

Pesticides in River and Tap Water in a Rice Production Area of Niigata, Japan

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Abstract Water samples collected in 1995 and 2007 from the Shinano and Agano rivers were examined to determine the types and concentrations of pesticides and their effects on tap water in typical rice production areas of Japan. Tap water originating from the Shinano River was also sampled in 2007, in Niigata City, Japan. Pesticides were present in the river and tap water throughout the year. Comparison of 13 pesticides common to both 1995 and 2007 series revealed that the frequency of individual pesticide occurrence and concentrations were decreasing. Riverine pesticides were classified into five groups according to the period of their appearance and changes in concentration. Pesticides were detected at the time of application to, and drainage from, paddy fields. Pesticide concentrations in tap water showed notable decline following rapid sand-filtration combined with granular activated carbon. The detection index (DI) for tap water and Shinano River water did not exceed a value of 1. Herbicides contributed most to the DI.

Keywords Pesticides · River water · Tap water · Granular activated carbon · Detection index (DI)

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1 Introduction

Japan is one of the main users of pesticides worldwide, with more than 480 active constituents distributed in 4,450 commercial products. Pesticide shipments for Japan in 2012 amounted to 232,915 tons, of which 10,551 tons (the fifth highest quantity in Japan) were for Niigata Prefecture (Japan Plant Protection Association 2012). The agricultural production and rice production of Niigata City for 2006 were worth 65.5 billion yen and 37.1 billion yen, respectively, which are the third and first highest in Japan (Ministry of Agriculture Forestry and Fisheries of Japan 2007).

The extensive application of pesticides to agricultural fields has led to serious issues of air, water, and soil contamination. An epidemiological study by Yamamoto et al. (1993) suggested that the heavy use of chlornitrofen was associated with increased occurrence of biliary tract cancer in Niigata Prefecture through the contamination of tap water. Their findings led to the nationwide suspension of chlornitrofen in Japan in 1996. Therefore, it is important to continue to monitor the behavior of pesticides in the environment and tap water.

The runoff of pesticides from agricultural fields is correlated with the amount applied within the drainage basin, its chemical properties, modes of application, and storm events following application (Richards and Baker 1993). Yamaguchi et al. (1992) showed that the behavior of pesticides generally followed two forms that mainly depended on pesticide usage. Kimbrough and Litke (1996) reported that pesticide concentrations were higher

at the time of their application, with maximum concentrations generally occurring in storm runoff. Nakano et al. (2004) reported that runoff rates of herbicides showed reasonable correlation with octanol–water partition coefficient. Sudo et al. (2002) carried out research in the Lake Biwa basin and detected molinate, simetryn, oxadiazon, and isoprothiolane at the higher frequencies with maximum concentrations of 0.1 to 1.1 $\mu\text{g/l}$ in the effluent river from lake. Mitobe et al. (1997) studied distribution of aerial spraying pesticides in river water at Niigata plain and detected 11 kinds of pesticides at 0.04 to 4.84 $\mu\text{g/l}$ in median. It was also reported that not only agricultural fields but also urban areas are sources for pesticide contamination of surface water (Hoffman et al. 2000; Derbalah et al. 2003). From these studies, it is clear that various kinds of pesticides are transported from agricultural fields and urban area into rivers. Therefore, it is probable that the consumption of tap water originating from rivers contaminated with pesticide has some effects on human health. Jerschow et al. (2012) showed that dichlorophenol, which is widely used as a component of pesticides and is formed as a disinfection by-product of chlorinated phenol in water treatment systems, may contribute to the increasing incidence of food allergies.

In this paper, the concentrations of 13 pesticides in the Shinano and Agano rivers (Niigata Prefecture, Japan) were studied in 1995, followed in 2007 by more detailed examination of 64 pesticides in the same rivers and in tap water originating from the Shinano River. The results were compared to determine the behavior of pesticides in river and tap waters, and the detection index (DI) was calculated.

2 Materials and Methods

2.1 Seasonal Pesticide Use in Paddy Fields

In most areas of Japan, rice is the main agricultural product. Wet-rice farming is carried out once in a year. The nursery period is about 3 weeks with seeding in mid-April. Fungicide is applied to prevent rice leaf blight. Young rice plants are planted in the first week of May. The water depth of a paddy field after planting is 3 to 4 cm until the rice plants spread their roots, after which it is reduced to 2 to 3 cm to promote higher water temperature. Herbicide is mainly applied during this

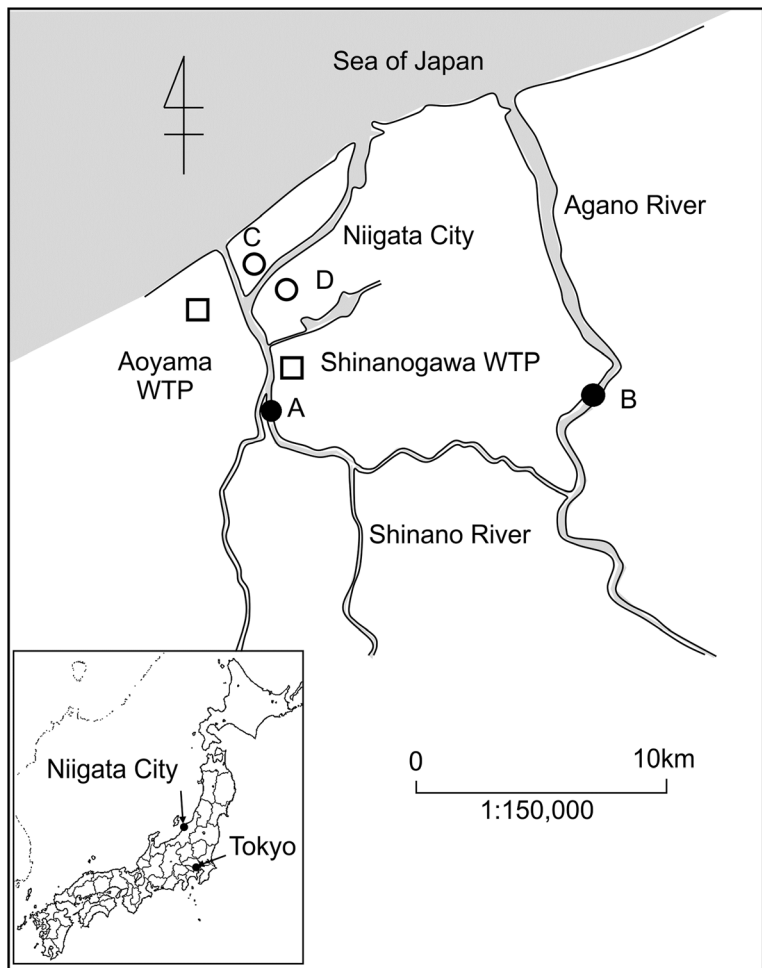
period, and there is no surface drainage for 4 to 5 days following application. At the beginning of June, about 1 month after planting, the paddy field is completely drained to suppress tillering; the field is not plowed and is subject to intermittent irrigation. Ears of rice appear at the beginning of August, when fungicides are sprayed to prevent panicle blast. From early- to mid-August, insecticides are sprayed to inhibit *Sogatella furcifera* and green rice leafhopper. After the appearance of ear shoots (around the end of August), the paddy field is entirely drained and the ears of rice are harvested.

