Bull Environ Contam Toxicol (2009) 82:705–710
DOI 10.1007/s00128-009-9695-7

Daily Variation of Pesticides in Surface Water of a Small River Flowing Through Paddy Field Area

Akiko Tanabe · Kuniaki Kawata

Received: 11 September 2008 / Accepted: 26 February 2009 / Published online: 17 March 2009

Abstract The daily variations in the insecticides, i.e., buprofezin, etofenprox, fenitrothion, fenobucarb and pyridaphenthion, and fungicides, i.e., flutolanil, isoprothiolane, mepronil, pencycuron, phthalide and tricyclazole, were investigated in order to evaluate the short periodic variations in the pesticide concentrations of small river waters. The mean and maximum concentrations were 0.05 μg/L (pyridaphenthion) – 1.2 μg/L (isoprothiolane) and 0.30 μg/L (pyridaphenthion) – 13 μg/L (flutolanil), respectively. The concentration at 10:00 a.m. could be regarded as the representative daily concentration of the day. However, the concentration could markedly vary during the day or the day following the pesticide application. Therefore, the mean concentrations at 10 a.m., 2 p.m. and 6 p.m. were recommended as the best representative values of the day.

Keywords Insecticide · Fungicide · Sampling · Concentration · River water

The movement of pesticides from cultivated areas into the water environment has been an ecological and human health concern (Liu et al. 2002). Since rivers are one of the most important water sources for industry and agriculture as well as for drinking water, there has been great concern of pesticide contaminations of the river waters (Struger et al. 2008; Wilson et al. 2007). Many studies have published the levels of pesticide residues in major rivers, including the Mississippi River (Rebich et al. 2004), the Danube River (Barth et al. 2007) and the Ganga River (Nayak et al. 1995). We have previously reported the seasonal and spatial variations of pesticides and their metabolites in water collected from the Shinano River, the longest river in Japan (Tanabe et al. 2001).

Paddy rice farming has been playing an important role in the food production in Japan. A large number of pesticides is applied to paddy fields. The pesticides applied to paddy fields were of great concern due to pesticide runoffs into the rivers, because a part of the applied pesticides flow from the paddy fields into the rivers. In particular, small rivers with cultivated areas in their basins are directly affected by these applied pesticides in the areas. Therefore, these small rivers could be used to evaluate the pesticide runoff events from the cultivated areas. However, the pesticide concentrations in the waters from these small rivers could markedly vary during short periods compared to the major rivers. In our previous report, the fungicide phthalide, which was aerially applied to the paddy fields, was significantly increased in concentration after its applications as well as after rain events (Shiota et al. 2006; Maeda et al. 2008).

The Shin River flows for 13.5 km through the northwest part of the Niigata Plain, Niigata, Japan, to the Sea of Japan. The contributory area includes 19,800 ha of cultivated areas and civilized areas. A number of pesticides are applied to paddy fields of 18,700 ha for rice cultivation in the contributory area. We have previously reported the weekly variation in the aerially applied pesticides in the river (Mitobe et al. 1999). However, pesticide concentrations could show a marked variation after their applications.

A. Tanabe
Faculty of Pharmaceutical Sciences, Niigata University
of Pharmacy and Applied Life Sciences, 265-1 Higashijima,
Akiha-Ku, Niigata 956-8603, Japan

K. Kawata (✉)
Faculty of Applied Life Sciences, Niigata University
of Pharmacy and Applied Life Sciences, 265-1 Higashijima,
Akiha-ku, Niigata 956-8603, Japan
e-mail: kawata@nupals.ac.jp

Therefore, it is hard to evaluate the appropriate variations in river waters by weekly samplings immediately after the applications. To evaluate the short periodic variations of the pesticide concentrations in the river waters and to recommend the best daily representative value, we studied the daily variations of the pesticide concentrations in river waters from the Shin River during July through August. The investigated pesticides included five insecticides, i.e., buprofezin, etofenprox, fenitrothion, fenobucarb and pyridaphenthion, together with six fungicides, flutolanil, isoprothiolane, mepronil, pencycuron, phthalide and tricyclazole. They were mainly aerially applied during the investigated period to the paddy fields in the contributory area (Kawata et al. 1996, 2005).

