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# Monitoring sources, discharges, and fluxes of, and assessing the risks from, pesticides in the Kurose and Ashida Rivers, Japan

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## Abstract

Because pesticide-contaminated water can harm living organisms, pesticide residues need to be monitored, their sources need to be identified, and the risks they pose should be assessed. In this study, the sources, fluxes, and discharges of, and risks from, pesticides were monitored and assessed during the rice-growing season (from April to October) in the Kurose and Ashida Rivers in Hiroshima, Japan. Water samples were collected monthly, subjected to solid-phase extraction, and then analyzed by gas chromatography–mass spectrometry and high-performance liquid chromatography to determine the presence and concentrations of pesticides. The fluxes of the detected pesticides were also estimated at each site in the Kurose and Ashida rivers, and the discharges of these pesticides from different sources were determined. The potential ecotoxicological risks from the detected pesticides to the aquatic systems were also evaluated. Thirteen pesticides were detected in the Kurose River. Of these, the mean concentrations of diroun (970 ng/L) and butamifos (4.7 ng/L) were the highest and the lowest, respectively. Eleven compounds were detected in the Ashida River. Again, the mean concentration of diuron (860 ng/L) was the highest, while that of flutolanil (5.5 ng/L) was the lowest. The pesticide fluxes were the highest in the Ashida and Kurose Rivers in October and May, respectively. The main sources of pesticide discharges were rice paddies, orchards, and vegetable fields. The results of the ecotoxicological risk assessment indicated that fenitrothion, diuron, dichlorvos, and benthioncarb posed high risks to the aquatic environment in the Ashida and Kurose Rivers.

**Keywords** Monitoring · Discharge source · Runoff load · River · Risk assessment · Pesticides

## Introduction

Considerable increases in the yield per unit have been achieved by applying chemical pesticides to agricultural land in Japan (Derbalah et al. 2003). Indeed, Japan is one of the largest users of pesticides in the world when ranked by pesticide consumption per unit area (Iwakuma et al. 1993;

Tsuda et al. 1994; Sakai 2003; Kaonga et al. 2017). While agricultural laws regulate pesticide use in Japan (Chikushi et al. 2009; Ohta 2013), their ongoing presence in the environment is a cause for concern, as many pesticides applied to land may eventually be discharged into river water (Tsuda et al. 1994; Nakano et al. 2004; Vu et al. 2006; Kondo et al. 2012; Kaonga et al. 2015; Chidya et al. 2018a, b).

Pollution by pesticide residues from nonpoint sources poses a threat to river water quality, the most important source of drinking water in most countries worldwide. Rice fields account for about 50% of Japanese agricultural land and are the main source of pesticide residues in Japanese rivers. Studies conducted to estimate pesticide residues in river waters in Japan have shown that the concentrations of a few pesticides that are commonly used in rice fields may reach several tens of  $\mu\text{g/L}$  (Tanabe et al. 2001; Sudo et al. 2002; Nakano et al. 2004; Vu et al. 2006). Further studies have shown that the pesticides applied to rice paddies during the rice cropping period are generally discharged into rivers (Tsuda et al. 2009; Tanabe and Kawata 2009; Phong et al. 2012; Narushima et al. 2014;

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Kaonga et al. 2015; Chidya et al. 2018a, b), because pesticides used in the rice fields move easily within the environment when the fields are flooded. More recently, researchers have reported that urban areas are also a source of pesticide pollution (Derbalah et al. 2003; Chidya et al. 2018a, b) and that the discharges of pesticides from roads and railways are higher than those from farmland because of the hard surfaces (Nitschke and Schussler 1998; Revitt et al. 2002; Blanchoud et al. 2004). For example, diuron, a herbicide widely used to control weeds on railways and roads, has been detected in rivers in urban areas, but few studies have investigated the levels of diuron in river water in Japan. While it is known that pesticides are discharged from different sources (farmland and urban areas) to rivers, there is a need for more specific information about the sources and amounts of different pesticides of concern and the contributions and potential impacts from each source.

Various anions and cations frequently found in water may affect the behavior and persistence of pesticides in natural water (El-Kabbany et al. 2000; Derbalah 2004). For example,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  may contribute to the photodegradation of organic compounds, thereby affecting their lifetimes and concentrations in stream water (Derbalah et al. 2003). Dissolved organic carbon (DOC) may also indicate pollution caused by organic compounds, such as pesticides, the target compounds in this study (Castilho et al. 2000).

Pesticide residues in the environment lead to ecological changes and pose significant risks to living organisms. They may also affect the health of people who have direct and/or indirect contact with pesticides (Wee and Aris 2017). The negative impacts and environmental risks of pesticide residues in aquatic environments should therefore be evaluated and assessed, so that these environments can be protected (Hela et al. 2005). Indeed, because of the potential risks to aquatic organisms from various pesticides (PPDB 2018; Derbalah et al. 2019), ecotoxicological risk assessments of the concentrations of pesticides in environmental media, such as rivers and other freshwater bodies, should be undertaken to ensure the safety of aquatic organisms and humans (ECC 2003). While there are numerous risk assessment methods, measured concentrations of pesticides are usually compared with the permitted limits for drinking water or environmental quality standards. Risk quotients are currently used in risk assessments (ECC 2003; Palma et al. 2014).

This study was carried out to evaluate the occurrence of pesticides in the Kurose and Ashida Rivers, the most contaminated rivers in Hiroshima Prefecture, Japan, during the rice-growing season (April to October, 2004). This study comprised various aspects, as follows. The fluxes of pesticides at various sampling sites in the Kurose and Ashida rivers were estimated, the sources of pesticides and discharges in Higashi-Hiroshima (the Kurose River) and Fukuyama and Sera-cho (the Ashida River) were assessed, and the potential ecotoxicological risks from the detected pesticides to the ecosystems in the Kurose and Ashida Rivers were also evaluated.

## Materials and methods

### Chemicals

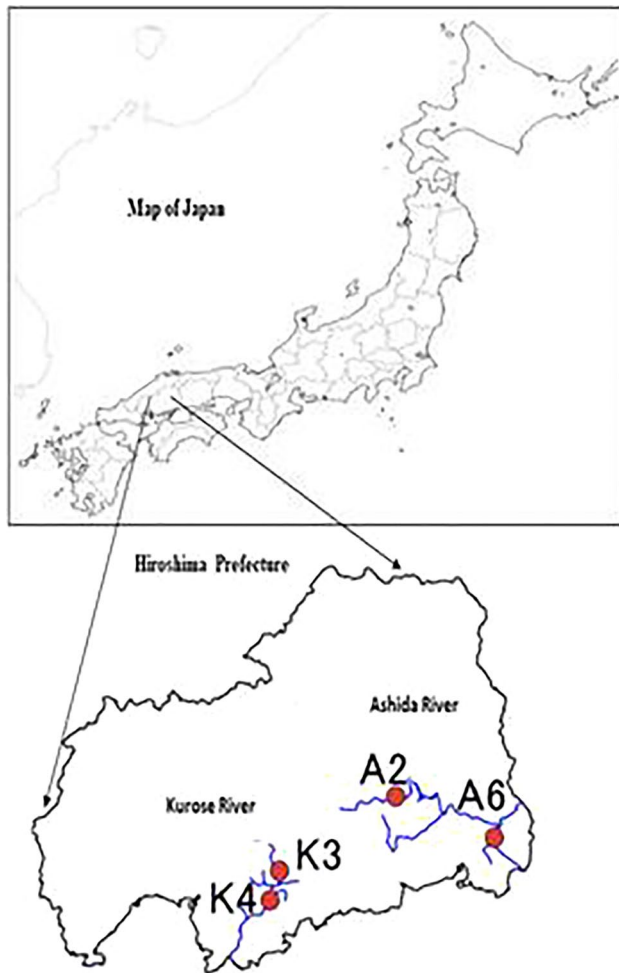
A diuron standard (purity of 99.9%) was obtained from the Kanto Chemical Co. Ltd. Japan. A standard mixture of 31 pesticides (pencycuron, simazine, propyzamide, diazinon, chlorothalonil, napropamide iprobenfos, terbucarb, tolclofos-methyl, metalaxyl, bensulide, dithiopyr, fenitrothion, chlorpyrifos, pendimethalin, methyldymron, captan, isofenphos, butamifos, flutolanil, isoprothiolane, triclopyr, isoxathion, mepronil, iprodione, dichlorvos, fenobucarb, benthocarb, chlornitrofen, EPN, and pyridiphenthion) was obtained from the Kanto Chemical Company, Tokyo, Japan. Pesticide analytical grade solvents (methanol, acetone, acetonitrile, and dichloromethane) were obtained from the Wako Company, Osaka, Japan, and the internal standard phenanthrene-d10 (97.5% purity) was obtained from the Supelco/SigmaAldrich Company, California, USA. Acetic acid (99.7% purity) was obtained from the Katayama Company (Japan). Sodium, potassium, magnesium, and calcium standard solutions, needed for cation analysis, were obtained from the Kanto Chemical Co. Ltd. Japan. Special reagent grade potassium hydrogen phthalate, hydrochloric acid: 2,6-pyridinedicarboxylic acid, sodium hydroxide, sodium chloride, potassium nitrate, sodium nitrite, and potassium sulfate, needed for anion analysis, were obtained from the Nacalai-Tesque Co. Ltd., Kyoto, Japan.