2.2 Sampling Sites

The sampling sites are shown in Fig. 1. In 1995 and 2007, river water was collected from two sites: (1) the Shinanogawa-ohashi Bridge across the Shinano River; and (2) the Ohun-bashi Bridge across the Agano River. The Shinanogawa-ohashi Bridge is located about 14 km upstream from the mouth of the Shinano River. The Shinano River is the longest river in Japan (approximately 367 km) and has a basin area of approximately 11,900 km^2 . Land use within the basin is approximately 70 % forest and wasteland, 19 % agriculture and paddy fields, 9 % urban, and 2 % lakes and other uses (Ministry of Land, Infrastructure, Transport and Tourism of Japan 2008). The Ohun-bashi Bridge is located about 10 km upstream from the mouth of the Agano River. The Agano River is the tenth longest river in Japan (approximately 210 km) and has a basin area of approximately 7,710 km^2 . Mountainous terrain occupies 87 % of the basin; approximately 10 % is agricultural paddy fields and 3 % of the area is urban (Ministry of Land, Infrastructure, Transport and Tourism of Japan 2007).

Samples of tap water were collected from the Aoyama and Shinanogawa water treatment plants (WTP). Both WTPs are owned and operated by the Niigata City administration and utilize the Shinano River for raw water. The water intakes for both WTPs are located about 2.3 km downstream from Shinanogawa-ohashi Bridge. Schematics of the water treatment system are shown in Fig. 2. The Aoyama WTP utilizes a rapid filtration process. In the summer season, powdered activated carbon is also added at the WTP inlet in order to remove disinfection by-products such as trihalomethanes (THMs). The Shinanogawa WTP was newly constructed in 2005 and operates a

Fig. 1 Sampling sites in Niigata City, Japan. **a** Shinanogawa-ohashi Bridge. **b** Ohun-bashi Bridge. **c** Tap water from Aoyama Water Treatment Plant (WTP). **d** Tap water from Shinanogawa WTP



granular activated-carbon tank between the sedimentation tank and the rapid sand-filtration tank.

2.3 Sampling

In the 1995 study, the river waters were sampled from April 29, 1995 to April 25, 1996, initially on alternate days and then at gradually longer intervals, reaching a frequency of once a week from mid-June onwards. In the 2007 study, river waters were sampled approximately twice weekly from April 18, 2007 to April 18, 2008. River waters were sampled from both rivers. Water samples were collected from the surface and the center of the river, using a bucket tied to a string. For tap water, two sampling points were selected in order to differentiate the performance of the two WTPs. One sampling point was from a hydrant in a private home that had no water storage tank and was located about 2 km from the

Aoyama WTP. The other hydrant shared the same conditions but was located about 4 km from the Shinanogawa WTP. Sampling was conducted after the water reached a constant temperature. Samples were stored in brown glass bottles. Residual chlorine was removed by adding 0.01 to 0.02 g of sodium ascorbate for every 1 mg of residual chlorine in the samples. In both the 1995 and 2007 studies, samples were refrigerated and immediately transferred to the laboratory for prompt pretreatment and analysis.

2.4 Number of Pesticides Measured

The 1995 study measured 13 pesticides that represented the standard and monitored chemicals in the Water Supply Act of 1992 (Ministry of Health, Labour and Welfare of Japan 1992). In the 2007 study, 64 pesticides were selected from 101 target chemicals for water

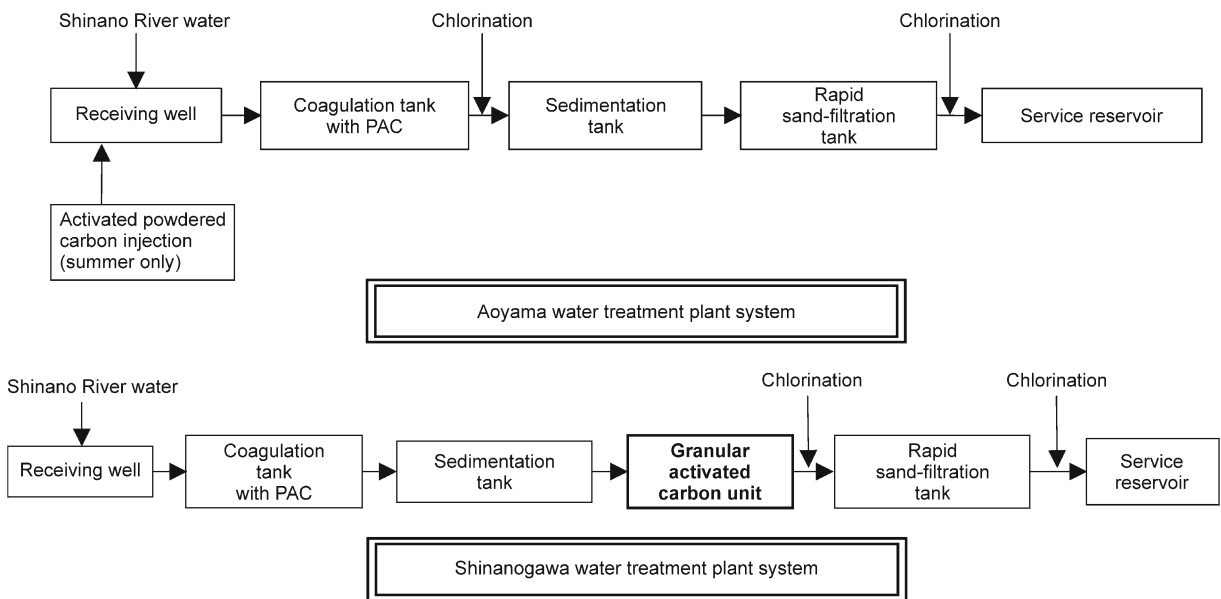


Fig. 2 Outline of water treatment system

quality standards in the Water Supply Act of 2003. Subsequently, water quality standards were revised several times, and in the current water quality standards that took effect in April 2014, the target chemicals for pesticides comprises 120 items (Ministry of Health, Labour and Welfare of Japan 2003; 2014). The pesticides measured in 1995 were also measured in 2007.

2.5 Method of Analysis

For pretreatment of the samples prior to gas chromatography–mass spectrometry (GC/MS) analysis, solid-phase extraction was used in accordance with Tap Water Testing Methods in Japan (Japan Water Works Association 2001). First, suspended solids were

removed from the river water samples by vacuum filtration using a glass-fiber filter paper with 1 μm pores. Numabe et al. (1992) reported that most pesticides were usually found only in dissolved solids, but that following periods of rain the resulting high concentrations of suspended solids can sometimes contain pesticides. Therefore, the present study only analyzed pesticides in filtrates. A solid-phase column (Sep-Pak Plus PS-2 cartridge) was used for separation and concentration of target pesticides. Each column was cleaned using 5 ml dichloromethane, 5 ml methanol, and 5 ml ion-exchanged water. Next, samples were passed through the column at 20 ml/min, and pesticides in the samples were adsorbed. The adsorption stages used 1,000 ml of the sample in 2007, and 400 ml in 1995. The column

Table 1 GC/MS operation conditions

Items	Operating Conditions of gas chromatography–mass spectrometry
Column:	DB-5MS (30 m \times 0.25 mm, ϕ :0.50 μm)
Column temperature in 2007:	50 $^{\circ}\text{C}$ (3 min) \rightarrow (20 $^{\circ}\text{C}/\text{min}$) \rightarrow 180 $^{\circ}\text{C}$ (5 min) \rightarrow (3 $^{\circ}\text{C}/\text{min}$) \rightarrow 290 $^{\circ}\text{C}$ (5 min)
Column temperature in 1995:	50 $^{\circ}\text{C}$ (2 min) \rightarrow (30 $^{\circ}\text{C}/\text{min}$) \rightarrow 200 $^{\circ}\text{C}$ \rightarrow (20 $^{\circ}\text{C}/\text{min}$) \rightarrow 270 $^{\circ}\text{C}$ (5 min)
Carrier gas:	He (1.7 ml/min)
Injection:	Splitless
Injection temperature:	250 $^{\circ}\text{C}$
Interface temperature:	250 $^{\circ}\text{C}$
Ion source temperature:	250 $^{\circ}\text{C}$
Ionization energy:	70 eV