Materials and Methods

The target pesticides were applied to the paddy fields in the contributory area from July 6 to August 9, 2001. The applied amounts are listed in Table 1. The aerial applications were performed from 5 to 8 a.m. The projected aerially applied pesticide amounts in the contributory area during the investigated period were 2,287 kg of buprofezin, 1,187 kg of etofenprox, 8,554 kg of fenitrothion, 201 kg of fenobucarb, 1,880 kg of pyridaphenthion, 641 kg of flutolanil, 740 kg of isoprothiolane, 898 kg of mepronil, 899 kg of pencycuron, 2,651 kg of phthalide and 1,456 kg of tricyclazole. The pesticides, except for buprofezin and flutolanil, were also directly applied to the ground in the area. The projected ground applied pesticide amounts during the period were 29.3 kg of etofenprox, 99.3 kg of fenitrothion, 13.6 kg of fenobucarb, 16.8 kg of pyridaphenthion, 30.5 kg of isoprothiolane, 29.2 kg of mepronil, 4.6 kg of pencycuron, 120 kg of phthalide and 26.3 kg of tricyclazole. The precipitation during the investigated period was 5 mm (3 mm at 8 a.m. and 2 mm at 9 a.m.) and 13 mm (2 mm at 5 a.m., 5 mm at 6 a.m., 5 mm at 7 a.m. and 1 mm at 8 a.m.) on August 9 and 12, respectively. The sampling point was located 2.6 km upstream from the river mouth (Mitobe et al. 1999). Water samples were collected at 10 a.m. from July 18 to August 6, 2001 and at 4 p.m. from July 26 to 28. Samples were also collected at 1–2 h intervals from 8:00 a.m. of August 7 to 10:00 a.m. of August 12. The collected samples were stored in 1-L glass bottles equipped with ground stoppers at 4°C without any headspace. All samples were analyzed within 24 h after collection.

A Waters Sep-Pak concentrator (Nippon Millipore, Tokyo, Japan) and an SPE manifold (J&W Scientific, Folsom, CA) were used for SPE and elution, respectively. A JEOL Model Automass 50 mass spectrometer (JEOL, Tokyo, Japan) equipped with a gas chromatograph, HP-5890 II (Hewlett Packard, Avondale, PA), was used for quantitative analysis. Waters Sep-Pak Plus PS-2 cartridges (Nippon Millipore) were washed with 5 mL acetone, followed by 5 mL distilled water prior to use. AGA-100 glass fiber filter, 1 µm pore size, 47 mm diameter (Toyo Roshi, Tokyo, Japan) was washed with acetone before use. The standard pesticides were purchased from GL Science (Tokyo, Japan), Kanto Kagaku (Tokyo, Japan) and Wako Pure Chemical Industries (Osaka, Japan). Other reagents were purchased from Wako. All solvents used were pesticide grade. A stock standard solution of each compound at 1,000 µg/mL was prepared in acetone. A mixed standard solution was prepared in acetone at a final concentration of 2 µg/mL for each pesticide. An acetone solution of polyethylene glycol (PEG) at 10 mg/mL prepared from PEG 200 and PEG 300 was used to obtain sharp and symmetrical chromatographic peaks for some pesticides. 1,4-Diiodobenzene and 9-bromoanthracene in acetone solution (200 µg/mL) were used as internal standards.