### Sampling sites and water collection

The Kurose River, about 43 km long, is a secondary river in Hiroshima Prefecture. It runs through urban areas, such as Higashi-Hiroshima City, and agricultural areas, on the Kamo Plateau, and flows into the Seto inland Sea. Higashi-Hiroshima, which extends from the upper to middle reaches of the Kurose River, is a leading breadbasket in Hiroshima, and thus there is potential for large discharges of agricultural chemicals during the rice-growing season. The Ashida River is the most polluted first-class river in Chugoku region. In its upper reaches, agriculture extends over the vast Sera Plateau, while Fukuyama, the second largest city in Hiroshima with a dense concentration of human activities, is in the lower reaches. The actual use of pesticides in the upper and lower reaches of the Ashida and Kurose Rivers may be different because of different agricultural activities and subsequently application of different pesticides.

Water sampling sites in the Kurose and Ashida Rivers are shown in Fig. 1. In the Kurose river, there were sampling sites at Misonou (K3), in the central part of Saijo-cho, and Hinotsume (K4), near the boundary between Saijo-cho and Kurose-cho in Higashi-Hiroshima. In the Ashida River, the sampling sites were in the vicinity of the Kozan Seiso





**Fig. 1** Locations of sampling sites in Ashida and Kurose rivers

Station (A2), close to the boundary between Sera-cho and Koyama-cho, and at Yamate-bashi (A6) in the central part of Fukuyama in the lower reaches of the river.

Site K3 was near high density residential and industrial areas, while site K4 was in a low population area, close to agricultural areas, mainly rice fields. Site A2 on the Ashida River was near the boundary between the urban areas of Sera and Koyama, surrounded by the Sera Plateau, a vast area of farmland. The site was upstream of the boundary between the two urban areas, so the water quality at A2 may have been influenced by discharges from Sera. Site A6, also in the Ashida River, was close to urban residential areas and approximately 5 km downstream from golf courses. The Yamate-Bashi Bridge site (A6) was close to the confluence of the Takaya River, which passes through Kannabe-Cho, where there are paddy fields.

The water samples were collected when the river water levels were stable, more than a day after a rainfall event. The samples were collected monthly from April to October in brown bottles and then were kept at 4 °C in an ice cooler and delivered to the analytical laboratory.

## Extraction of the target pesticides from water

Water samples were filtered through glass fiber filters (GC-50, diameter: 47 mm; pore size: 0.5  $\mu\text{m}$ , Advantec) that were subsequently ultrasonically extracted with acetone and combined with filtered samples. Pesticides in the filtered samples were then extracted by solid-phase extraction using an OasisHLB3 cc (60 mg) cartridge (Waters Corporation, USA). After conditioning the cartridges with 5 mL of dichloromethane, 5 mL of methanol, and 5 mL of ultrapure water, the samples were passed through the cartridges at a flow rate of 10–20 mL/min under reduced pressure using an aspirator. To extract 1 L samples, two cartridges were used for each 1 L sample to prevent clogging, which would have slowed the water flow rate considerably. The solid-phase cartridge was dried for approximately 1 h using an aspirator after the sample had passed through. Once dry, the substances adsorbed to the cartridge were eluted into a centrifuge tube with 5 mL of dichloromethane per cartridge and the eluates from the corresponding pairs of cartridges were then mixed to give 10 mL samples. The sample was then concentrated under nitrogen gas, after which phenanthrene solution (10 ppm) was added (50  $\mu\text{L}$ ) as an internal standard in 1 mL acetone. This was then concentrated to approximately 200  $\mu\text{L}$  under nitrogen gas and measured by GC/MS. Each sample was extracted in triplicate. The target compounds were spiked into 200 mL Milli-Q water at levels of 1  $\mu\text{g/L}$  and 0.1  $\mu\text{g/L}$  to calculate the recovery and detection limits, respectively. Another recovery test was carried out using a 1 L spike volume at the same concentration level. The water was acidified to pH 3.0 immediately after this operation, and the water samples were extracted with an automated solid-phase extraction (SPE) apparatus. The detection limit was taken as the concentration that gave a signal-to-noise ratio of three, following the method of Azevedo et al. (2000). The tests to determine the recovery efficiency and the detection limit were repeated five times to obtain accurate values. Ultrapure Milli-Q water was used as a blank without spiking with pesticides to ensure there was no contamination and the results showed that no pesticides were detected in the blank.

## GC–MS analysis

Samples were analyzed with a gas chromatograph (Hewlett Packard HP 5973 series) equipped with a mass selective detector (HP 5973), as described by Derbalah et al. (2003). The main molecular ions of the target pesticides that were used in the GC–MS analysis are shown in Table 1. The total pesticide concentration was calculated by summing the concentrations of the individual compounds.



## HPLC analysis for diuron

Diuron was determined by HPLC, following the method described by Field et al. (1997) and Goody et al. (2002). The water samples were first pretreated in the same manner as the samples to be analyzed by GC/MS. The HPLC system consisted of a pump (LC-10Ai, Shimadzu), a sample injector (Rheodyne Model 1296, sample size 50  $\mu$ L) and an UV–VIS detector (SPD-10A, Shimadzu), with a 250-mm-long column with a particle size 5 of  $\mu$ m, and a diameter of 250 mm (Ultron VX-ODS Suplecasil LC-18, Supelco). A 10-mm-long guard

column, with a particle size of 5  $\mu$ m and a diameter of 4.6 mm (Suplecasil LC-18), was fitted to the front of the analytical column. A mixture of acetonitrile (HPLC grade) and Milli-Q water (35:65) was used as the mobile phase under the isocratic elution mode. The flow rate was maintained at 1.0 mL/min, and the UV detector wavelength was 252 nm.

## Analysis of water quality parameters

At the sampling sites, the conductivity and pH were measured with a pH/conductivity meter (D-24, Horiba, Ltd.,

**Table 1** Retention time, determination and confirmation ion, recovery rate and detection limit of tested pesticides based on GC–MS and HPLC analysis