Table 2 Summary of pesticides concentration in river and tap waters, together with detection frequencies

Pesticides	2007						1995						DL		
	Shinano River (n=104)		Agano River (n=104)		Aoyama WTP (n=104)		Shinanogawa WTP (n=104)		Shinano River (n=61)		Agano river (n=61)				
	Concentration (ng/l)	Fr (%)	Concentration (ng/l)	Fr (%)	Concentration (ng/l)	Fr (%)	Concentration (ng/l)	Fr (%)	Concentration (ng/l)	Fr (%)	Concentration (ng/l)	Fr (%)			
	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean			
Herbicides															
Thiobencarb	35	11	2.6	2.6	<2	1.0	<2	<2	80	27	16	120	40	13	2
Molinate	450	84	120	34	<2	17	<2	<2	-	-	-	-	-	-	2
Cafenstrole	140	47	79	29	45	23	10	<10	-	-	-	-	-	-	10
Pyributicarb	7.5	7.1	<3	<3	<3	<3	<3	<3	-	-	-	-	-	-	3
Alachlor	30	16	42	42	<2	1.0	<2	<2	-	-	-	-	-	-	2
Mefenacet	220	69	57	32	8.6	8.6	1.0	<4	-	-	-	-	-	-	4
Thenylchlor	17	8.2	<3	<3	<3	<3	<3	<3	-	-	-	-	-	-	3
Dimethametryn	49	10	22	7.9	<3	11	<3	<3	-	-	-	-	-	-	3
Bromobutide	6200	720	4400	430	1900	490	30	110	32	95	32	110	32	95	6
Dichlobenil	52	8.6	21	3.0	23	5.2	86	1.4	0.87	13	0.87	1.4	0.87	13	1
Simetryn	210	49	38	18	<2	10	<2	<2	-	-	-	-	-	-	2
Esprocarb	100	32	<6	<6	<6	<6	<6	<6	-	-	-	-	-	-	6
Simazine	<1	<1	<1	<1	<1	<1	<1	<1	55	23	8.2	60	60	1.6	1
Propyzamide	<3	<3	<3	<3	<3	<3	<3	<3	73	42	11	<3	<3	<3	3
Chlomitrofen	<27	<27	<27	<27	<27	<27	<27	<27	76	76	1.6	<27	<27	<27	27
Dithiopyr	<2	<2	<2	<2	<2	<2	<2	<2	-	-	-	-	-	-	2
Terbucarb	<2	<2	<2	<2	<2	<2	<2	<2	-	-	-	-	-	-	2
Napropamide	<4	<4	<4	<4	<4	<4	<4	<4	-	-	-	-	-	-	4
Butamifos	<30	<30	<30	<30	<30	<30	<30	<30	-	-	-	-	-	-	30
Benfluralin	<4	<4	<4	<4	<4	<4	<4	<4	-	-	-	-	-	-	4
Pendimethalin	<4	<4	<4	<4	<4	<4	<4	<4	-	-	-	-	-	-	4
Methyl-daimuron	<6	<6	<6	<6	<6	<6	<6	<6	-	-	-	-	-	-	6
Anilofos	<22	<22	<22	<22	<22	<22	<22	<22	-	-	-	-	-	-	22
Atrazine	<1	<1	<1	<1	<1	<1	<1	<1	-	-	-	-	-	-	1
Dimepiperate	<3	<3	<3	<3	<3	<3	<3	<3	-	-	-	-	-	-	3
Piperophos	<16	<16	<16	<16	<16	<16	<16	<16	-	-	-	-	-	-	16

Table 2 (continued)

Water source	2007												1995				DL		
	Shinano River (n=104)			Agano River (n=104)			Aoyama WTP (n=104)			Shinanogawa WTP (n=104)			Shinano River (n=61)		Agano river (n=61)				
	Concentration (ng/l)	Fr (%)	Mean	Concentration (ng/l)	Fr (%)	Mean	Concentration (ng/l)	Fr (%)	Mean	Concentration (ng/l)	Fr (%)	Mean	Concentration (ng/l)	Fr (%)	Mean	Concentration (ng/l)		Fr (%)	Mean
Pesticides																			
Trifluralin	<4			<4			<4			<4			<4						
Insecticides																			
Dichlorvos	110	28	28	12	12	1.0	80	26	29	80	26	80	57	18	38	20	11	6.6	2
Fenobucarb	43	11	30	15	7.1	8.7	12	5.9	19	<2	12	5.9	540	84	23	54	21	15	2
Isoprocarb	7.5	5.5	1.9	<2			6.1	5.8	1.9	<2	6.1	5.8							2
Dimethoate	66	52	1.9	<14			<14			<14									14
Diazinon	<6			<6			<6			<6			530	100	23	220	160	8.2	6
Fenitrothion	<10			<10			<10			<10			220	97	9.8	110	110	1.6	10
Isoxathion	<42			<42			<42			<42			1200	670	3.3	280	280	1.6	42
EPN	<13			<13			<13			<13			240	170	3.3	<13			13
Isofenphos	<6			<6			<6			<6									6
Chlorpyrifos	<6			<6			<6			<6									6
Pyridaphenthion	<36			<36			<36			<36									36
Methidathion	<8			<8			<8			<8									8
α-Endosulfan	<12			<12			<12			<12									12
β-Endosulfan	<11			<11			<11			<11									11
Ethofenprox	<17			<17			<17			<17									17
Fenthion	<2			<2			<2			<2									2
Malathion	<4			<4			<4			<4									4
Phenthoate	<4			<4			<4			<4									4
Buprofezin	<6			<6			<6			<6									6
Disulfoton	<10			<10			<10			<10									10
Pyriproxyfen	<15			<15			<15			<15									15
Fungicides																			
Isoprothiolane	200	50	36	120	40	22	32	21	6.7	<4			870	150	25	290	93	16	4
Chlorothalonil	44	9.0	13	7.3	7.1	1.9	19	12	3.8	<4			77	45	3.3	78	77	3.3	4
Flutolanil	41	15	22	3.0	3.0	1.0	13	7.8	4.8	<2									2

Table 2 (continued)

Pesticides	2007		1995				DL						
	Shinano River (n=104)		Agano River (n=104)		Aoyama WTP (n=104)			Shinanogawa WTP (n=104)		Shinano River (n=61)		Agano river (n=61)	
	Concentration (ng/l)	Fr (%)	Concentration (ng/l)	Fr (%)	Concentration (ng/l)	Fr (%)		Concentration (ng/l)	Fr (%)	Concentration (ng/l)	Fr (%)	Concentration (ng/l)	Fr (%)
	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	
Mepronil	320	320	1.0	<13	<13	<13	<13	<13	-	-	-	-	
Pyroquilon	1300	86	51	1500	150	79	100	23	21	5.4	12	-	
Fthalide	62	16	21	16	9.3	11	20	8.0	7.7	<2	<2	-	
Iprobenfos	<10			<10			<10			<10	81	6.6	
Iprodione	<30			<30			<30			<30	-	-	
Etridiazole	<3			<3			<3			<3	-	-	
Captan	<20			<20			<20			<20	-	-	
Chloroneb	<2			<2			<2			<2	-	-	
Tolclofos-methyl	<3			<3			<3			<3	-	-	
Pencycuron	<8			<8			<8			<8	-	-	
Metalaxyl	<2			<2			<2			<2	-	-	
Edifenphos	<150			<150			<150			<150	-	-	
Procymidone	<2			<2			<2			<2	-	-	

Max maximum concentration, Fr detected frequency, DL detection limits

was then dried with vacuum suction for more than 60 min. Dichloromethane 3 ml was gently poured through from the top of the column to elute the pesticide components to a 10-ml centrifuge tube. Then 1 ml of 1 mg/l 9-bromoanthracene was added to the elute as an internal standard. The solution was then warmed at 40 °C in a heating block, using nitrogen gas to condense the content to less than 1 ml. This content was made up to 1 ml with dichloromethane. Following pretreatment, quantitative analysis was performed using a GC/MS (GC17A/QP-5000, Shimadzu Corporation). The analytical conditions are shown in Table 1. To insure against contamination, each series first analyzed a procedural blank, none of which indicated the presence of pesticides.