Table 1 Pesticide concentrations in waters from the Shin River

	Concentration (µg/L)				R[a] (%)	Amount[b] (kg)
	Median	Mean	Min	Max		
Insecticide						
Buprofezin	0.49	0.71	0.02	4.2	97	2,287
Etofenprox	<0.01	0.01	0.01	0.16	22	1,217
Fenitrothion	0.39	0.92	0.02	8.1	100	8,654
Fenobucarb	0.07	0.08	0.01	0.34	86	214
Pyridaphenthion	0.03	0.05	0.02	0.30	66	1,897
Fungicide						
Flutolanil	0.36	0.95	0.05	13	100	641
Isoprothiolane	0.81	1.2	0.40	8.8	100	771
Mepronil	0.07	0.33	0.02	5.9	95	927
Pencycuron	0.16	0.38	0.03	5.9	99	903
Phthalide	0.73	0.95	0.04	5.3	100	2,771
Tricyclazole	0.10	0.23	0.05	3.0	82	1,482

[a] Percentile ratio of sample number of detections to that of analyses

[b] Projected amount of application in the contributory area during the investigated period

The pesticides were determined by a previously published method (Tanabe et al. 2000). Briefly, water samples were filtered through a glass fiber filter (1 µm pore size). A 500 mL volume of the filtered water was passed through a series of 2 cartridges at a flow rate of 10 mL/min. After the cartridges were washed with 10 mL distilled water, they were dried by passing air through them for 15 min with an aspirator. The target compounds collected on the cartridges were eluted with 3 mL acetone, 3 mL hexane, and 3 mL ethyl acetate under reduced pressure. The combined eluates were concentrated under a stream of nitrogen, and the volume was adjusted to 1 mL with acetone. A 10 µL volume of

