1.9	2.3
2,3',4,4',5'-PeCB (#118)	2500	82	110	14	20	30	68	110	100	13	130	110	110	84	120	58	68	70
2',2,3,4,4',5'-PeCB (#123)	71	2.4	2.9	0.42	0.64	0.63	1.5	3.6	2.2	0.31	3.3	2.7	3.2	2.2	3.2	1.4	1.8	1.8
3,3',4,4',5'-PeCB (#126)	9.1	1.3	1.3	0.12	0.27	0.23	0.54	4.2	0.89	0.13	1.4	0.86	1.0	0.76	5.0	1.3	0.77	0.86
2,3,3',4,4',5'-HxCB (#156)	210	11	13	1.0	2.2	4.1	9.1	26	14	1.9	19	14	15	10	23	7.9	10	11
2,3,3',4,4',5'-HxCB (#157)	49	3.3	3.5	0.26	0.50	1.1	2.3	8.7	3.7	0.59	5.0	3.7	3.5	2.7	5.8	1.7	2.4	2.7
2,3',4,4',5',5'-HxCB (#167)	73	4.3	5.1	0.41	0.87	1.7	3.6	10	5.3	0.77	7.4	5.6	5.8	3.9	8.7	N.D.	4.5	5.3
3,3',4,4',5,5'-HxCB (#169)	0.25	0.78	0.41	N.D.	N.D.	N.D.	0.09	2.5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	6.5	0.82	0.22	0.18
2,3,3',4,4',5,5'-HpCB (#189)	8.3	2.2	0.90	0.08	0.18	0.33	0.93	5.7	0.70	0.09	1.0	0.90	0.70	0.50	14	1.6	1.4	1.7
WHO-TEQ₂₀₀₆^b (pg-TEQ/L)	1.9	4.5	2.8	0.11	0.23	0.15	0.23	8.3	1.1	0.11	0.78	0.73	0.68	0.35	50	4.7	0.60	0.69

^a The IUPAC No. of each DL-PCB congener is provided in parentheses; ^b the values were obtained using TEFs proposed by WHO in 2006; ^c samples were collected on 9th September, 2003; ^d samples were collected on 13th January, 2005; ^e samples were collected on 15th November, 2005; ^f not detected.

WHO-TEQ value of 41,000 ng-TEQ/kg dw was detected at location 32. The value was 270 times as high as the Japanese environmental standard. Regarding the PCDD/PCDF profiles, Table 3 shows that the dominant homologues at locations 27–34 were hexa–octaCDFs (50%) and octaCDD (12%). Further, as shown in Fig. 4, the average contribution ratio of sum of 2,3,7,8-substituted hexaCDFs and 2,3,4,7,8-pentaCDF to the WHO-TEQ values was 64% in sediments from these locations. Thus, significantly high WHO-TEQ values and larger contributions of 2,3,4,7,8-pentaCDF and 2,3,7,8-substituted hexaCDFs to the WHO-TEQ values were obtained mainly in the sediment samples collected near the ISWIs. These facts strongly indicate that the small waterway could have been seriously polluted by the dumping of incineration-related wastes from the ISWIs. Considering the facts that similar characteristics were observed at the downstream

sites in proximity to the ISWIs (Figs. 2 and 3), the wastes from the ISWIs were considered to have strongly affected the dioxin pollution possibilities in river waters from those sites located downstream.

2.4 Contribution of the three typical dioxin sources in Japan to the WHO-TEQ values using a TEQ apportionment method

In order to estimate the impact of incinerator-related wastes on WHO-TEQs, a TEQ apportionment method, which was newly established by Minomo et al. (2010) to understand the contribution of Japanese typical sources (pyrogenic sources, herbicides (CNP and PCP) and commercial PCBs) to WHO-TEQ values, was applied to river waters and sediments from the Kanzaki River Basin. Average ratios of estimated WHO-TEQs relative to analyzed WHO-TEQs were 0.93 for water samples and 0.76 for

Table 3 Concentrations of PCDD/PCDF and DL-PCB congeners and WHO-TEQ values in sediment samples from Sangamaki Waterway