2.6 Calculation of the Detection Index

The Japanese Government presently sets criteria for 120 types of pesticide (Ministry of Health, Labour and Welfare of Japan 2014). In this DI system, rural administrations that include sources of water can select important pesticides from those listed. The DI for operation of WTPs in Japan should not exceed 1, as calculated by the following equation.

$$DI = \sum \left(\frac{DV_i}{GV_i} \right) < 1$$

Here, DI is the detection index; DV is the detected value for a pesticide i ; and GV_i is the guideline value for pesticide i . GV is defined by the following equation (World Health Organization 2008; Research Institute of Environmental Management, Administration and Maintenance of JAPAN 2009),

$$GV = \frac{ADI \cdot bw \cdot P}{C}$$

where ADI is acceptable daily intake; bw is body weight (50 kg as per the Water Supply Act in Japan); P is the allocation to drinking water (=10 %); and C is daily drinking water consumption (=2 l).

3 Results and Discussion

3.1 Concentrations of Pesticides in River Water

The results, maximum and average concentrations are summarized in Table 2. In 1995, of the 13 pesticides analyzed, all were detected in the Shinano River, compared with 10 in the Agano River. In the 2007 study, 22 pesticides were detected in the Shinano River and 16 in the Agano River. Therefore, overall, only 22 of the 64 tested pesticides were present in 2007.

Of the 13 pesticides found in 1995, five (thiobencarb, dichlorvos, fenobucarb, isoprothiolane, and chlorothalonil) were also found in 2007. The remaining 8 pesticides were not detected in 2007, that is, simazine, propyzamide, chlornitrofen, iprobenfos, diazinon, fenitrothion, isoxathion, and ethyl 4-nitrophenyl phenylphosphonothioate (EPN).

The concentrations were compared for the five pesticides present (Table 2). The results showed that the maximum and average concentrations of dichlorvos from the Shinano River in 2007 were 190 and 200 % higher than in 1995, respectively. However, the other four pesticides showed concentrations that were 8, 60, 20, and 80 % lower than in 1995, respectively. For the Agano River, the five pesticides showed declines of 2 to 60 % in maximum concentrations and 0.5 to 60 % in mean concentrations in 2007 compared with 1995.

As seen in Fig. 3, between pesticide fiscal years 1993 and 2004, substantially reduced quantities of pesticides

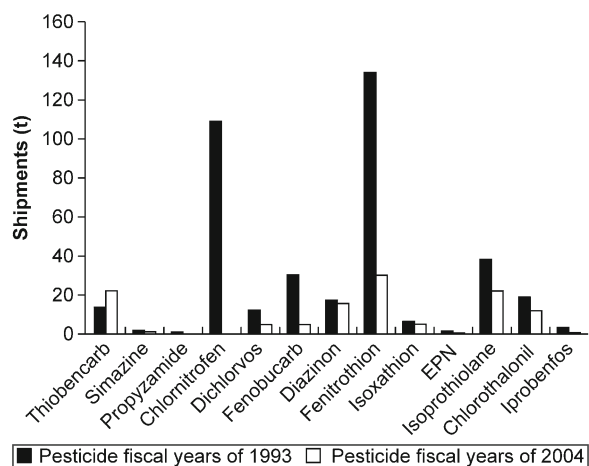


Fig. 3 Shipments of pesticides into Niigata Prefecture in fiscal years 1993 and 2004 Pesticide fiscal year 1993: October 1992 to September 1993. Pesticide fiscal year 2004: October 2003 to September 2004

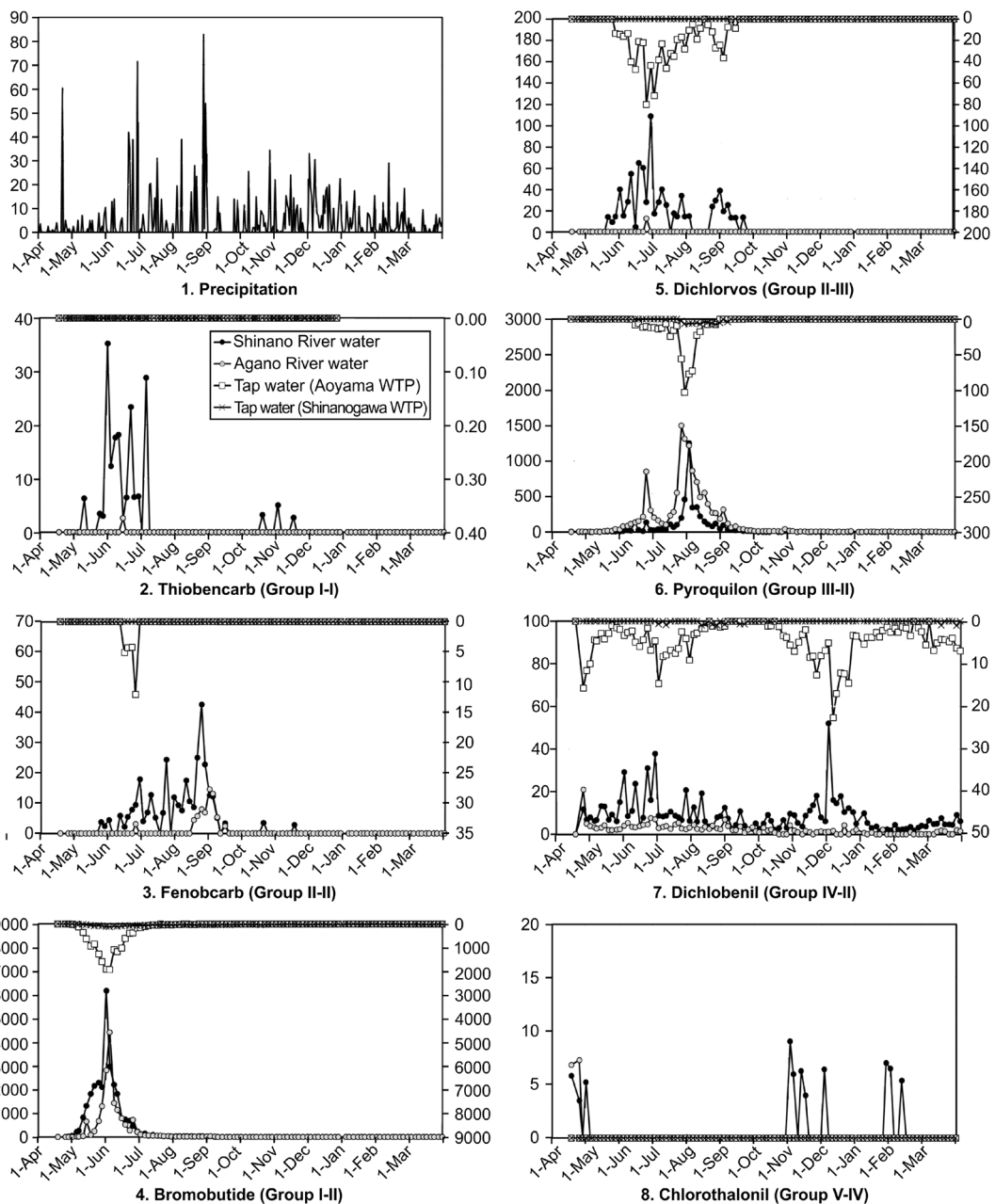


Fig. 4 a Changes in precipitation in Niigata City and pesticide concentrations in Shinano River, Agano River water and tap water in 2007. Units for precipitation are mm per day; concentration units for pesticides are nanograms per liter. *Left graph axis* is concentration in river water; *right axis* is tap water. **b** Changes in