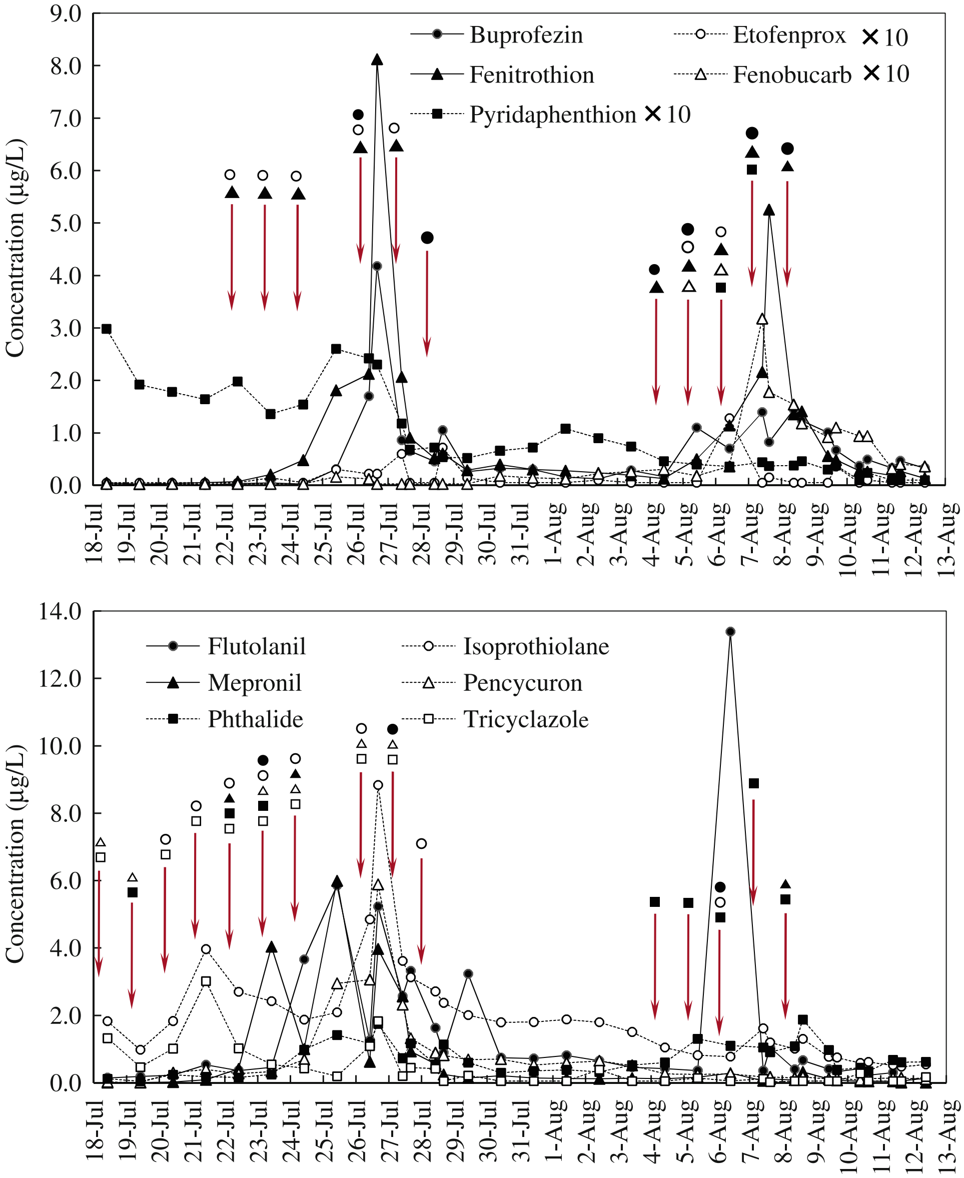


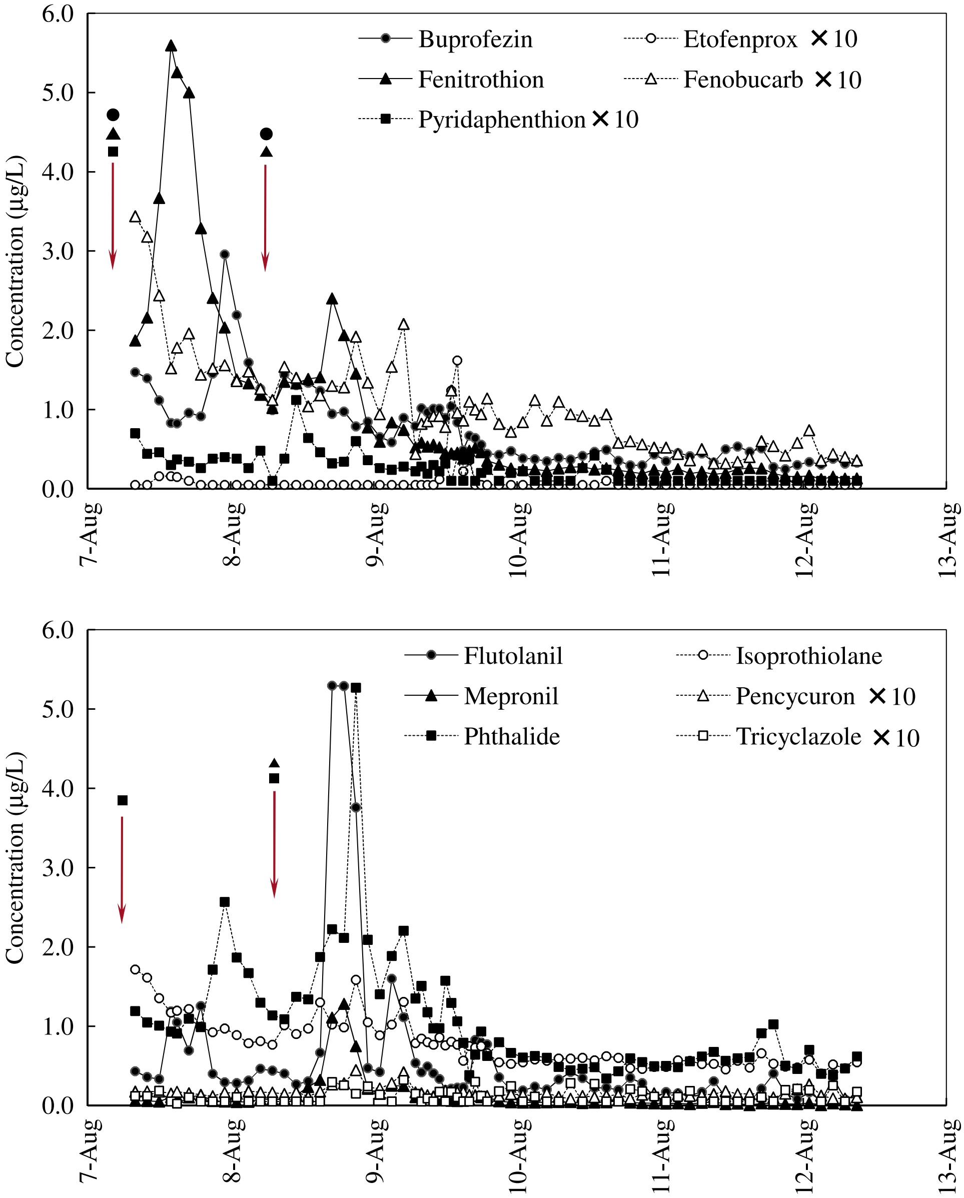
Fig. 1 Daily variations in pesticide concentrations in river waters. *Arrows* indicate pesticide applications