Congeners	Concentration (ng/kg dw)															
	No.27-M	No.28-M	No.29-M	No.30-M	No.30-L	No.31-R	No.31-M	No.32-R	No.32-M	No.33-R	No.33-M	No.34-R	No.34-M	No.35-M	No.36-M	No.36-L
PCDD congeners																
1,3,6,8-TeCDD	2100	2100	8700	9000	6500	2400	7600	6100	37000	8000	6200	2500	2700	5700	2100	2700
1,3,7,9-TeCDD	1000	1300	6100	4500	3600	1400	3600	3900	26000	5400	3900	820	970	2000	770	940
2,3,7,8-TeCDD	23	80	300	210	160	100	180	170	620	270	190	4.8	8.9	3.2	1.3	5.2
TeCDDs	3800	4900	23000	17000	14000	5800	15000	14000	76000	21000	15000	3600	3700	8600	3100	4100
1,2,3,7,8-PeCDD	180	410	1400	1100	980	490	1200	1000	4000	2100	1600	41	53	15	7.7	12
PeCDDs	4000	9100	42000	24000	22000	11000	27000	30000	140000	45000	34000	1100	1300	990	430	530
1,2,3,4,7,8-HxCDD	410	1000	3800	2700	2400	1100	2900	2300	11000	5300	4500	86	99	23	10	11
1,2,3,6,7,8-HxCDD	730	1700	7200	4200	3800	1800	5200	4300	17000	9100	7900	140	180	45	22	27
1,2,3,7,8,9-HxCDD	480	1200	4500	3300	2400	1200	3400	2800	13000	6300	5200	110	140	34	15	19
HxCDDs	10000	26000	110000	67000	54000	26000	77000	92000	380000	140000	110000	2000	2600	590	280	350
1,2,3,4,6,7,8-HpCDD	5300	16000	67000	37000	29000	14000	47000	35000	170000	78000	66000	1400	1600	560	250	270
HpCDDs	10000	31000	140000	74000	56000	28000	94000	70000	330000	150000	130000	2700	3200	1200	520	560
OCDD	14000	32000	140000	81000	57000	27000	100000	80000	310000	160000	130000	7000	8900	8500	3600	3700
total PCDDs	42000	100000	450000	260000	200000	97000	320000	290000	1200000	520000	420000	16000	20000	20000	7900	9200
PCDF congeners																
2,3,7,8-TeCDF	120	340	1400	890	890	530	900	1100	3200	1400	1100	34	35	16	8.5	13
TeCDFs	4100	10000	46000	25000	23000	15000	26000	29000	85000	42000	33000	1100	1100	670	370	460
1,2,3,7,8-PeCDF	450	1100	4000	2700	2400	1300	3400	3200	10000	5300	4600	130	130	43	24	33
2,3,4,7,8-HxCDF	750	1900	7400	4500	4100	2100	5900	4700	16000	9000	7900	170	190	43	24	30
PeCDFs	8500	22000	90000	50000	46000	26000	64000	58000	180000	94000	85000	2000	2200	600	350	430
1,2,3,4,7,8-HxCDF	1600	4700	18000	11000	9400	5200	15000	11000	46000	21000	20000	410	430	77	47	47
1,2,3,6,7,8-HxCDF	2000	5300	22000	12000	10000	5400	17000	12000	48000	23000	24000	420	460	73	39	46
1,2,3,7,8,9-HxCDF	150	66	1200	540	460	70	820	480	2800	1400	1000	24	35	5.0	4.0	7.3
2,3,4,6,7,8-HxCDF	4300	12000	52000	29000	23000	12000	42000	31000	110000	53000	55000	760	960	110	57	58
HxCDFs	19000	54000	230000	130000	100000	56000	180000	130000	500000	240000	240000	4300	4900	810	480	480
1,2,3,4,6,7,8-HpCDF	12000	36000	150000	77000	57000	32000	120000	71000	310000	130000	150000	2300	2800	410	300	240
1,2,3,4,7,8,9-HpCDF	1600	5300	25000	13000	9600	5100	20000	12000	51000	24000	27000	340	440	38	12	16
HpCDFs	19000	63000	270000	140000	100000	57000	220000	130000	550000	260000	280000	4000	5000	700	420	380
OCDF	18000	58000	270000	120000	88000	50000	210000	120000	470000	240000	280000	3100	4300	540	200	230
Total PCDFs	69000	210000	900000	460000	370000	200000	700000	470000	1800000	880000	920000	15000	17000	3300	1800	2000
DL-PCB congeners^a																
3,3',4,4'-TeCB (#77)	800	1400	1800	1700	1900	930	1700	1300	3200	1900	1700	970	870	1500	530	520
3,4,4',5-TeCB (#81)	37	78	180	150	170	81	200	130	340	290	190	47	42	57	28	38
2,3,3',4,4'-PeCB (#105)	1500	1900	1800	2500	2900	1400	2500	1300	3100	1900	2000	2000	1700	2500	1300	1200
2,3,4,4',5-PeCB (#114)	92	130	160	220	230	110	200	110	300	220	180	150	120	170	91	86
2,3',4,4',5-PeCB (#118)	5000	5300	4400	5200	6600	2800	5000	2500	5900	3100	5000	4300	3700	4900	2700	2600
2',3,4,4',5-PeCB (#123)	110	110	150	130	190	67	130	73	210	150	120	98	83	120	64	60
3,3',4,4',5-PeCB (#126)	190	420	1000	840	860	470	1100	790	2600	1500	1100	190	78	71	40	43
2,3,3',4,4',5-HxCB (#156)	1400	1500	1300	1300	1600	690	1400	790	2400	1300	1500	790	630	830	450	440
2,3,3',4,4',5'-HxCB (#157)	290	350	520	450	490	260	560	350	1200	620	580	180	150	170	94	96
2,3',4,4',5'-HxCB (#167)	690	650	540	460	570	240	480	280	950	380	600	290	250	320	180	170
3,3',4,4',5,5'-HxCB (#169)	160	360	1100	820	740	460	1200	950	2900	1500	1300	150	142	21	14	13
2,3,3',4,4',5,5'-HpCB (#189)	520	710	1400	1000	980	550	1400	1100	3500	1700	1600	110	120	110	64	61
WHO-TEQ _{sum} ^b	1600	4400	18000	11000	8900	4600	14000	11000	41000	20000	19000	370	420	92	49	61