Compounds	Retention time (min)	Quantitative ion (m/z)	Confirmation ion (m/z)	Recovery (%)	Standard deviation (ppb)	Detection limits (ppb)
<i>Fungicides</i>						
Pencycuron	16.90	125	180	115 $\pm$ 3	0.0200	0.0110
Chlorothalonil	19.80	266	264	90 $\pm$ 8	0.0130	0.0170
Iprobenfos	19.92	91	204	90 $\pm$ 5	0.0360	0.0180
Tolclofos-methyl	21.10	265	267	73 $\pm$ 2	0.0130	0.0150
Metalaxyl	21.45	206	132	80 $\pm$ 2	0.0088	0.0130
Captan	24.29	79	149	79 $\pm$ 2	0.0088	0.0090
Isoprothiolane	26.04	118	162	81 $\pm$ 2	0.0150	0.0240
Flutolanil	26.11	173	145	81 $\pm$ 2	0.0130	0.0024
Mepronil	28.42	119	91	79 $\pm$ 3	0.0150	0.0110
Iprodione	30.72	314	316	87 $\pm$ 1	0.0069	0.0150
<i>Insecticides</i>						
Dichlorvos	8.84	109	185	116 $\pm$ 5	0.0350	0.023
Fenobucarb	15.30	121	150	86 $\pm$ 4	0.0270	0.0099
Diazinon	19.17	137	179	63 $\pm$ 3	0.0230	0.0093
Fenitrothion	22.00	277	109	118 $\pm$ 5	0.0350	0.0240
Chlorpyrifos	22.79	199	97	64 $\pm$ 2	0.0110	0.0160
Isofenphos	24.36	58	121	73 $\pm$ 1	0.0047	0.0064
Isoxathion	27.01	105	177	85 $\pm$ 3	0.0190	0.0130
Pyridaphenthion	30.82	97	77	81 $\pm$ 4	0.0170	0.0160
EPN	30.94	157	169	90 $\pm$ 3	0.0190	0.0370
<i>Herbicides</i>						
Simzaine	18.18	201	186	109 $\pm$ 3	0.020	0.0320
Porpyzamide	18.92	173	175	92 $\pm$ 5	0.033	0.0094
Terbucarb	20.95	205	220	79 $\pm$ 2	0.0089	0.0052
Bensulide	21.44	77	131	82 $\pm$ 1	0.0031	0.0150
Dithiopyr	21.93	306	354	77 $\pm$ 2	0.0082	0.0096
Benthiocarb	22.33	100	72	77 $\pm$ 3	0.0240	0.010
Pendimethalin	24.00	252	253	63 $\pm$ 2	0.0094	0.0073
methylmeron	24.26	107	106	75 $\pm$ 2	0.0096	0.0160
Napropamide	25.79	72	100	76 $\pm$ 1	0.0080	0.0098
Triclopyr	26.82	57	85	73 $\pm$ 1	0.0060	0.0210
Chlornitrofen	28.6	319	317	76 $\pm$ 1	0.0068	0.0220
Butamifos	28.83	286	200	77 $\pm$ 1	0.0073	0.0044
Phenanthrine-d10	18.79	188				
<i>HPLC analysis</i>						
Diuron	17.64	–	–	86 $\pm$ 3	0.024	0.021



Japan), while the temperature and water temperature were measured with a mercury thermometer. The water flow rate was measured using a Hiroi-type water flow meter (Mikasa, Japan). Anions ( $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ ) and cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) were measured by ion chromatography (Dionex, DX500), with different columns for anions (Ion Pac AS11) and cations (Ion Pac CS12A). Dissolved organic carbon (DOC) was measured using a total organic carbon analyzer (TOC 5000-A, Shimadzu Comp. Japan). DOC, and the anions and cations were measured on filtered water samples.

### Calculation of pesticide fluxes

The flux is defined as the mass of the compound transported in a stream in a specific time period. The fluxes of the target compounds at each sampling point were estimated as the product of the compound concentration and the water flow rate for each month (Derbalah et al. 2003). The monthly fluxes were summed to give the total pesticide flux, as described by Larson et al. (1995).

### Estimation of pesticide discharges

The pesticide discharge estimated for Hiroshima Prefecture was used to estimate the discharges (ton/year) of pesticides from the municipalities with sampling sites, namely Higashi-Hiroshima, Fukuyama, and Sera-cho. The estimated discharges of individual pesticides (ton/year) from different sources (rice fields, orchards, vegetables, houses, forests, golf courses, and other non-crop land) to the environments in Hiroshima Prefecture were reported by the Ministry of the Environment, Japan (NIES 2000). The estimated discharges of pesticides from different sources (except golf courses) in each municipality are estimated using Eq. 1:

$$D = A \times B/C \quad (1)$$

where  $D$  is the discharge for a specific municipality,  $A$  is the estimated discharge from Hiroshima Prefecture,  $B$  is the area of each municipality, and  $C$  is the total area of Hiroshima Prefecture.

Because there were no data about discharges from golf courses, the pesticide discharges from golf courses in specific municipalities are estimated using Eq. 2:

$$G = E \times F/I \quad (2)$$

where  $G$  is the discharge from the golf courses in the municipalities,  $E$  is the discharge from all the golf courses in Hiroshima Prefecture,  $F$  is the number of golf courses in the municipalities, and  $I$  is the number of golf courses in Hiroshima Prefecture.

### Ecotoxicological risk assessment of the detected pesticides

The toxicity exposure ratio, or risk quotient (RQ), which is defined as the measured environmental concentration divided by the predicted no-effect concentration (PNEC), is commonly used in risk assessments. Here, the risks from the detected pesticides were assessed using RQs. The chemical properties of the pesticides and the ecotoxicological risk assessment data for the pesticides are shown in Table 1S.

The  $\text{RQ}_i$  for pesticide  $i$  is calculated using Eq. (3):

$$\text{RQ}_i = \frac{\text{MEC}}{\text{PNEC}} \quad (3)$$

where MEC (mg/L) is the measured environmental concentration and PNEC is the predicted no-effect concentration. Each PNEC (mg/L) was calculated from a critical concentration such as the concentration lethal to 50% of test organisms ( $\text{LC}_{50}$ ), 50% effective concentration ( $\text{EC}_{50}$ ), or no-observed-effect concentration (NOEC). Previously published standards were used for the calculations (ECC 2003; Vryzas et al. 2009; Palma et al. 2014).

To account for uncertainty and any missing data when calculating the toxicity parameters, PNECs were estimated for organisms at three trophic levels (algae, crustaceans, and fish) using assessment factors (AFs). The equations used to calculate the critical concentrations ( $\text{PNEC} = \text{NOEC}/\text{AF}$ ,  $\text{PNEC} = \text{LC}_{50}/\text{AF}$ , or  $\text{PNEC} = \text{EC}_{50}/\text{AF}$ ) were selected depending on whether NOEC,  $\text{LC}_{50}$ , or  $\text{EC}_{50}$  data were available for algae, aquatic invertebrates, and fish. An AF of 1000 was used when at least 1 short-term assay result was available for 1 trophic level, an AF of 100 was used when data from 1 long-term assay were available for fish or zooplankton, and AFs of 50 and 10 were used when data from 2 and 3 long-term assays, respectively, were available (ECC 2003). Data for the NOEC,  $\text{LC}_{50}$ ,  $\text{EC}_{50}$ , and log octanol–water partition coefficients were taken from reputable databases (JACC 2010; USEPA 2016; PPDB 2018). The RQs were used to classify the pesticides as low risk ( $0.01 \leq \text{RQ} < 0.1$ ), medium risk ( $0.1 \leq \text{RQ} < 1$ ), or high risk ( $\text{RQ} \geq 1$ ) (Sánchez-Bayo et al. 2002; Vryzas et al. 2011).

## Results and discussion

### Results

#### Method validation

The results of the GC–MS analysis showed that all 31 pesticides listed in Table 1 were separated by the GC column and eluted in a reasonable time. Moreover, the recoveries of most of the tested pesticides were between 70 and 115%, as shown in Table 1, with only lower recoveries for diazinon



(63%) and pendimethalin (63%). The relative standard deviation was around 10% and was always below 30%, in line with the guidance of the United States Environmental Protection Agency (Azevedo et al. 2000). This method, with a detection limit of between 0.004 and 0.003  $\mu\text{g/L}$ , was very sensitive to all the tested pesticides. The HPLC analysis method showed a high sensitivity for diuron, with detection and quantification limits of 0.021 and 0.02  $\mu\text{g/L}$ , respectively. The percentage recovery of diuron was 86%, and the relative standard deviation was below 10%.