the PEG solution and 5 µL of the internal standard solution were added to the extract, and a 4 µL aliquot of the resulting mixture was injected into the GC/MS instrument. GC/MS conditions were as follows: column, fused-silica, HP-5 Trace Analysis (0.25 µm film thickness, 30 m length, 0.32 mm id); column temperature, programmed from 50°C, held for 1 min, to 150°C at a rate of 20°C/min, then from 150 to 280°C at a rate of 10°C/min, held for 4 min; injector temperature, 250°C; injection mode, splitless; ionization mode, electron impact; ionization current, 350 µA; electron energy, 70 eV; resolution, 0.8–1.1 amu; scan range, 50–450 amu; source temperature, 230°C; interface temperature, 230°C. Ions used for the quantitation and confirmation were *m/z* 172 and 105 for buprofezin, *m/z* 163 and 376 for etofenprox, *m/z* 109 and 125 for fenitrothion, *m/z* 150 and 122 for fenobucarb, *m/z* 199 and 340 for pyridaphenthion, *m/z* 145 and 281 for flutolanil, *m/z* 204 and 290 for isoprothiolane, *m/z* 119 and 91 for mepronil, *m/z* 125 and 180 for pencycuron, *m/z* 243 and 272 for phthalide, and *m/z* 135 and 136 for tricyclazole, respectively. Ions for the internal standards were *m/z* 330 for 1,4-diiodobenzene and *m/z* 256 for 9-bromoanthracene. The ratios of the peak areas of the ions to that of the internal standard were used for quantification of the pesticides.

Results and Discussion

The pesticide concentrations in the river waters are summarized in Table 1. Based on the investigations from 1995 to 1997 (Mitobe et al. 1999), the target pesticides were detected at annual maximum from June through August. The annual

Fig. 2 Hourly and bihourly variations in pesticide concentrations in river waters. *Arrows* indicate pesticide applications