^a The IUPAC No. of each DL-PCB congener is provided in parentheses; ^a the values were obtained using TEFs proposed by WHO in 2006; ^c L, M and R represent left side, middle and right sides respectively, and samples were collected on 29th June, 2007.

sediment samples. These results suggest that the estimated values were approximately in agreement with the analyzed values. Continuously, contribution of the three typical sources in Japan to WHO-TEQs is shown in Fig. 5. In terms of sediment samples from Sangamaki Waterway, the pyrogenic sources accounted for ca. 90% of the WHO-TEQ values at site numbers 27–34. This shows that the toxicity of the dioxin congeners in the tributary had been largely the result of the dumping of solid material wastes by the ISWIs. Higher contributions from combustion sources were also observed in water samples from sites located downstream from the ISWIs (locations 5–9, 16, 21, 27 and 31), whereas at the other sites, contributions of herbicides and/or PCB products became higher than those of pyrogenic sources. As discussed above, the PCDD/PCDF characteristics at the downstream sites were essentially prominent for locations around the ISWIs. Above all, the

higher WHO-TEQ values in waters from the mainstream Kanzaki River were significantly attributed to the dumping of incinerator-related wastes into Sangamaki Waterway by the ISWIs.

3 Conclusions

For the first time, the author has elucidated the distribution and causes of PCDD/PCDFs and DL-PCBs in waters from the Kanzaki River Basin, which is one of the most heavily polluted rivers in Japan. In the mainstream, the WHO-TEQ values in SP plus DP were seen to exceed the Japanese environmental standard. Further, abnormally high WHO-TEQ values were detected in a water (50 pg-TEQ/L) and a sediment sample (41,000 ng-TEQ/kg dw) collected from the vicinity of the ISWIs. These facts indicate that the high values could have been a result of the dumping of