precipitation in Niigata City and pesticide concentrations in Shinano and Agano river water in 1995. Units for precipitation are mm per day; units for pesticide concentration are nanograms per liter

were shipped to Niigata Prefecture (12 of the 13 pesticides, except thiobencarb) (Japan Plant Protection Association 1994, 2005). Propyzamide and chlornitrofen (registration for the latter was revoked in 1996) were not shipped at all in pesticide fiscal year

2004. It was concluded that the changes in the type of pesticides and reduction in the amounts used accounted for the reduced number of compounds and concentrations detected in 2007. We attributed the reduced usage and changes in pesticide type to a decline in planted area

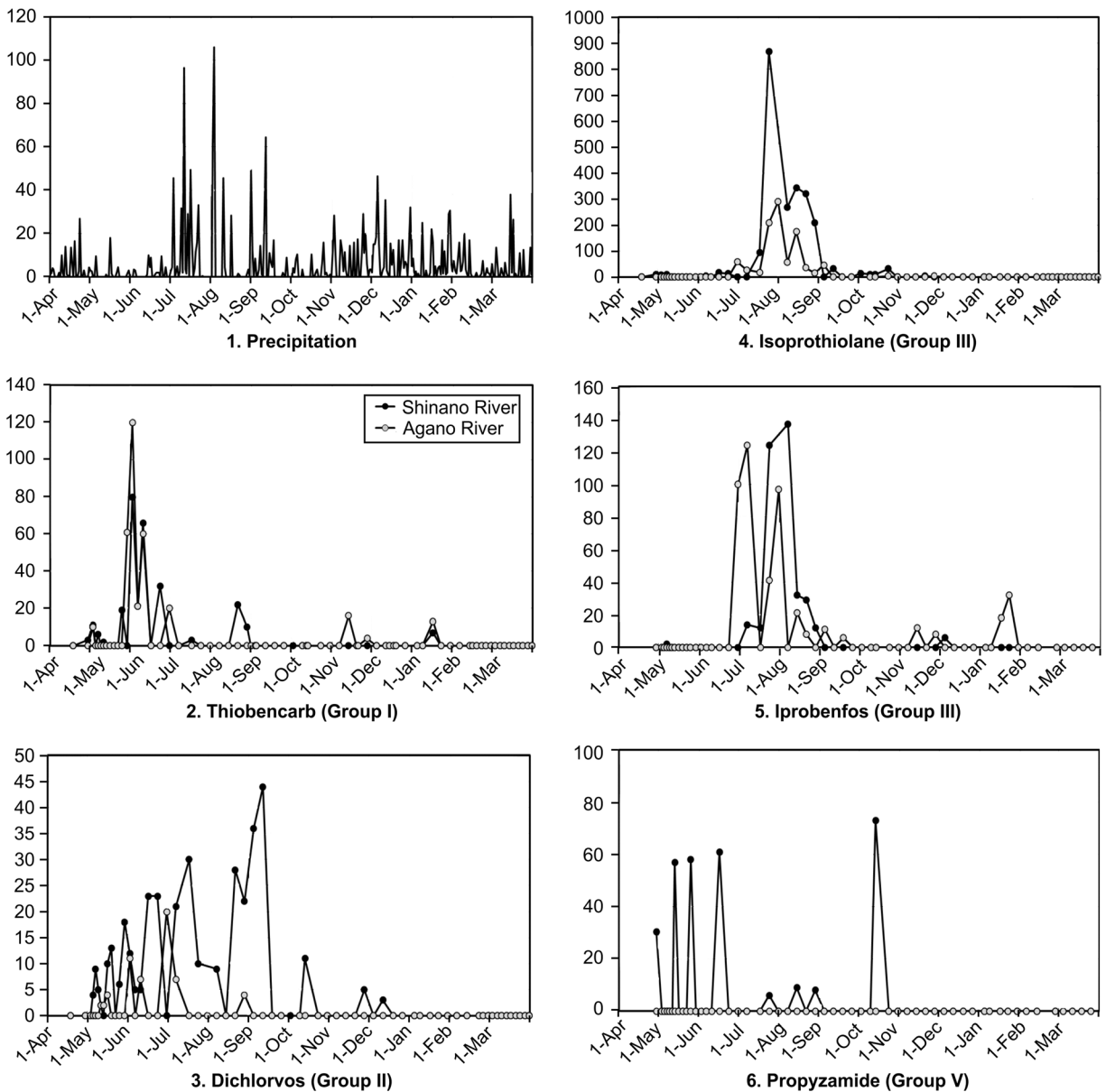


Fig. 4 (continued)

together with greater consumer demand for reduced pesticide input in agricultural production.

The changes in pesticide concentrations in the Shinano and Agano rivers and change of precipitation are shown in Fig. 4a, b. The pesticides detected were classified into five groups (I–V) according to their temporal distribution and frequency of detection in the Shinano River (see Table 3).

Group I represents pesticides detected from the beginning of May to the middle of July with a peak at the

beginning of June, comprising eight herbicides for paddy fields: molinate, simetryn, esprocarb, dimethametryn, mefenacet, bromobutide, cafenstrole, and thiobencarb. The representative pesticides are shown in Fig. 4a, b. As mentioned in Section 2.1, herbicides are applied to paddy fields during the second half of May, and drainage of the fields is completed at the beginning of June. The temporal occurrence of these compounds corresponds with the application and drainage periods for paddy fields.

Table 3 Classification of pesticides found in river and tap waters

Study year	2007				1995
	i	ii	iii	iv	
Tap water [→]					
River water [↓]					
I	Thiobencarb Molinate Simetryn Esprocarb Dimethametryn	Mefenacet Bromobutide Cafenstrole			Thiobencarb
II		Fenobucarb	Dichlorvos		Dichlorvos Fenobucarb
III		Isoprothiolane Flutolanil Pyroquilon Fthalide			Isoprothiolane Iprobenfos
IV		Dichlobenil			
V				Pyributicarb Alachlor Thenylchlor Isoprocab Dimethoate Chlorothalonil Mepronil	Simazine Chlornitrofen Fenitrothion Isoxathion EPN Propyzamide Diazinon Chlorothalonil

Classification of pesticides found in river water in 2007 and 1995

I - Detected from the beginning of May to the middle of July

II - Detected from the middle of May to the end of September

III - Detected from the beginning of June to September

IV - Detected throughout the year

V - Low detection frequency

Classification of pesticides found in tap water in 2007

i - Detected in raw water, but not in tap water

ii - Detected in both raw and tap water: lower concentration in tap water than raw water

iii - Detected in both raw and tap water: similar concentrations in tap water and raw water

iv - Low detection frequency

Tanabe et al. (2001) found 53 pesticides in their 1996 study in the Shinano River and detected herbicides after application during May and June, and loading peaked at the beginning of June. Morohashi et al. (2012) reported that runoff of bromobutide was caused mainly by the drainage of paddy waters several days after application and by rainfall. As shown in Fig. 4a, b, the periods of peak precipitation and herbicide concentration did not coincide, which we attributed to the combined effects of

both drainage and application as well as storm events in causing runoff of herbicides from paddy fields.