maximum values of the insecticides in 1995, 1996 and 1997 were 0.82, 0.24 and 0.02 μg/L for buprofezin, 0.15, 0.05 and 0.12 μg/L for etofenprox, 1.5, 0.82 and 4.2 μg/L for fenitrothion, 0.29, 0.16 and 1.9 μg/L for fenobucarb and 1.9, 10 and 2.5 μg/L for pyridaphenthion, respectively. The maximum concentrations of etofenprox and fenitrothion in this study were almost comparable to those in 1995–1997, while those of buprofezin, fenobucarb and pyridaphenthion were 5.1, 0.18 and 0.030 times those in 1995–1997, respectively. On the other hand, the annual maximum values of the fungicides in 1995, 1996 and 1997 were 2.7, 0.12 and 3.9 μg/L for flutolanil, 3.4, 3.7 and 5.3 μg/L for isoprothiolane, 6.6, 0.80 and 0.78 μg/L for mepronil, 2.3, 0.59 and 1.6 μg/L for pencycuron, 1.8, 2.1 and 3.9 μg/L for phthalide and 5.1, 0.03 and 1.8 μg/L for tricyclazole, respectively. The maximum concentrations of the fungicides in this study were almost comparable to those in 1995–1997. Regarding phthalide, the maximum concentration was much higher than those of 0.68 and 0.86 μg/L in the Anno River, Niigata, in 2005 and 2006, respectively (Shiota et al. 2006; Maeda et al. 2008).

Figure 1 shows the variations in the pesticide concentrations in the river water collected at 10 a.m. from July 18 to August 12 together with those at 4 p.m. from July 26 to 28 and from August 7 to 12. The pesticides were detected at relatively high concentrations after their applications. The differences in the times between the applications and high concentrations depended on the distances of the applied area and the sampling site as well as their properties and applied amounts. Regarding pyridaphenthion, it was detected in the river water from July 18 to August 4, although it was aerially

Table 2 Differences in pesticide concentrations for representative values

		Concentration (μg/L)					
		7 Aug.[e]	8 Aug.	9 Aug.	10 Aug.	11 Aug.	12 Aug.[f]
Buprofezin	a	1.4	1.4	1.0	0.37	0.33	0.33
	b	1.1	1.3	0.82	0.43	0.40	
	c	1.1	1.2	0.80	0.40	0.46	
	d	1.3	1.2	0.74	0.39	0.40	0.33
Etofenprox	a	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	b	0.01	<0.01	0.02	<0.01	<0.01	
	c	0.01	<0.01	0.06	<0.01	<0.01	
	d	<0.01	<0.01	0.02	<0.01	<0.01	<0.01
Fenitrothion	a	2.2	1.4	0.56	0.27	0.18	0.13
	b	3.7	1.4	0.51	0.27	0.22	
	c	4.3	1.7	0.49	0.25	0.23	
	d	3.5	1.4	0.50	0.24	0.21	0.14
Fenobucarb	a	0.32	0.15	0.09	0.09	0.03	0.04
	b	0.25	0.14	0.10	0.09	0.04	
	c	0.22	0.13	0.09	0.08	0.04	
	d	0.21	0.14	0.10	0.08	0.04	0.05
Pyridaphenthion	a	0.04	0.04	0.03	<0.02	<0.02	<0.02
	b	0.04	0.04	0.03	<0.02	<0.02	
	c	0.04	0.04	0.03	0.02	<0.02	
	d	0.04	0.05	0.02	<0.02	<0.02	<0.02
Flutolanil	a	0.36	0.40	0.40	0.42	0.30	0.13
	b	0.70	0.53	0.41	0.32	0.18	
	c	0.75	2.00	0.47	0.28	0.20	
	d	0.67	1.49	0.52	0.26	0.17	0.16
Isoprothiolane	a	1.6	1.0	0.77	0.59	0.52	0.54
	b	1.4	1.2	0.77	0.61	0.50	
	c	1.3	1.0	0.76	0.59	0.58	
	d	1.2	1.0	0.78	0.56	0.53	0.50
Mepronil	a	0.06	0.08	0.11	0.04	0.04	<0.01
	b	0.08	0.20	0.09	0.04	0.02	
	c	0.09	0.47	0.09	0.05	0.03	
	d	0.08	0.36	0.11	0.04	0.02	0.02
Pencycuron	a	0.18	0.14	0.11	0.08	0.14	0.10
	b	0.17	0.16	0.13	0.10	0.15	
	c	0.16	0.17	0.13	0.11	0.14	
	d	0.16	0.21	0.17	0.12	0.14	0.13
Phthalide	a	1.0	1.1	0.97	0.44	0.68	0.62
	b	0.98	1.5	0.78	0.39	0.64	
	c	1.0	1.6	0.99	0.45	0.73	
	d	1.3	1.9	1.1	0.51	0.63	0.51
Tricyclazole	a	0.12	0.10	0.07	0.28	0.06	0.17
	b	0.07	0.08	0.09	0.15	<0.05	
	c	0.08	0.15	0.10	0.14	0.06	
	d	0.10	0.12	0.14	0.13	0.10	0.13