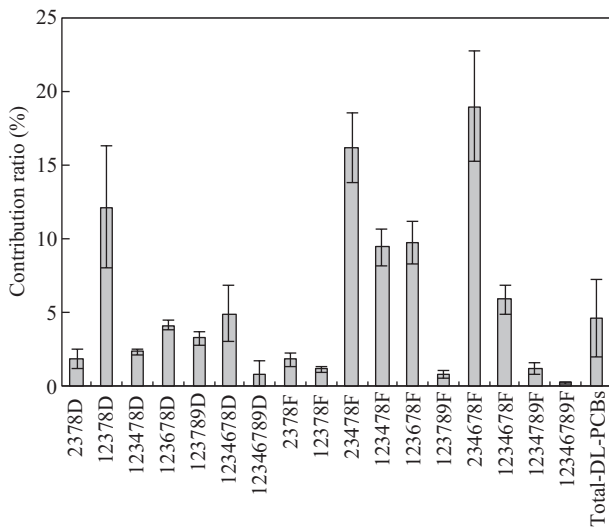


Fig. 3 Average contribution ratios of 2,3,7,8-substituted PCDD/PCDFs and total DL-PCBs to the WHO-TEQ values in water samples from site numbers 16, 21, 27 and 31 in tributary small waterways. D and F in horizontal axis represent PCDDs and PCDFs, respectively.

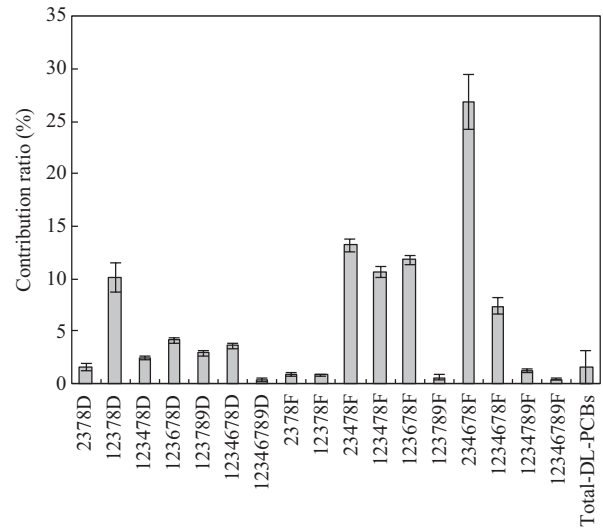


Fig. 4 Average contribution ratios of 2,3,7,8-substituted PCDD/PCDFs and total DL-PCBs to the WHO-TEQ values in sediment samples from site numbers 27–34 in a tributary small waterway (Sangamaki Waterway). D and F in horizontal axis represent PCDDs and PCDFs, respectively.