Group II consists of insecticides detected over the longer term, from mid-May to mid-September, and includes fenobucarb and dichlorvos (Fig. 4a, b). Fenobucarb concentration peaked at the end of August whereas dichlorvos peaked at the end of June. Fenobucarb is used in paddy fields to control *S. furcifera* and green rice leafhopper in August, as

mentioned in Section 2.1, but is also used in forests against pine wilt nematode (PWN) and in urban areas against termites. Dichlorvos is used in agricultural fields except for paddy fields. We attributed the multiple peaks and long-term presence of group II insecticides to their wide range of uses.

Group III consists of pesticides detected from the end of June to September, peaking at the end of July. This group consists of five fungicides: isoprothiolane, flutolanil, pyroquilon, fthalide, and iprobenfos. The representative pesticides are shown in Fig. 4a, b. These fungicides are used in paddy fields from July to August for control of panicle blast. Thus, the runoff of group III coincided with the timetable for pesticide spraying.

Group IV includes only dichlobenil, which was detected continually at various concentrations throughout the sampling period. We attributed the continuous presence of dichlobenil to its use throughout the year in controlling weeds in agricultural and nonagricultural fields

Group V consists of 14 pesticides: pyributicarb, alachlor, thenylchlor, isoprocarb, dimethoate,

chlorothalonil, mepronil, simazine, chlornitrofen, fenitrothion, isoxathion, EPN, propyzamide, and diazinon. All were detected infrequently, with no consistent tendency observed in the detection period.

3.2 Pesticides in Tap Water

The 2007 study examined the concentrations of pesticides in tap water. The results are summarized in Table 2, and changes in the concentrations of representative pesticides are shown in Fig. 4a. Tap water from the Aoyama WTP, which does not operate granular activated-carbon filtration, showed 12 pesticides (Fig. 2). In comparison with the pesticide concentration detected from the Shinano River raw water, based on the detection frequency and the extent of the reduction in concentration, these pesticides were classified into four groups, shown in Table 3.

Group i consists of five pesticides detected in raw water but not in Aoyama WTP tap water: thiobencarb, molinate, simetryn, esprocarb, and dimethametryn. Group ii consists of nine pesticides detected in raw water and at lower concentrations in Aoyama WTP tap

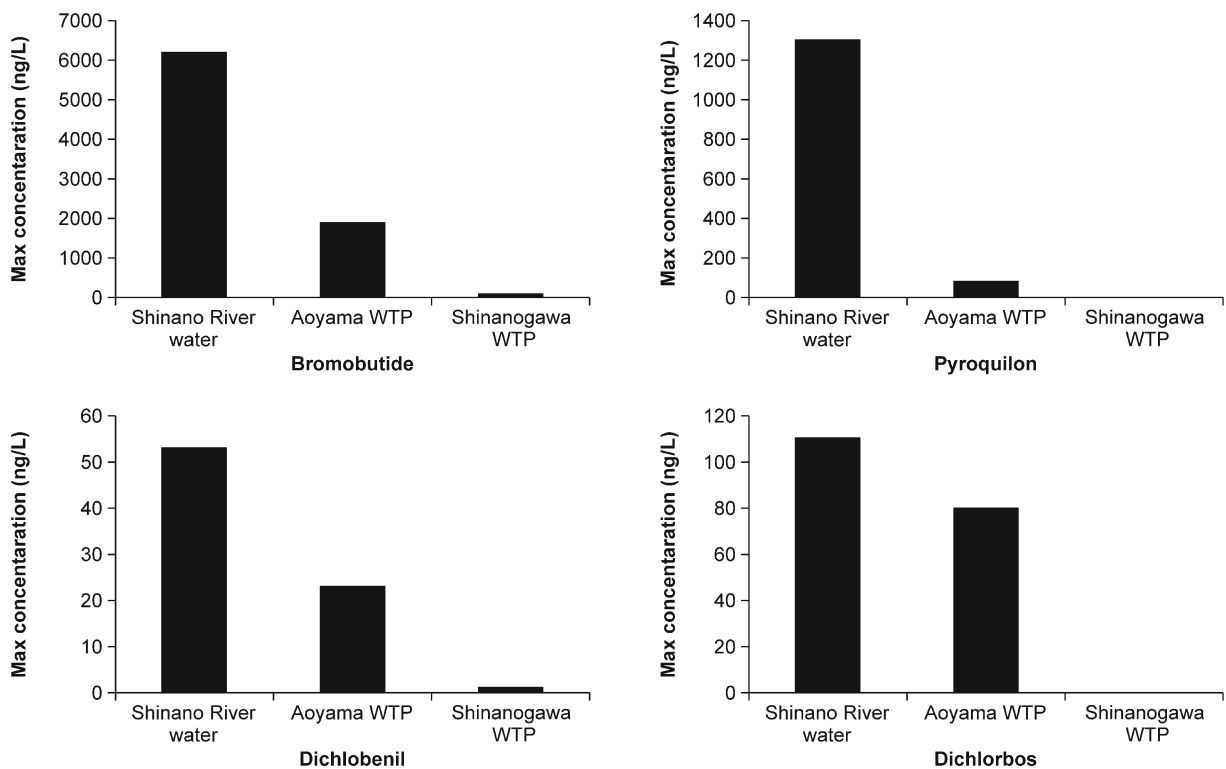


Fig. 5 Maximum pesticide concentration in river and tap water samples Shinano River water is supplied to both water treatment plants (WTP). Aoyama WTP does not have granular activated-carbon unit. Shinanogawa WTP has granular activated-carbon unit

water: mefenacet, bromobutide, cafenstrole, fenobucarb, isoprothiolane, flutolanil, pyroquilon, fthalide, and dichlobenil. The maximum concentration of group ii pesticides was about 7 to 40 % in raw water, as shown in Fig. 4a and Table 2. The reduction in the concentrations of group i and ii pesticides is attributable to either coagulation and sedimentation with the aid of coagulant polyaluminium chloride (PAC) during the water treatment process, or to complete or incomplete oxidation by hypochloride. Takahashi and Morita (1993) reported that chlorobenzyl alcohol, chlorotoluene, and other chemicals are newly produced during the reaction between thiobencarb and chlorine. Dichlorvos in group iii was detected in both Shinano River raw water and Aoyama WTP tap water from May until September. These findings for dichlorvos demonstrate that it is not removed by the use of rapid sand-filtration alone. Group iv consists of pesticides detected infrequently in both tap and raw water during the study period: in tap water, isoprocab was detected twice and chlorothalonil was detected four times.

Figure 5 shows the maximum concentrations of bromobutide, pyroquilon, dichlobenil, and dichlorvos in raw and tap waters. Tap water from Shinanogawa WTP (with granular activated-carbon filtration) contained three pesticides from group ii: bromobutide, pyroquilon, and dichlobenil (Fig. 2). However, the maximum concentrations of these three were very low, at 0.6 to 2 % in raw water, and 6 to 7 % in Aoyama WTP tap water. For group iii, dichlorvos was not detected in the Shinanogawa WTP tap water. Our results indicate that the addition of a granular activated-carbon adsorption unit to the rapid sand-filtration system resulted in a marked reduction in pesticide concentrations compared to the sole use of the rapid sand-filtration system.