[a] Concentration at 10 a.m., [b] Mean of concentrations at 10 a.m. and 4 p.m., [c] Mean of concentrations at 10 a.m. 2 p.m. and 6 p.m., [d] Mean of concentrations from 2 a.m. to 12 p.m., [e] Measured from 8 a.m. to 12 p.m., [f] Measured from 2 a.m. to 10 a.m.

applied from July 4 to 9 and not applied from July 18 to August 5. This implies that the unprojected ground applications of the insecticide could be performed before and/or during the test period. The maximum concentrations during this study were detected from July 18 to August 6 except for etofenprox, fenobucarb and phthalide.

The variations in the pesticide concentrations collected during 8:00 a.m. on August 7 to 10 a.m. on August 12 are shown in Fig. 2. The maximum concentrations of etofenprox, fenobucarb and phthalide, which do not appear in Fig. 1, were observed at 2 p.m. on August 9, 12 a.m. on August 8 and 10 p.m. on August 9, respectively. Moreover, the daily maximum concentrations were observed at different times in the days. For instance, the daily maximum concentrations of buprofezin and fenitrothion on August 7, and flutolanil and phthalide on August 8 were observed at 12 p.m. and 2 p.m., and at 6 p.m. and 10 p.m., respectively. Although the pesticide concentrations could increase with rainfall due to the runoff (Fox et al. 2007; Maeda et al. 2008) or pesticides in the rain (Guo et al. 2004), the rainfall events on August 9 and 12 did not remarkably affect the increases in the pesticide concentrations.

Table 2 shows the four kinds of concentrations of the target pesticides for the daily representative values from August 7 to 12. The pesticide concentrations at 10 a.m. and the mean values at 10 a.m. and 4 p.m. were within 70%–150% of the daily mean concentrations except for the following cases. The concentrations at 10 a.m. of fenitrothion and flutolanil on August 7, and those of flutolanil, mepronil and phthalide on August 8 were <70% of the corresponding daily mean concentrations; the mean values at 10 a.m. and 4 p.m. of flutolanil and mepronil on August 8 were also <70% of the corresponding daily mean concentrations. In these cases, the pesticide concentrations increased from 6 to 10 p.m. Regarding tricyclazole, the concentration at 10 a.m. on August 9 and 11, and the means at 10 a.m. and 4 p.m. on August 8–9 were <70% of the corresponding daily mean concentrations, because the concentration increased from 6 p.m. on August 8 to 8 a.m. on August 9 and 10–12 p.m. on August 11. Moreover, the concentrations at 10 a.m. for flutolanil on August 10 and 11, that for mepronil on August 11, and that of tricyclazole on August 10 were >150% of the corresponding daily means, because the concentrations increased around 10 a.m. In these cases, the pesticide applications during the day or the previous day caused significant variations in their concentrations in the river waters. On the other hand, the mean values at 10 a.m., 2 p.m. and 6 p.m. were within 70%–150% of the daily mean concentrations. In conclusion, the concentration at 10:00 a.m. could be regard as the representative daily value in many cases. However, the concentration could be different from the daily mean value during the day or on the day following the pesticide application. Therefore, the mean concentrations at 10 a.m., 2 p.m. and 6 p.m. of a day were recommended as the best representative value of the day.