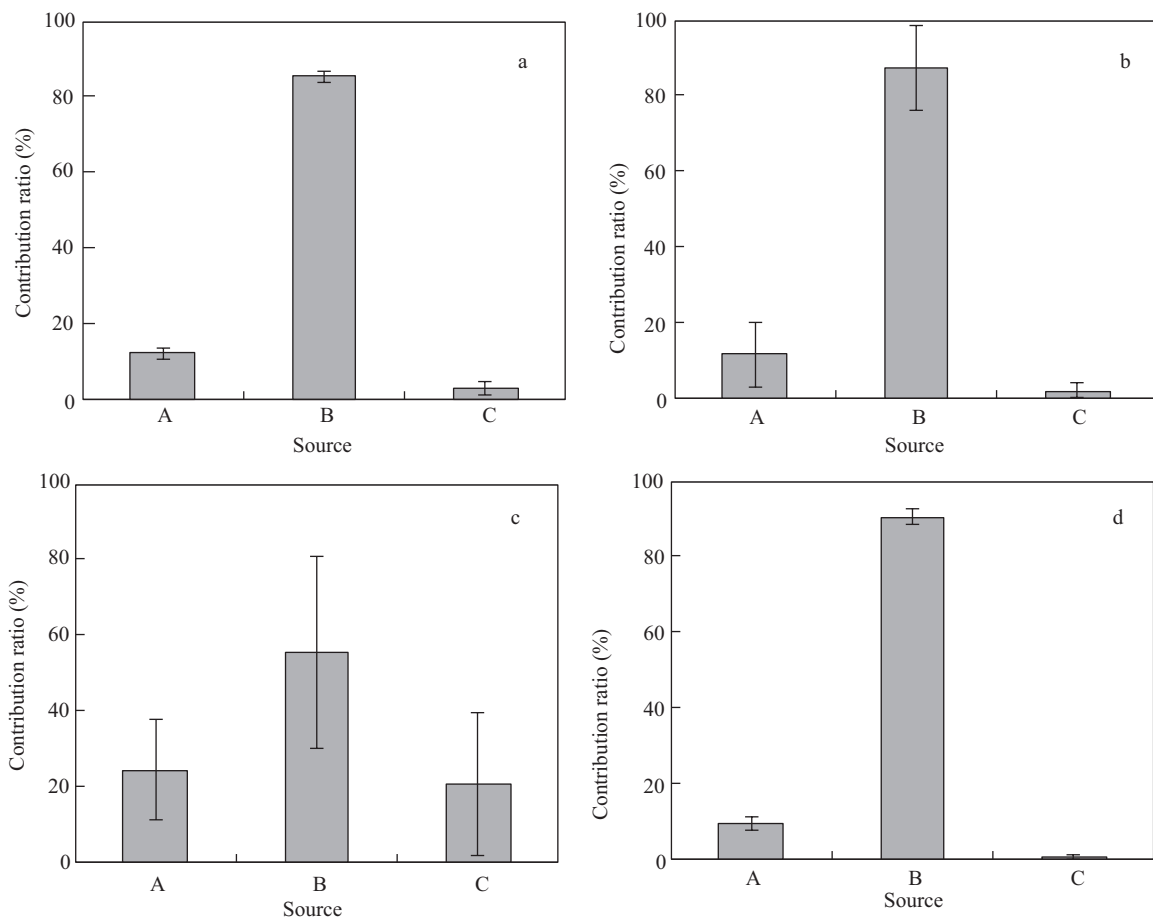


Fig. 5 Average contribution ratio of the three typical sources of dioxins in Japan to the WHO-TEQ values in water and sediment samples from Kanzaki River Basin obtained using a TEQ apportionment method. (a) water samples (dissolved plus suspended phases) from site numbers 5–9 in mainstream Kanzaki River, (b) water samples from site numbers 16, 21, 27 and 31 in tributary small waterways, (c) water samples from sites except for site numbers 5–10, 16, 21, 27 and 31 in tributary small waterways, (d) sediment samples from site numbers 27–34 in a tributary small waterway (Sangamaki Waterway). A, B and C in horizontal axis represent herbicides (CNP plus PCP), pyrogenic sources and commercial PCBs, respectively. Error bars show SDs.

incinerator-related wastes by the ISWIs. Using a TEQ apportionment method, it was found that the high values of the WHO-TEQ in the mainstream could be significantly attributed to dumping of the wastes into its tributary small waterway by the ISWIs. Thus, It was found that one of the heaviest pollution of dioxins in river waters from Japan can be attributed to the runoff of sediments which had already been affected by the incinerator-related wastes dumped into the small tributary.