### Water quality indicators in both rivers

The flow rate and the water quality data (average, minimum, and maximum values) from the different sampling sites and sampling events in the Kurose and Ashida Rivers are shown in Table 2S. The average flow rate was the highest at site A6 in the Ashida River (8.6  $\text{m}^3/\text{s}$ ) on the day of water sampling, and the lowest at site K3 in the Kurose River (1.4  $\text{m}^3/\text{s}$ ). Generally, the water flow rates were higher at the Ashida River sampling sites than at the Kurose River sampling sites. Also, the water temperature and pH values at the Ashida River sampling sites were higher than at the Kurose River sampling sites. The average pH was the highest at site A6 (8.6) in the Ashida River, and the lowest (7.4) at site K4 of the Kurose River. The average water temperature was the highest at site A6 (25.7) in the Ashida River and the lowest (23.7) at site K4 in the Kurose River. The mean electrical conductivity values were higher at the sampling sites in the Kurose River than in the Ashida River. The average EC was the highest at site K4 (25.0) in the Kurose River, and the lowest (10.2) at site A2 in the Ashida River. The average DOC values at the Kurose River sampling sites were higher than those at sites in the Ashida River. The average DOC value was the highest at site K4 (2.7) in the Kurose River and was the lowest (2) at site A6 in the Ashida River. The average values of cations and anions were higher at the Kurose River sites than at the Ashida River sites. In both rivers, the average cation concentrations were higher than the anion concentrations at all sampling sites. The concentrations of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  were also higher at the Kurose River sites than at the Ashida River sites.

### Detection and levels of pesticides residues in the Kurose and Ashida Rivers

The occurrence frequency and residue levels (average, minimum, and maximum) of the pesticides detected in the Ashida and Kurose Rivers at all sampling sites are summarized in Table 2. Overall, 13 pesticides were detected at the Kurose River sampling sites and 11 were detected at the Ashida River sampling sites. The pesticide detection rates were higher at sites K4 and A6 than that at sites K3 and A2. Of the detected pesticides, the detection rate was the highest for diuron and

the lowest for butamifos in both rivers. When split into categories of pesticides, the insecticides detection rate was higher than the rate for fungicides and herbicides in both rivers. The number of fungicides detected was the highest, followed by herbicides and insecticides. Of the detected pesticides, the concentration of diuron (3.60  $\mu\text{g/L}$ ) was the highest, while that of pendimethalin was the lowest (0.01  $\mu\text{g/L}$ ), in both rivers. Furthermore, the mean value was the highest for diuron (0.970  $\mu\text{g/L}$ ) and the lowest for butamifos (0.0047  $\mu\text{g/L}$ ) in both rivers. In the Kurose River, the mean concentrations of fungicides, insecticides, and herbicides ranged from 0.01 to 0.05, 0.03 to 0.10, and from 0.005 to 0.97  $\mu\text{g/L}$ , respectively. In the Ashida River, the mean concentrations of fungicides, insecticides, and herbicides ranged from 0.06 to 0.13, 0.04 to 0.21, and from 0.04 to 0.86  $\mu\text{g/L}$ , respectively. The total detected pesticides at all sampling sites varied monthly, as summarized in Fig. 1S. The total pesticide concentration was the highest at site A2 in the Ashida River and the lowest at site K3 in the Kurose River. The total pesticide concentrations were the highest in April, May, and June in both the Kurose and Ashida Rivers, except at site A2, for which the total concentration was the highest in August and October.

### Fluxes of pesticides at the different sampling sites in the Ashida and Kurose Rivers

The changes in the fluxes of the detected fungicides, insecticides, and herbicides over the sampling period for each site are shown in Figs. 2, 3, and 4, respectively. Generally, the fluxes of the fungicides, insecticides, and herbicides were higher in the Ashida River than in the Kurose River.

The results showed that the fluxes of all fungicides were the highest in May, June, August, and September (Fig. 2). Of the fungicides, the flux of iprobenfos in June was the highest and that of metalaxyl was the lowest in May. When taken together, the fluxes of iprobenfos at all sampling sites were the highest while those of flutolanil were the lowest. However, the fluxes of all insecticides were the highest in April, July, August, and September (Fig. 3). Of the insecticides at all sampling periods and sampling sites, the flux of fenobucarb in August was the highest and that of dichlorvos in May was the lowest. The fluxes of all the estimated herbicides were the highest in June, July, August, and September (Fig. 4), and, for all sampling sites and sampling periods, the flux of diuron was the highest and that of butamifos was the lowest. With the exception of pendimethalin and butamifos, the fluxes of all the herbicides in the Ashida River were higher than in the Kurose River. The changes in the fluxes of total pesticides over the sampling period at each sampling site are shown in Fig. 2S. The pesticide fluxes were the highest in the Ashida River in August, September, and October, and were the highest in the Kurose River in May and June. The fluxes of pesticides were the highest in August and June at sites A2 and A6,



**Table 2** Detection rate, maximum and average concentrations of pesticides detected at each sampling point of the Kurose and Ashida rivers

Kurose river	K3				K4			
	N.D./N.S.	Detection rate (%)	Highest conc. (ppb)	Average conc. (ppb)	N.D./NS	Detection rate (%)	Highest conc. (ppb)	Average conc. (ppb)
<i>Fungicides</i>								
Chlorthalonil	2/30	7.0	0.05	0.02	0/7	0	–	–
Iprobenfos	3/30	10	0.07	0.02	1/7	14	0.04	0.02
Metalaxyl	2/30	7.0	0.12	0.02	2/7	29	0.02	0.01
Isoprothiolane	12/30	40	0.12	0.04	5/7	71	0.10	0.05
Flutolanil	9/30	30	0.29	0.02	3/7	43	0.07	0.02
Mepronil	0/30	0	–	–	0/7	0	–	–
<i>Insecticides</i>								
Dichlorvos	1/30	3	0.03	0.02	1/7	14	0.03	0.02
Fenobucarb	30/30	100	1.00	0.10	7/7	100	0.08	0.03
Fenitrothion	23/30	77	0.25	0.08	6/7	86	0.13	0.05
<i>Herbicides</i>								
Simzaine	0/30	0	–	–	0/7	0	–	–
Benthiocarb	17/30	57	0.79	0.11	4/7	57	0.46	0.09
Pendamethaline	2/30	7.0	0.01	0.01	1/7	14	0.01	0.01
Butamifos	1/30	3.0	0.02	0.01	0/7	0	–	–
Diuron	29/29	100	3.60	0.97	7/7	100	1.10	0.59
Ashida river	A2		A6					
<i>Fungicides</i>								
Chlorthalonil	0/7	0	–	–	0/7	0	–	–
Iprobenfos	0/7	0	–	–	3/7	43	0.54	0.11
Metalaxyl	1/7	14	0.04	0.02	1/7	14	0.02	0.01
Isoprothiolane	5/7	71	0.47	0.13	6/7	86	0.09	0.05
Flutolanil	2/7	29	0.01	0.01	3/7	43	0.02	0.01
Mepronil	1/7	14	0.16	0.04	2/7	29	0.15	0.04
<i>Insecticides</i>								
Dichlorvos	2/7	29	0.25	0.06	0/7	0	–	–
Fenobucarb	5/7	71	0.50	0.09	6/7	86	0.12	0.04
Fenitrothion	6/7	86	1.10	0.21	6/7	86	0.08	0.04
<i>Herbicides</i>								
Simazine	0/7	0	–	–	1/7	14	0.06	0.04
Benthiocarb	3/7	43	0.41	0.07	4/7	57	0.23	0.05
Pendimethalin	0/7	0	–	–	0/7	0	–	–
Butamifos	0/7	0	–	–	0/7	0	–	–
Diuron	7/7	100	2.10	0.86	7/7	100	0.48	0.35

N.D. number of detections, N.S. number of samples

Average concentration, concentration below the detection limit, calculated by the value of the detection limit