3.3 Pesticides DI in Tap Water and Shinano River Raw Water

In this study, DI was calculated for tap water and Shinano River raw water. Table 4 shows the guideline value for each selected pesticide in this study, and Fig. 6 shows the changes of DI in 2007. The DI for Shinano River raw water in 2007 increased from the beginning of May, peaked at 0.2 at the beginning of June, and subsequently decreased (Fig. 6a). This trend coincided with that for the application of herbicide to paddy fields. Molinate contributed most to the DI (peak value 0.09), followed by bromobutide (0.06). In other words, 45 %

of the DI is attributed to the DI_i of molinate, and 30 % to that of bromobutide, both of which are herbicides and show peak values at the beginning of June. The DI for tap water from Aoyama WTP was lower than that for raw water (maximum 0.027, average 0.003) but showed a similar pattern of variation (Fig. 6b). The DI_i for bromobutide was the highest (maximum 0.019) and accounted for more than 50 % of the DI when it increased between May and July. The DI for tap water from the Shinanogawa WTP (maximum 0.001, average 0.0003) was lower than that for tap water from Aoyama

Table 4 Guideline values (GV) of selected pesticides in this study (Ministry of Health, Labour and Welfare, 2014)

Pesticides	GV (mg/l)
Herbicides	
Thiobencarb	0.02
Molinate	0.005
Cafenstrole	0.008
Pyributicarb	0.02
Alachlor	0.01
Mefenacet	0.02
Thenylchlor	0.2
Dimethametryn	0.02
Bromobutide	0.10
Dichlobenil	0.01
Simetryn	0.03
Esprocarb	0.03
Simazine	0.003
Propyzamide	0.05
Chlomitrofen	0.0001
Insecticides	
Dichlorvos	0.008
Fenobucarb	0.03
Isoprocab	0.01
Dimethoate	0.05
Diazinon	0.005
Fenitrothion	0.003
Isoxathion	0.008
EPN	0.004
Fungicides	
Isoprothiolane	0.3
Chlorothalonil	0.05
Flutolanil	0.2
Mepronil	0.1
Pyroquilon	0.04
Fthalide	0.1
Iprobenfos	0.09

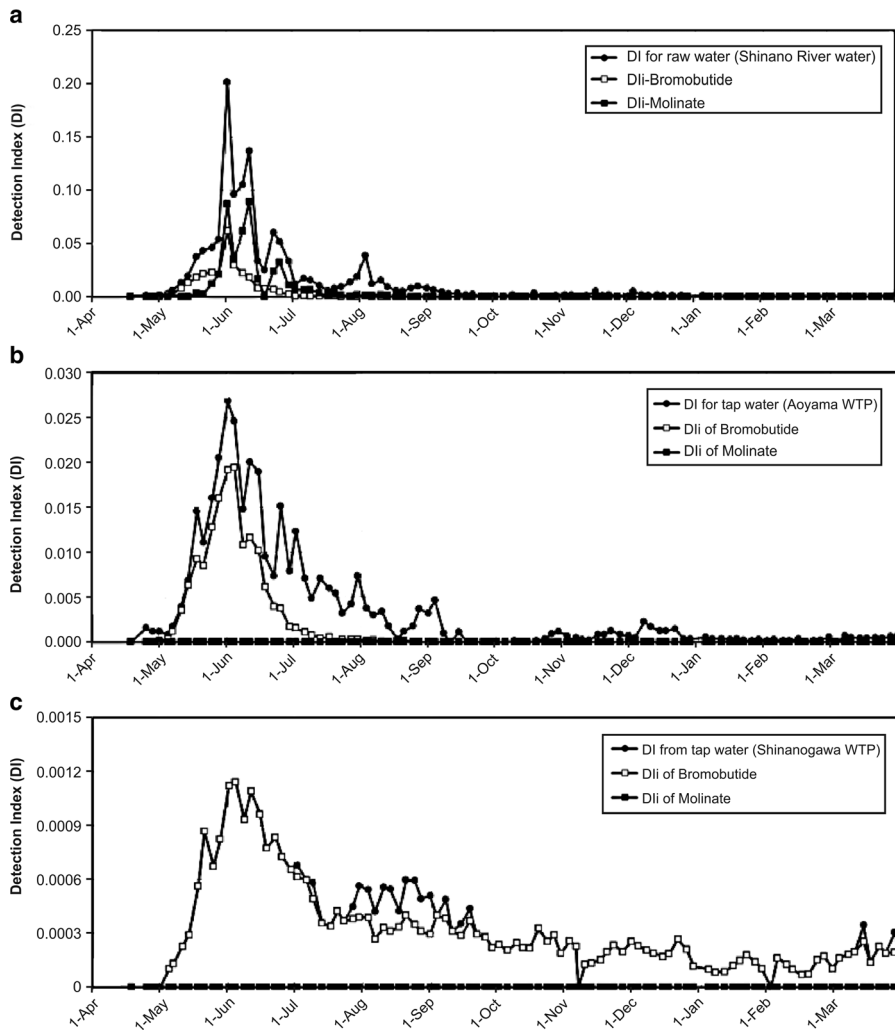


Fig. 6 Changes of detection index (DI) for raw and tap waters in 2007, together with changes of DI_i of molinate and bromobutide. **a** Raw water sample from Shinano River. **b** Tap water sample from Aoyama WTP. **c** Tap water sample from Shinanogawa WTP

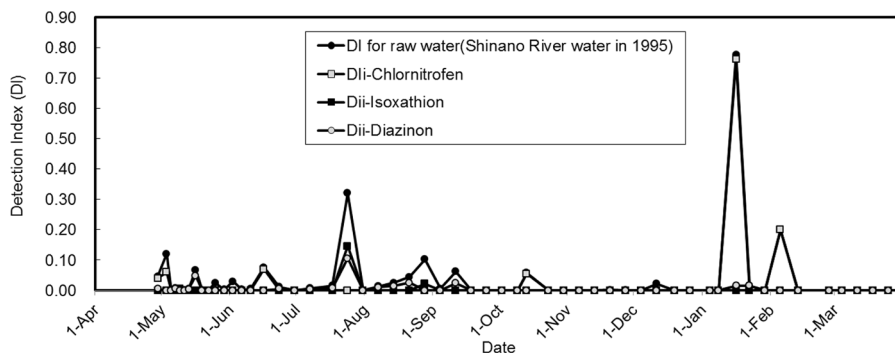


Fig. 7 Changes of detection index (DI) for raw waters in 1995, together with changes of DI_i of chlornitrofen, isoxathion, and diazinon

WTP (Fig. 6b, c). Most of the DI for tap water from the Shinanogawa WTP derives from the DI_i of bromobutide. The DI did not exceed 1 throughout the year for tap waters and Shinano River raw water.

Figure 7 shows the DI for Shinano River raw water in 1995. Chlornitrofen contributed for most to the DI for Shinano River raw water in 1995. We considered that the contribution of chlornitrofen for DI in 1995 depended on its lowest GV value of 0.0001 (Table 4). The DI in 1995 was attributed to the pesticides chlornitrofen, isoxathion, and diazinon, which were not detected in 2007. This showed that pesticide usage had changed to types with lower DI.