References

- Broman D, Naef C, Rolff C, Zebühr Y, 1991. Occurrence and dynamics of polychlorinated dibenzo-*p*-dioxins and dibenzofurans and polycyclic aromatic hydrocarbons in the mixed surface layer of remote coastal and offshore waters of Baltic. *Environmental Science and Technology*, 25(11): 1850–1864.
- Examination Committee for Environmental Dioxin Pollution (ECFEDP), 2007. A report of a survey on dioxin pollution in sediment samples from Sangamaki Waterway, Osaka Prefectural Government. Osaka, Japan.
- Götz R, Enge P, Friesel P, Roch K, Kjeller L O, Kulp S E et al., 1994. Sampling and analysis of water and suspended particulate matter of the River Elbe for polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs). *Chemosphere*, 28(1): 63–74.
- Japan Plant Protection Association (JPPA), 2011. Handbook of Agricultural Chemicals. Tokyo, Japan.
- Kakimoto H, Oka H, Miyata Y, Yonezawa Y, Niikawa A, Kyudo H et al., 2006. Homologue and isomer distribution of dioxins observed in water samples collected from Kahokugata Lagoon and inflowing rivers, Japan. *Water Research*, 40(10): 1929–1940.
- Kiguchi O, Kobayashi T, Wada Y, Satoh K, Ogawa N, 2007. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in paddy soils and river sediments in Akita, Japan. *Chemosphere*, 67(3): 557–573.
- Kim Y S, Eun H, Katase T, 2008. Historical distribution of PCDDs, PCDFs, and coplanar PCBs in sediment core of Ariake Bay, Japan. *Archives of Environmental Contamination and Toxicology*, 54(3): 395–405.
- Kishida M, Imamura K, Takenaka N, Maeda Y, Viet P H, Kondo A et al., 2010a. Characteristics of the abundance of polychlorinated dibenzo-*p*-dioxin and dibenzofurans, and dioxin-like polychlorinated biphenyls in sediment samples from selected Asian regions in Can Gio, Southern Vietnam and Osaka, Japan. *Chemosphere*, 78(2): 127–133.
- Kishida M, Maekawa T, Bandow H, 2010b. Effect of extraction temperature on pressurized liquid extraction of polychlorinated dibenzo-*p*-dioxin and dibenzofurans, and dioxin-like polychlorinated biphenyls from a sediment sample using polar and non-polar solvents. *Analytica Chimica Acta*, 659(1-2): 186–193.
- Kishida M, Nishikawa A, Fujimori K, Shibutani Y, 2011. Gas-particle concentrations of atmospheric polycyclic aromatic hydrocarbons at an urban and a residential site in Osaka, Japan: Effect of the formation of the atmospherically stable layer on their temporal change. *Journal of Hazardous Materials*, 192(3): 1340–1349.
- Liu Y L, Peng P, Li X M, Zhang S K, Ren M, 2008. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in water and suspended particulate matter from the Xijiang River, China. *Journal of Hazardous Materials*, 152(1): 40–47.
- Lohmann R, Nelson E, Eisenreich S J, Jones K C, 2000. Evidence of dynamic air-water exchange of PCDD/Fs: A study in the Raritan Bay/Hudson River estuary. *Environmental Science and Technology*, 34(15): 3086–3093.
- Masunaga S, Takasuga T, Nakanishi J, 2001a. Dioxin and dioxin-like PCB impurities in some Japanese agrochemical formulations. *Chemosphere*, 44(4): 873–885.
- Masunaga S, Yao Y, Osuga I, Nakai S, Kanai Y, Yamamuro M et al., 2001b. Identifying sources and mass balance of dioxin pollution in Lake Shinji Basin, Japan. *Environmental Science and Technology*, 35(10): 1967–1973.
- Ministry of the Environment (MOE), Government of Japan, 1998. Manual for the determination of PCDD/Fs and Co-PCBs in water samples. Tokyo, Japan.
- Ministry of the Environment (MOE), Government of Japan, 2012. Countermeasures against dioxins in the environment. Tokyo, Japan. <http://www.env.go.jp/chemi/dioxin/index.html>.
- Minomo K, Ohtsuka N, Hosono S, Nojiri K, Kawamura K, 2010. Apportionment of TEQs from four major dioxin sources in Japan on the basis of five indicative congeners. *Chemosphere*, 81(8): 985–991.
- Minomo K, Ohtsuka N, Hosono S, Nojiri K, Kawamura K, 2011. Seasonal change of PCDDs/PCDFs/DL-PCBs in the water of Ayase River, Japan: Pollution sources and their contribution to TEQ. *Chemosphere*, 85(2): 188–194.
- Osaka Prefectural Government, 2004. Osaka Prefectural Program for PCB Waste Treatment. Osaka, Japan.
- Osaka Prefectural Government, 2012a. Ecogallery. Osaka, Japan. <http://www.pref.osaka.jp/kannosuisoken/ecogallery/>.
- Osaka Prefectural Government, 2012b. Committee for River Maintenance. Osaka, Japan. <http://www.pref.osaka.jp/kasenseibi/keikaku/seibiinkai.html>.
- Saito N, Harada K, Inoue K, Sasaki K, Yoshinaga T, Koizumi A, 2004. Perfluorooctanoate and perfluorooctane sulfonate concentrations in surface water in Japan. *Journal of Occupational Health*, 46(1): 49–59.
- Sakai M, Seike N, Kobayashi J, Kajihara H, Takahashi Y, 2008. Mass balance and long-term fate of PCDD/Fs in a lagoon sediment and paddy soil, Niigata, Japan. *Environmental Pollution*, 156(3): 760–768.
- Suarez M P, Rifai H S, Palachek R, Dean K, Koenig L, 2006. Distribution of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in suspended sediments, dissolved phase and bottom sediment in the Houston Ship Channel. *Chemosphere*, 62(3): 417–429.
- Sugimae A, 1980. Atmospheric concentrations and sources of rare earth elements in the Osaka area, Japan. *Atmospheric Environment*, 14(10): 1171–1175.
- Uebori M, Takahashi K, Kamada A, Kishida M, Shimizu T, Tamura T et al., 2002. PCDD/PCDF and DL-PCB concentrations in the environment in Osaka: Part 2. *Annual report of Environmental Pollution Control Center, Osaka Prefectural Government*, 22: 71–79.