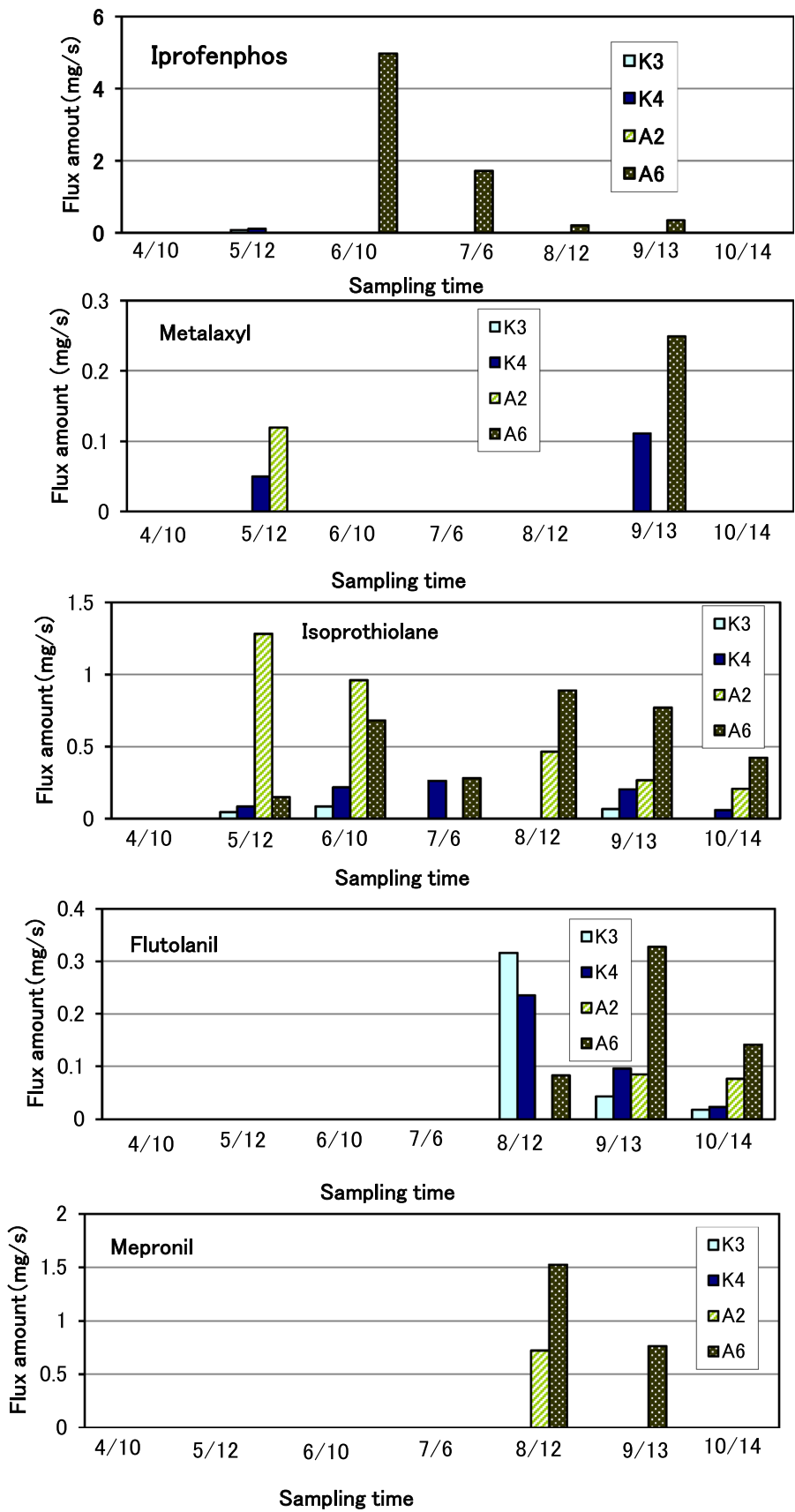
respectively. In the Kurose River, the fluxes were the highest in June and May at sites K4 and K3, respectively.

**Sources and amounts of pesticides discharged into the rivers**

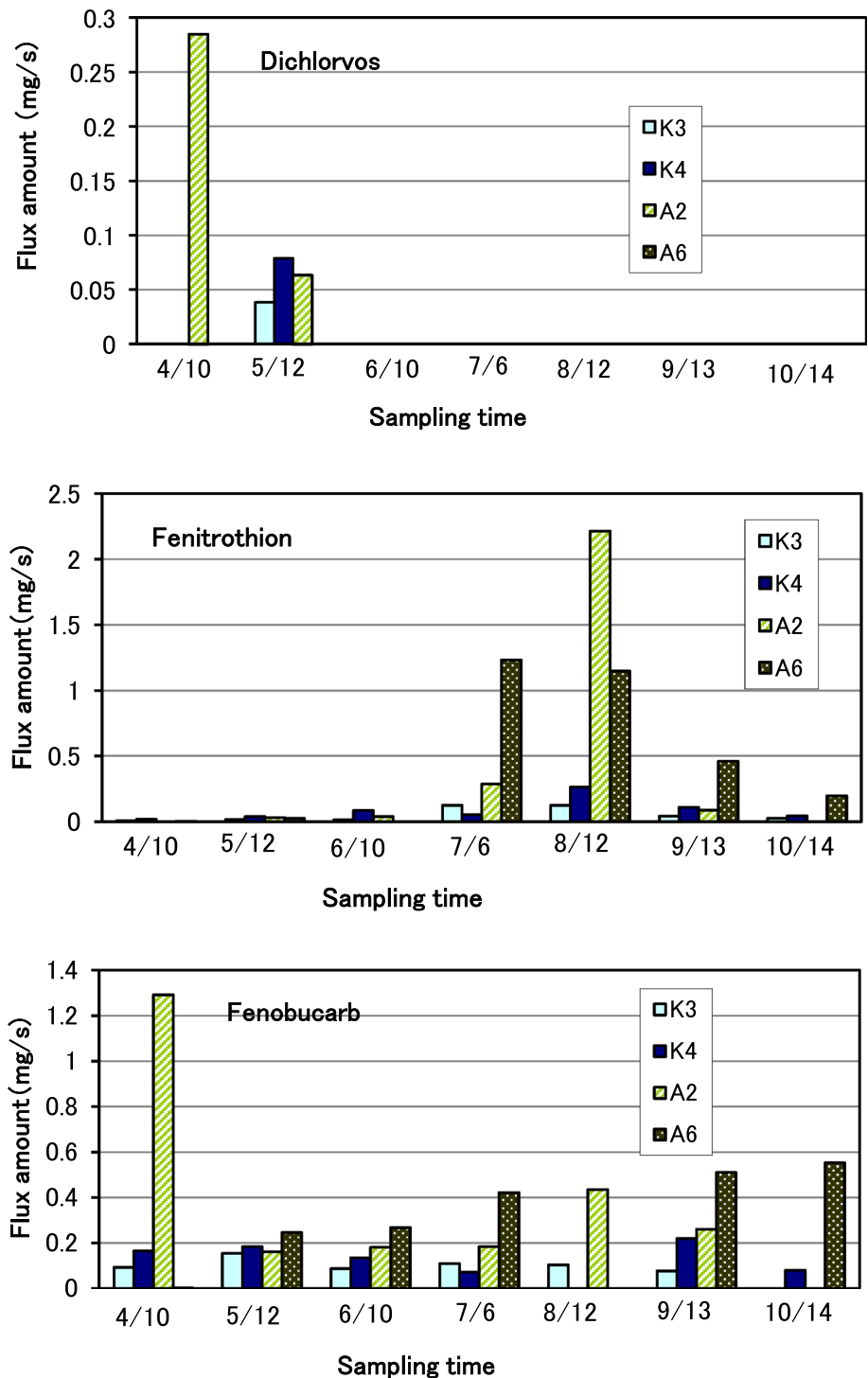
The amounts of pesticides discharged from different sources in Higashi-Hiroshima (which represented all the Kurose River), Fukuyama (used to represent the middle reaches

of the Ashida River), and Sera-cho (used to represent the downstream reach of the Ashida River) are summarized in Tables 3, 4 and 5, respectively. The results showed that the discharges of total insecticides were the higher than those of fungicides and herbicides in all cities. Of the pesticides, the total discharge of fenitrothion was the highest, while the discharges of iprodione, metalaxyl, and mepronil were the lowest in Higashi-Hiroshima, Fukuyama, and Sero-cho, respectively.