References

Barth JAC, Steidle D, Kuntz D, Gocht T, Mouvet C, von Tümpling W, Lobe I, Langenhoff A, Albrechtsen H-J, Janniche GS, Morasch B, Hunkeler D, Grathwohl P (2007) Deposition, persistence and turnover of pollutants: first results from the EU project AquaTerra for selected river basins and aquifers. Sci Total Environ 376:40–50. doi:10.1016/j.scitotenv.2007.01.065

Fox GA, Pulijala SH, Sabbagh GJ (2007) Influence of rainfall distribution on simulations of atrazine, metolachlor, and isoxaflutole/metabolite transport in subsurface drained fields. J Agric Food Chem 55:5399–5407. doi:10.1021/jf063753z

Guo L, Nordmark CE, Spurlock FC, Johnson BR, Li L, Lee JM, Goh KS (2004) Characterizing dependence of pesticide load in surface water on precipitation and pesticide use for the Sacramento River watershed. Environ Sci Technol 38:3842–3852. doi:10.1021/es0351241

Kawata K, Mukai H, Tanabe H, Yasuhara H (1996) Annual variation of insecticides in precipitation in rural Japan. Bull Environ Contam Toxicol 57:853–858. doi:10.1007/s001289900268

Kawata K, Asada T, Tanabe A, Oikawa K (2005) Runoff of clomeprop and oxaziclomefone from a paddy field. Bull Environ Contam Toxicol 75:922–928. doi:10.1007/s00128-005-0838-1

Liu B, Mcconnell LL, Torrents A (2002) Herbicide and insecticide loadings from the Susquehanna River to the northern Chesapeake Bay. J Agric Food Chem 50:4385–4392. doi:10.1021/jf010133j

Maeda T, Iwashita M, Hori T, Asada T, Oikawa K, Kawata K (2008) Variation of 4,5,6,7-tetrachlorophthalide in water after aerial application to rice cultivation area. Bull Environ Contam Toxicol 80:399–402. doi:10.1007/s00128-008-9371-3

Mitobe H, Ibaraki T, Tanabe A, Kawata K, Sakai M, Kifune I (1999) Variation of pesticides in a river flowing through paddy fields area. J Environ Chem 9:311–320

Nayak AK, Raha R, Das AK (1995) Organochlorine pesticide residues in middle stream of the Ganga River, India. Bull Environ Contam Toxicol 54:68–75. doi:10.1007/BF00196271

Rebich RA, Coupe RH, Thurman EM (2004) Herbicide concentrations in the Mississippi River basin—the importance of chloroacetanilide herbicide degradates. Sci Total Environ 321:189–199. doi:10.1016/j.scitotenv.2003.09.006

Shiota N, Hori T, Nissato K, Asada T, Oikawa K, Kawata K (2006) Runoff of aerially applied phthalide from paddy fields. Bull Environ Contam Toxicol 77:508–515. doi:10.1007/s00128-006-1093-9

Struger J, Thompson D, Staznik B, Martin P, McDaniel T, Marvin C (2008) Occurrence of glyphosate in surface waters of southern Ontario. Bull Environ Contam Toxicol 80:378–384. doi:10.1007/s00128-008-9373-1

Tanabe A, Mitobe H, Kawata K, Sakai M, Yasuhara A (2000) A new monitoring system for 90 pesticides and related compounds in river water by solid-phase extraction with gas chromatography/mass spectrometry. J AOAC Int 83:61–77

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. J Agric Food Chem 49:3847–3852. doi:10.1021/jf010025x

Wilson PC, Boman B, Foos JF (2007) Norflurazon and simazine losses in surface runoff water from flatwoods citrus production areas. Bull Environ Contam Toxicol 78:341–344. doi:10.1007/s00128-007-9202-y