- United Nations Environment Programme (UNEP), 1999. Dioxin and Furan. Inventories, National and Regional Emissions of PCDD/PCDF. Geneva, Switzerland.
- Watanabe I, Kashimoto T, Tatsukawa R, 1986. Confirmation of the presence of the flame retardant decabromobiphenyl ether in river sediment from Osaka, Japan. *Bulletin of Environmental Contamination and Toxicology*, 36(1): 839–842.
- Yasuhara A, Ito H, Morita M, 1987. Isomer-specific determination of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in incinerator-related environmental samples. *Environmental Science and Technology*, 21(10): 971–979.

Editorial Board of Journal of Environmental Sciences

Editor-in-Chief

Hongxiao Tang Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China

Associate Editors-in-Chief

Jiuhui Qu Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China
Shu Tao Peking University, China
Nigel Bell Imperial College London, United Kingdom
Po-Keung Wong The Chinese University of Hong Kong, Hong Kong, China

Editorial Board

Aquatic environment

Baoyu Gao
Shandong University, China
Maohong Fan
University of Wyoming, USA
Chihpin Huang
National Chia Tung University
Taiwan, China
Ng Wun Jern
Nanyang Environment &
Water Research Institute, Singapore
Clark C. K. Liu
University of Hawaii at Manoa, USA
Hokyong Shon
University of Technology, Sydney, Australia
Zijian Wang
Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China
Zhiwu Wang
The Ohio State University, USA
Yuxiang Wang
Queen's University, Canada
Min Yang
Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China
Zhifeng Yang
Beijing Normal University, China
Han-Qing Yu
University of Science & Technology of China

Terrestrial environment

Christopher Anderson
Massey University, New Zealand
Zucong Cai
Nanjing Normal University, China
Xinbin Feng
Institute of Geochemistry,
Chinese Academy of Sciences, China
Hongqing Hu
Huazhong Agricultural University, China
Kin-Che Lam
The Chinese University of Hong Kong
Hong Kong, China
Erwin Klumpp
Research Centre Juelich, Agrosphere Institute
Germany
Peijun Li
Institute of Applied Ecology,
Chinese Academy of Sciences, China