**Fig. 2** Changes in the flux amount of fungicides applied during the sampling of the Kurose



**Fig. 3** Changes in the flux of insecticides at the time of water sampling in the Kurose and Ashida

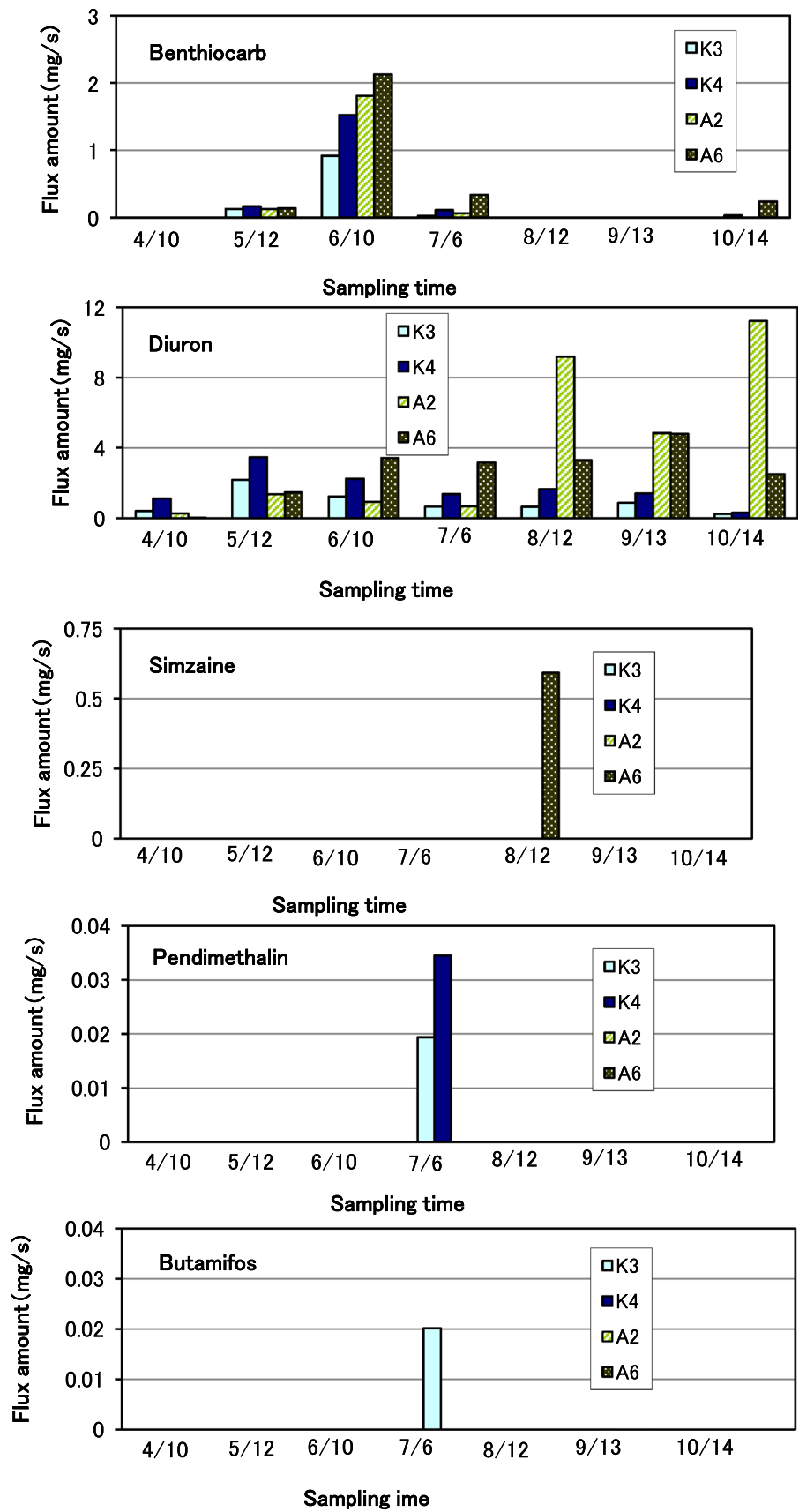


Of the fungicides, chlorothalonil was the only compound discharged in high amounts from different sources in all cities. In Higashi-Hiroshima, most of the fungicide discharges were from rice fields, apart from captan and iprodione, which were mainly from golf courses. In Fukuyama, most of the fungicides were discharged from rice fields, except for iprodione, captan, and mepronil, which were mainly discharged from orchards, vegetable farms, and golf courses, respectively. In

Sera-Cho, most of the fungicides discharged were from rice fields, apart from captan and iprodione, which were mainly discharged from orchard fields. In Sera-cho and Fukuyama, metalaxyl was mainly discharged from vegetable fields.

Of the insecticides, the total discharges of fenitrothion from different sources were the highest in all three cities. For the insecticides, the main sources of fenobucarb, diazinon, fenitrothion, and EPN were rice fields, while dichlorvos

**Fig. 4** Changes in the flux of herbicides at the time of water sampling in the Kurose and Ashida rivers



**Table 3** Estimated discharge of pesticides (kg/year) in Higashi-Hiroshima

Name	Rice fields	Orchards	Vegetables	House	Golf course	Forests	Others non-crop-land	Total
<i>Fungicides</i>								
Chlorothalonil	185.1	7.4	70.2	88.7	122.1	–	–	473.5
Iprobenfos	94.2	–	–	–	–	–	–	94.2
Tolclofos-methyl	–	–	–	–	–	–	–	–
Metalaxyl	11.3	–	5.1	–	–	–	–	16.4
Captan	–	3.0	9.0	–	22.8	–	–	34.9
Isoprothiolane	168.4	–	–	–	–	–	–	168.4
Flutolanil	73.1	–	–	–	–	–	–	73.1
Mepronil	21.7	–	–	–	50.4	–	–	72.1
Iprodione	–	2.5	2.7	–	9.1	–	–	14.3
<i>Insecticides</i>								
Dichlorvos	–	19.0	45.4	–	–	–	3.0	67.4
Fenobucarb	1096.7	–	0.1	–	–	–	2.2	1099.1
Diazinon	235.3	3.3	56.1	–	84.4	–	–	379.2
Fenitrothion	1335.4	33.3	14.0	101.5	47.6	246.6	180.6	1959.1
Chlorpyrifos	–	1.1	2.0	–	13.9	–	–	16.9
Isofenphos	–	–	–	–	–	–	–	–
Isoxathion	16.9	2.3	29.3	41.6	–	–	–	90.1
Pyridafenthion	–	0.6	0.1	–	0.6	–	1.1	2.3
EPN	16.8	–	2.7	–	–	–	–	19.5
<i>Herbicides</i>								
Simazine	–	0.5	4.5	9.1	4.3	–	–	18.5
Propyzamide	–	–	0.2	–	33.9	–	–	34.1
Terbucarb	–	–	–	–	–	–	–	–
Bensulide	–	–	–	–	–	–	–	–
Dithiopyr	–	–	–	–	–	–	–	–
Benthiocarb	1313.5	–	29.8	–	–	–	–	1343.2
Pendimethalin	–	–	13.1	–	–	–	–	13.1
Methyldimeron	–	–	–	–	–	–	–	–
Napropamide	–	–	–	–	–	–	–	–
Triclopyr	–	–	–	–	10.2	21.3	7.2	38.7
Chlorinetofen	–	–	–	–	–	–	–	–
Butamifos	11.9	–	7.0	–	8.8	–	–	27.7
Diuron	–	7.1	13.2	143.3	–	–	150.0	313.6

was mainly discharged from vegetables in both Higashi-Hiroshima and Fukuyama and Sera-cho. In Higashi-Hiroshima, golf courses were the main source of chlorpyrifos, non-cropland was the main source of pyridiphenthion, and residential homes were the main source of isoxathion. However, in Fukuyama, vegetable fields were the main source of isoxathion, while in Sero-cho, orchard fields were the main sources of chlorpyrifos and pyridaphenthion and vegetable fields were the main source of isoxathion.

Of the herbicides, the total discharges of benthiocarb were the highest, and simazine and diuron were discharged from various sources in all cities. Rice fields were the main source of benthiocarb, while vegetable fields were the main source of butamifos and pendimethalin in all cities. In Higashi-Hiroshima,

the main sources of simazine, propyzamide, triclopyr, diuron, and fenobucarb were houses, golf courses, forests, non-cropland, and rice fields, respectively. In Fukuyama, houses were the main source of simazine and diuron, while forests and golf courses were the main sources of triclopyr and propyzamide, respectively. In Sera-cho, vegetables were the main source of simazine and propyzamide, non-cropland was the main source of diuron, and forests were the main source of triclopyr.