4 Conclusions

The 1995 study detected 13 pesticides in the Shinano River, of which 10 occurred in the Agano River. The 2007 study tested for 64 pesticides, detecting 22 in the Shinano River and 16 in the Agano River. Comparing the 13 kinds of pesticide which were studied in common in 2007 and 1995, it is evident that the number of detected pesticide and their concentration were reduced in 2007. It is concluded that this was due to changes in the kinds of pesticides in use and reductions in the amounts applied. Pesticides in Shinano River water were classified into five groups, according to the observed change. The detection periods for all pesticides found in river water coincided with their application periods. Pesticides applied to paddy fields were transported to river systems by application and drainage. In tap water, 12 pesticides were detected at the Aoyama WTP, and three at the Shinanogawa WTP in 2007. In the case of Aoyama WTP, thiobencarb and molinate were not found in treated waters. The concentration of dichlorvos was similar in both river water and tap water. The concentrations of bromobutide and pyroquilon were reduced by WTP treatment. Few pesticides were detected in tap water from Shinanogawa WTP, which uses a granular activated carbon unit. DI never exceeded 1 throughout the entire year of this study. The changes in DI corresponded with the concentrations of herbicides applied to paddy fields.

In this study, high concentrations of herbicides were detected during the standard periods of their application to, and drainage from, paddy fields. In addition, it was clear that paddy-field herbicides contribute most to the DI. Therefore, in order to reduce risks to humans and

adverse environmental effects, the amounts of pesticides applied to paddy fields should be reduced and appropriate methods of water management should be developed in order to confine pesticides within paddy fields. The 2007 study did not detect chlornitrofen, which in drinking water is claimed to increase rates of biliary tract cancer (Yamamoto et al. 1993) and is regarded as a major source of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans in paddy soil (Kobayashi et al. 2008). This absence from the 2007 data was attributed to the ban on chlornitrofen in 1996, following greater public awareness of its human and environmental effects.

Compared with a conventional rapid sand-filtration system, the WTP incorporating an additional granular activated-carbon unit showed marked reductions of pesticide concentrations in tap water. Therefore, in order to reduce the risks to humans associated with pesticides in tap water, it is important to select an appropriate water treatment system.

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References

- Derbalah, A. S. H., Nakatani, N., & Sakugawa, H. (2003). Distribution, seasonal pattern, flux and contamination source of pesticides and nonylphenol residues in Kurose River water, Higashi-Hiroshima, Japan. *Geochemical Journal*, 37, 217–232.
- Hoffman, R. S., Capel, P. D., & Larson, S. J. (2000). Comparison of pesticides in eight U.S. urban streams. *Environmental Toxicology and Chemistry*, 19(9), 2249–2258. doi:10.1002/etc.5620190915.
- Japan Plant Protection Association. (1994). *Pesticide handbook (Noyaku yoran)*. Tokyo: Japan Plant Protection Association.
- Japan Plant Protection Association. (2005). *Pesticide handbook (Noyaku yoran)*. Tokyo: Japan Plant Protection Association.
- Japan Plant Protection Association. (2012). *Pesticide handbook (Noyaku yoran)*. Tokyo: Japan Plant Protection Association.
- Japan Water Works Association. (2001). *Tap water testing methods in Japan*. Tokyo: Japan Water Works Association.
- Jerschow, E., McGinn, A. P., de Vos, G., Vernon, N., Jariwala, S., Hudes, G., et al. (2012). Dichlorophenol-containing pesticides and allergies: results from the US National Health and Nutrition Examination Survey 2005–2006. *Annals of Allergy, Asthma & Immunology*, 109(6), 420–425. doi:10.1016/j.anai.2012.09.005.
- Kimbrough, R. A., & Litke, D. W. (1996). Pesticides in streams draining agricultural and urban areas in Colorado. *Environmental Science & Technology*, 30(3), 908–916. doi:10.1021/es950353b.

- Kobayashi, J., Sakai, M., Kajihara, H., & Takahashi, Y. (2008). Temporal trends and sources of PCDD/Fs, pentachlorophenol and chlornitrofen in paddy field soils along the Yoneshiro River basin, Japan. *Environmental Pollution*, *156*(3), 1233–1242. doi:10.1016/j.envpol.2008.03.012.
- Ministry of Agriculture, Forestry and Fisheries of Japan. (2007). *Amount of agricultural output in 2006: statistics on agriculture, forestry and fisheries*. Tokyo: Ministry of Agriculture, Forestry and Fisheries.
- Ministry of Health, Labour and Welfare of Japan (1992). Concerning the Ministerial Directive on Water Quality Standards and the revision of the rules of practice in the Water Supply Act.
- Ministry of Health, Labour and Welfare of Japan (2003). Concerning the Ministerial Directive on Water Quality Standards and the partial revision of the rules of practice in the Water Supply Act.
- Ministry of Health, Labour and Welfare of Japan (2014). Concerning the revision of the Ministerial Directive on Water Quality Standards in the Water Supply Act.
- Ministry of Land, Infrastructure, Transport and Tourism of Japan. (2007). *Basic maintenance policy for the Agano River water system rivers*. Tokyo: Ministry of Land, Infrastructure, Transport and Tourism.
- Ministry of Land, Infrastructure, Transport and Tourism of Japan. (2008). *Overview of the Shinano River water system basin and rivers*. Tokyo: Ministry of Land, Infrastructure, Transport and Tourism.
- Mitobe, H., Tanabe, A., Kawata, K., & Sakai, M. (1997). Distribution of aerially sprayed pesticides in river water. *Journal of Environmental Chemistry*, *7*, 507–513.
- Morohashi, M., Nagasawa, S., Enya, N., Suzuki, K., Kose, T., & Kawata, K. (2012). Behavior of bromobutide in paddy water and soil after application. *Bulletin of Environmental Contamination and Toxicology*, *88*, 521–525.
- Nakano, Y., Miyazaki, A., Yoshida, T., Ono, K., & Inoue, T. (2004). A study on pesticide runoff from paddy fields to a river in rural region—1: field survey of pesticide runoff in the Kozakura River, Japan. *Water Research*, *38*(13), 3017–3022. doi:10.1016/j.watres.2004.02.013.
- Numabe, A., Inoue, T., & Ebise, S. (1992). Estimation on the runoff amounts of pesticides applied after transplanting of rice plant by drainage river. *Journal of Japan Society on Water Environment*, *15*(10), 662–671.
- Research Institute of Environmental Management, Administration and Maintenance of Japan. (2009). *Guideline of water quality standards for drinking water*. Tokyo: Maruzen Co., Ltd.
- Richards, R. P., & Baker, D. B. (1993). Pesticide concentration patterns in agricultural drainage networks in the Lake Erie basin. *Environmental Toxicology and Chemistry*, *12*(1), 13–26. doi:10.1002/etc.5620120104.
- Sudo, M., Kunimatsu, T., & Okubo, T. (2002). Concentration and loading of pesticide residues in Lake Biwa basin (Japan). *Water Research*, *36*, 315–329.
- Takahashi, Y., & Morita, M. (1993). Chlorination degradation of benthocarb in aqueous water. *Journal of Japan Society on Water Environment*, *16*(3), 190–201. doi:10.2965/jswe.16.190.
- Tanabe, A., Mitobe, H., Kawata, K., Yasuhara, A., & Shibamoto, T. (2001). Seasonal and spatial studies on pesticide residues in surface waters of the Shinano River in Japan. *Journal of Agricultural and Food Chemistry*, *49*(8), 3847–3852.
- World Health Organization (2008). *Guidelines for drinking-water quality - Volume 1: Recommendations. Incorporating first and second addenda* (3 ed., pp. 145–156b): World Health Organization.
- Yamaguchi, Y., Fukushima, M., Fujita, T., Yamamoto, T., & Yamada, A. (1992). Distribution and seasonal variation of pesticide residues in Yodo River basin, Japan. *Water Science and Technology*, *25*(11), 61–68.
- Yamamoto, M., Endoh, K., Nakadaira, H., Mano, H., Katagiri, M., Yamazaki, O., et al. (1993). Epidemiology of biliary tract cancer in Japan: analytical studies. *Acta Medica et Biologica*, *41*(3), 127–138.