Michael Schloter

German Research Center for Environmental Health
Germany

Xuejun Wang

Peking University, China

Lizhong Zhu

Zhejiang University, China

Atmospheric environment

Jianmin Chen

Fudan University, China

Abdelwahid Mellouki

Centre National de la Recherche Scientifique
France

Yujing Mu

Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China

Min Shao

Peking University, China

James Jay Schauer

University of Wisconsin-Madison, USA

Yuesi Wang

Institute of Atmospheric Physics,
Chinese Academy of Sciences, China

Xin Yang

University of Cambridge, UK

Environmental biology

Yong Cai

Florida International University, USA

Henner Hollert

RWTH Aachen University, Germany

Christopher Rensing

University of Copenhagen, Denmark

Bojan Sedmak

National Institute of Biology, Ljubljana

Lirong Song

Institute of Hydrobiology,
the Chinese Academy of Sciences, China

Chunxia Wang

National Natural Science Foundation of China

Gehong Wei

Northwest A&F University, China

Daqiang Yin

Tongji University, China

Zhongtang Yu

The Ohio State University, USA

Environmental toxicology and health

Jingwen Chen

Dalian University of Technology, China

Jianying Hu

Peking University, China

Guibin Jiang

Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China

Jae-Seong Lee

Hanyang University, South Korea

Sijin Liu

Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China

Tsuyoshi Nakanishi

Gifu Pharmaceutical University, Japan

Willie Peijnenburg

University of Leiden, The Netherlands

Chonggang Wang

Xiamen University, China

Bingsheng Zhou

Institute of Hydrobiology,
Chinese Academy of Sciences, China

Environmental catalysis and materials

Hong He

Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China

Junhua Li

Tsinghua University, China

Wenfeng Shangguan

Shanghai Jiao Tong University, China

Yasutake Teraoka

Kyushu University, Japan

Ralph T. Yang

University of Michigan, USA

Environmental analysis and method

Zongwei Cai

Hong Kong Baptist University,
Hong Kong, China

Jiping Chen

Dalian Institute of Chemical Physics,
Chinese Academy of Sciences, China

Minghui Zheng

Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China

Municipal solid waste and green chemistry

Pinjing He

Tongji University, China

Environmental ecology

Rusong Wang

Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China

Editorial office staff

Managing editor Qingcai Feng
Editors Zixuan Wang Suqin Liu Zhengang Mao
English editor Catherine Rice (USA)

JOURNAL OF ENVIRONMENTAL SCIENCES

(<http://www.jesc.ac.cn>)

Aims and scope

Journal of Environmental Sciences is an international academic journal supervised by Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. The journal publishes original, peer-reviewed innovative research and valuable findings in environmental sciences. The types of articles published are research article, critical review, rapid communications, and special issues.

The scope of the journal embraces the treatment processes for natural groundwater, municipal, agricultural and industrial water and wastewaters; physical and chemical methods for limitation of pollutants emission into the atmospheric environment; chemical and biological and phytoremediation of contaminated soil; fate and transport of pollutants in environments; toxicological effects of terrorist chemical release on the natural environment and human health; development of environmental catalysts and materials.

For subscription to electronic edition

Elsevier is responsible for subscription of the journal. Please subscribe to the journal via <http://www.elsevier.com/locate/jes>.

For subscription to print edition

China: Please contact the customer service, Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China. Tel: +86-10-64017032; E-mail: journal@mail.sciencep.com, or the local post office throughout China (domestic postcode: 2-580).

Outside China: Please order the journal from the Elsevier Customer Service Department at the Regional Sales Office nearest you.

Submission declaration

Submission of an article implies that the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere. The submission should be approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out. If the manuscript accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

Submission declaration

Submission of the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere. The publication should be approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out. If the manuscript accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

Editorial

Authors should submit manuscript online at <http://www.jesc.ac.cn>. In case of queries, please contact editorial office, Tel: +86-10-62920553, E-mail: jesc@263.net, jesc@rcees.ac.cn. Instruction to authors is available at <http://www.jesc.ac.cn>.

Journal of Environmental Sciences (Established in 1989)

Vol. 25 No. 3 2013

Supervised by	Chinese Academy of Sciences	Published by	Science Press, Beijing, China
Sponsored by	Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences		Elsevier Limited, The Netherlands
Edited by	Editorial Office of Journal of Environmental Sciences P. O. Box 2871, Beijing 100085, China Tel: 86-10-62920553; http://www.jesc.ac.cn E-mail: jesc@263.net , jesc@rcees.ac.cn	Distributed by	Domestic Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China Local Post Offices through China
Editor-in-chief	Hongxiao Tang	Foreign	Elsevier Limited http://www.elsevier.com/locate/jes
CN 11-2629/X	Domestic postcode: 2-580	Printed by	Beijing Beilin Printing House, 100083, China
		Domestic price per issue	RMB ¥ 110.00

ISSN 1001-0742



www.jesc.ac.cn