#### Ecotoxicological risk assessment of the pesticides detected in the Kurose and Ashida Rivers

The results of the ecotoxicological risk assessment (as  $RQ_{\text{mean}}$  values) derived from the mean measured



**Table 4** Estimated discharge of pesticides (kg/year) in Fukuyama

Name	Rice fields	Orchards	Vegetables	House	Golf course	Forests	Others non-cropland	Total
<i>Fungicides</i>								
Chlorothalonil	174.0	65.5	411.9	333.4	122.1	–	–	1106.8
Iprobenfos	88.6	–	–	–	–	–	–	88.6
Tolclofos-methyl	–	–	–	–	–	–	–	–
Metalaxyl	10.6	–	30.0	–	–	–	–	40.6
Captan	–	26.7	53.1	–	22.8	–	–	102.5
Isoprothiolane	158.3	–	–	–	–	–	–	158.3
Flutolanil	68.7	–	–	–	–	–	–	68.7
Mepronil	20.4	–	–	–	50.4	–	–	70.8
Iprodione	–	21.8	15.8	–	9.1	–	–	46.7
<i>Insecticides</i>								
Dichlorvos	–	168.1	266.4	–	–	–	6.7	441.2
Fenobucarb	1031.1	–	0.6	–	–	–	5.1	1036.8
Diazinon	221.2	29.6	328.9	–	84.4	–	–	664.1
Fenitrothion	1255.5	295.1	82.2	381.5	47.6	634.9	409.4	3106.2
Chlorpyrifos	–	9.6	11.6	–	13.9	–	–	35.1
Isofenphos	–	–	–	–	–	–	–	–
Isoxathion	15.9	20.7	171.8	156.3	–	–	–	364.7
Pyridafenthion	–	4.9	0.5	–	0.6	–	2.5	8.5
EPN	15.8	–	15.8	–	–	–	–	31.6
<i>Herbicides</i>								
Simazine	–	4.7	26.4	34.3	4.3	–	–	69.8
propyzamide	–	–	1.3	–	33.9	–	–	35.2
Terbucarb	–	–	–	–	–	–	–	–
Bensulide	–	–	–	–	–	–	–	–
Dithiopyr	–	–	–	–	–	–	–	–
Benthiocarb	1234.9	–	174.5	–	–	–	–	1409.4
Pendimethalin	–	–	76.7	–	–	–	–	76.7
Methyldimeron	–	–	–	–	–	–	–	–
Napropamide	–	–	–	–	–	–	–	–
Triclopyr	–	–	–	–	10.2	54.9	16.3	81.4
Chlorinetofen	–	–	–	–	–	–	–	–
Butamifos	11.2	–	40.8	–	8.8	–	–	60.8
Diuron	–	62.9	77.5	538.4	–	–	340.0	1018.8

NA not available

concentrations of the detected pesticides in the Kurose and Ashida Rivers are shown in Table 6. For both rivers, the RQ was the lowest for simazine in the Ashida River (0.0033) and was the highest for fenitrothion in the Ashida River (143), respectively. The RQ values of the pesticides detected in the Kurose and Ashida Rivers ranged from 0.001 to 139 and from 0.00033 to 143, respectively. The RQ values of fenitrothion, diuron, dichlorvos, and butamifos were higher ( $RQ > 1$ ) than those of the other detected pesticides in both rivers. The RQ values of fenitrothion, diuron, and dichlorvos were 139 and 143, 75 and 42, and 32 and 90 in the Kurose and Ashida Rivers, respectively. The RQ values of benthiocarb were  $> 1$  in both rivers, while the RQ values of the remaining pesticides (iprobenfos, metalaxyl, flutolanil,

mepronil, isoprothiolane, and simazine) were  $< 1$  in both rivers.

## Discussion

The results of this study showed that there were different types of pesticides, such as insecticides (fenitrothion, diazinon, chlorpyrifos, isofenphos, and pyridaphenthion), herbicides (simazine, propyzamide, pendimethalin, and butamifos), and fungicides (flutolanil, mepronil, tolclofos-methyl, mepronil, iprodione, isoxathion, chlorothalonil, and isoprothiolane), in water from the Kurose and Ashida Rivers. These pesticides have been detected in numerous other rivers in Japan previously (Itagaki et al. 2000; Kondoh et al.



**Table 5** Estimated discharge (kg/year) of pesticides in Sera-Cho

Name	Rice fields	Orchards	Vegetables	House	Golf course	Forests	Others non-cropland	Total
<i>Fungicides</i>								
Chlorothalonil	68.2	39.4	72.8	11.9	–	–	–	192.3
Iprobenfos	34.7	–	–	–	–	–	–	34.7
Tolclofos-methyl	–	–	–	–	–	–	–	–
Metalaxyl	4.2	–	5.3	–	–	–	–	9.5
Captan	–	16.0	9.4	–	–	–	–	25.4
Isoprothiolane	62.1	–	–	–	–	–	–	62.1
Futolanil	26.9	–	–	–	–	–	–	26.9
Mepronil	8.0	–	–	–	–	–	–	8.0
Iprodione	–	13.1	2.8	–	–	–	–	15.9
<i>Insecticides</i>								
Dichlorvos	–	101.2	47.1	–	–	–	0.9	149.2
Fenobucarb	404.3	–	0.1	–	–	–	0.7	405.1
Diazinon	86.8	17.8	58.1	–	–	–	–	162.7
Fenitrothion	492.3	177.6	14.5	13.6	–	146.1	52.5	896.6
Chlorpyrifos	–	5.8	2.1	–	–	–	–	7.8
Isofenphos	–	–	–	–	–	–	–	–
Isoxathion	6.2	12.5	30.4	5.6	–	–	–	54.6
Pyridafenthion	–	3.0	0.1	–	–	–	0.3	3.4
EPN	6.2	–	2.8	–	–	–	–	9.0
<i>Herbicides</i>								
Simazine	–	2.8	4.7	1.2	–	–	–	8.7
porpyzamide	–	–	0.2	–	–	–	–	0.2
Terbucarb	–	–	–	–	–	–	–	–
Bensulide	–	–	–	–	–	–	–	–
Dithiopyr	–	–	–	–	–	–	–	–
Benthiocarb	484.3	–	30.9	–	–	–	–	515.1
Pendimethalin	–	–	13.6	–	–	–	–	13.6
Methyldimeron	–	–	–	–	–	–	–	–
Napropamide	–	–	–	–	–	–	–	–
Triclopyr	–	–	–	–	–	12.6	2.1	14.7
Chlorinetofen	–	–	–	–	–	–	–	–
Butamifos	4.4	–	7.2	–	–	–	–	11.6
Diuron	–	37.9	13.7	19.2	–	–	43.6	114.3

2001; Tanabe et al. 2001; Sudo et al. 2002; Derbalah et al. 2003; Nakano et al. 2004; Vu et al. 2006; Tanabe and Kawata 2009; Kondo et al. 2012; Phong et al. 2012; Narushima et al. 2014; Kaonga et al. 2015; Chidya et al. 2018a, b).

The residual levels of the pesticides detected in this study varied considerably. The levels of fungicides in river water were the highest, perhaps because these fungicides are used relatively widely on most crops, especially rice, to control a wide range of fungal diseases (Derbalah et al. 2003). The considerable variability is not surprising, given the diversity in the physical properties of pesticides, the application practices, soil characteristics, topography, and weather (Larson et al. 1995; Montuori et al. 2016), and the effective dissipation processes during transport in surface water (Sudo et al. 2002). The concentrations of the detected pesticides were

the lowest in both the Kurose and Ashida Rivers and may have been affected by water quality ions such as  $\text{NO}_3^-$  and  $\text{NO}_2^-$  anions, which are considered a major source of hydroxyl radicals in natural water (Mopper and Zhou 1990; Derbalah et al. 2003) and have a role in the photodegradation of pesticides, thereby affecting their lifetimes and concentrations. The stability of pesticides in water is closely related to the pH, with pesticides most stable in slightly acidic water (pH 4–6) (Petroff 2000). Thus, because of the environmental conditions, the concentrations of some heavily used compounds may be low while those of other infrequently used compounds may be high (Derbalah et al. 2003).

Examination of the temporal variation showed that the total concentrations of pesticides were the highest in April, May, and June in the Kurose and Ashida Rivers, perhaps



**Table 6** Ecotoxicological risk assessment results (risk quotients) for detected pesticides in Kurose and Ashida rivers (calculated using mean values)

Compounds	Mean values			RQ <sub>m</sub> Kurose river	RQ <sub>m</sub> <sup>a</sup> Ashida river
	MEC (mg/L) Kurose river	MEC (mg/L) Ashida river	PNEC (mg/L)		
Chlorthalonil	0.00008	–	0.000900	0.089	–
Iprobenfos	0.000315	0.000055	0.001200	0.263	0.04583
Metalaxyl	0.00025	0.0000505	0.000960	0.260	0.05260
Isoprothiolane	0.000585	0.000495	0.004850	0.121	0.10206
Flutolanil	0.00026	0.00001765	0.018000	0.014	0.00098
Mepronil	0.00008	0.0001795	0.010000	0.008	0.01795
Dichlorvos	0.000345	0.000125	0.000004	90.789	32.89474
Fenobucarb	0.001145	0.000522	0.001700	0.674	0.30706
Fenitrothion	0.001085	0.001122	0.000008	139.103	143.84615
Simzaine	0.00008	0.0000195	0.060000	0.001	0.00033
Benthiocarb	0.000513	0.000436	0.000340	1.509	1.28235
Pendimethalin	0.0000875	–	0.000300	0.292	–
Butamifos	0.00485	–	0.000025	19.40	–
Diuron	0.00405	0.002275	0.000054	75.000	42.12963

RQ<sub>m</sub> risk quotient based on mean concentrations, PNEC predicted no-effect concentration, MEC measured environmental concentration (mean)

<sup>a</sup>RQ classification: low risk  $0.01 \leq RQ < 0.1$ ; medium risk  $0.1 \leq RQ < 1$ ; high risk  $RQ \geq 1$

reflecting the timing of the pesticide applications to the rice fields (Derbalah et al. 2003). Many studies have reported high concentrations of herbicides during the rice planting season, and that the discharges of herbicides were the highest at this time. Studies have also shown that the concentrations of insecticides and fungicides peaked later than those of herbicides. Nakano et al. (2004) reported that the herbicide concentrations were the highest after paddy rice was transplanted in the Koise River in Ibaraki Prefecture, but were almost lower than the LOD 1 month later. In their two-year survey of the Ishikari River, Kondoh et al. (2001) reported that the concentrations of herbicides and insecticides corresponded with the timing of applications and peaked between June and July and between July and August, respectively (Kondoh et al. 2001). In addition, Numabe et al. (1992) noted that the concentration of an insecticide peaked 1 week after that of a herbicide. Derbalah et al. (2003) reported that the pesticide concentrations were relatively high in the Kurose River between April and September, during the rice-growing season.

There were obvious variations in the detection frequencies of each of the detected pesticides. For example, of the fungicides, the detection rate for isoprothiolane was the highest at each sampling site, especially at A2, perhaps because this compound is widely used to control some plant pathogens in rice (Iwafune et al. 2010). However, of the detected herbicides, the detection rate at all sampling sites was the highest for diuron, probably because this herbicide is often used both in non-farmland areas such as roads and railways and in agricultural fields to control some weeds. Moreover, the use of pesticides on non-agricultural land may

result in pesticide pollution of rivers (Nitschke and Schussler 1998; Revitt et al. 2002; Blanchoud et al. 2004). Also, of the detected insecticides, fenitrothion was frequently detected at all sampling sites, possibly because fenitrothion is extensively used in agriculture to control of a wide range of insects, and also as an insecticide in households and forestry applications (Derbalah et al. 2003; Kaonga et al. 2015; Chidya et al. Chidya et al. 2018a, b).

The fluxes of the detected pesticides were high during May, June, July, and August in both rivers, which may reflect the high concentrations of detected pesticides and high flow rates in both rivers (Derbalah et al. 2003). Moreover, the fluxes of pesticides were higher in the Ashida River than in the Kurose River, perhaps because the flow was higher in the Ashida River than in the Kurose River. Derbalah et al. (2003) reported that the Kurose River was known for its low water flow rate (estimated at 0.91 m<sup>3</sup>/s). Compared with the fluxes of all the pesticides, the flux of diuron was high, reflecting its high concentrations in both rivers.

By evaluating the discharge amounts of pesticides from different sources in Higashi-Hiroshima, Sera-cho, and Fukuyama, we found that agricultural fields where rice was cultivated, orchards and fields where vegetables were cultivated were the main sources of pesticide discharges into river water (Derbalah et al. 2003), while golf courses, forests, and residential buildings were secondary sources. The results also showed that non-cropland was the main discharge source of diuron, perhaps because it is used extensively to control weeds in roads and railways (Nitschke and Schussler 1998; Revitt et al. 2002; Blanchoud et al. 2004). The large amounts of fungicides discharged such as





metalaxyl, iprobenfos, mepronil, flutolanil, and isoprothiolane from rice fields may reflect the use of these fungicides to control several plant pathogens in rice crops, including those responsible for rice blight and root rot (Shiraishi et al. 1988; Derbalah et al. 2003; Iwafune et al. 2010). The large amounts of captan and iprodione discharged from orchards and vegetables fields reflect the fact that they are widely applied to fruits and vegetables to control a wide range of plant pathogens. Conversely, the amounts of fenitrothion, fenobucarb, and diazinon discharged were large because they are extensively used to control sucking insects when cultivating rice (Derbalah et al. 2003; Iwafune et al. 2010). However, the discharges of isoxathion and dichlorvos from vegetables fields were large because they were widely used to control sucking and leafminer insects in vegetable crops. The discharge of thiobencarb from rice fields was high, perhaps reflecting the heavy use of this herbicide to control broadleaved weeds mainly in rice (Shiraishi et al. 1988; Sudo et al. 2002; Iwafune et al. 2010), while the high discharges of pendimethalin and butamifos from vegetables fields may reflect their widespread application to control annual weeds in vegetable crops.

The results from the risk assessment showed that there may be considerably more ecotoxicological risks from dichlorvos, benthocarb, diuron, and fenitrothion than from other pesticides in both rivers, which may have adverse effects on aquatic organisms (algae, aquatic invertebrates, and fish) and subsequently human health. Because of the risks they pose, these pesticides, especially organophosphorus insecticides (dichlorvos and fenitrothion), should be managed as a priority (Derbalah et al. 2019). The RQs indicated that attention should be paid to the potential risks from iprobenfos, metalaxyl, flutolanil, mepronil, and isoprothiolane, even though their ROs were currently  $< 1$ . Also, some fractions of these pesticides may accumulate in sediments; therefore, the risks posed by the aqueous and particulate phases could be more significant (Ma et al. 2006; Tien and Chen 2012). Also, the Kurose and Ashida Rivers flow into the Seto Inland Sea and so these rivers will transport pesticides that may affect aquatic organisms, especially fish, into the Seto Inland Sea, with possible indirect effects on human health (Derbalah et al. 2019). A priority for the future therefore is to improve the accuracy of the risk assessments of pesticide residues to river ecosystems. Improved assessments are only possible when the data of the concentrations of pesticides and their byproducts are improved and when there is better information about the toxicological effects of these pesticides, especially on endemic species. With improved information, it will then be possible to improve assessments of the ecological risks from pesticides and how they change on a seasonal basis (Hela et al. 2005; Derbalah et al. 2019).

## Conclusion

Thirteen pesticides were detected in the Kurose River. Of these, the mean concentrations of diroun and butamifos were the highest and the lowest, respectively. Eleven compounds were found in the Ashida River, and the mean concentrations of diroun and flutolanil were the highest and the lowest, respectively. The concentrations of pesticides were the highest at site K3 in the Kurose River and at site A6 in the Ashida River. The fluxes of pesticides were the highest in the Ashida River in August, September, and October, and in the Kurose River in April, May, and June. The main sources of pesticide discharges were rice fields, orchards, and vegetable fields. The ecotoxicological risk assessment indicated that there were considerable risks to the aquatic environments in the Ashida and Kurose Rivers from fenitrothion, diuron, dichlorvos, and benthocarb.

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