Estimation of pesticide runoff from paddy fields to rural rivers

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Abstract The runoff characteristics of pesticides from paddy fields to rural rivers were investigated over a period of three years in Hokkaido Prefecture, Japan. High pesticide concentrations were usually observed in rivers during pesticide application periods. In one year, the growth of rice seedlings slowed down after transplantation owing to low temperatures and lack of sunshine, and many farmers delayed herbicide application. In that year, high-concentration runoff of herbicides in rivers was observed 1–3 weeks later than in average years. The pesticide runoff rates ranged from 0.3% for fenthion to 42% for benfuresate. The runoff rates of pesticides applied post-flood were large. Furthermore, the larger the water solubility of the pesticide, the larger the runoff rate. The highest concentrations of herbicides in paddy water were observed on the day of application or 1–2 days later, and the concentrations decreased exponentially afterwards. The half-lives of the herbicides ranged from 1.2 days for pretilachlor and esprocarb to 5 days for simetryn; the concentrations of the herbicides in paddy water had decreased to 1/10 of their initial concentrations by about 7 days after application. Therefore, the runoff amounts of pesticides from paddy fields could be decreased by improving irrigation-water management.
Keywords Herbicide concentrations; irrigation water management; paddy fields; paddy water; pesticide runoff; runoff rate

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Introduction

Approximately 500 chemicals are currently used as pesticides in Japan. The pesticides, both singly and in combination, are diluted and formulated as dusts, granules, emulsions, wettable powders, and so on. About 350,000 tons of pesticide formulations are purchased every year. Ninety-eight per cent of all the formulations sold are for agriculture and forestry uses, and 50% of those are applied to paddy fields. Pesticides applied to paddy fields run off into environmental waters more easily than pesticides applied to upland fields, because paddy water is discharged directly into rivers and lakes.

Irrigation water for paddy fields is usually managed artificially. Therefore, if irrigation discharges are carefully timed after pesticide applications, high-concentration runoff of pesticides can be controlled. However, most previous studies have indicated that high concentrations and large loadings of pesticides in river and lake waters are observed immediately after pesticide application and during rainfall-runoff events (Numabe *et al.*, 1992; Ebise *et al.*, 1993; Nagafuchi *et al.*, 1994; Sasagawa *et al.*, 1996). In agricultural regions where most farmers have office or factory jobs, pesticides are applied to paddy fields during weekends. Therefore, high concentrations and large loadings of pesticides are observed in drainage rivers at the beginning of the week (Numabe *et al.*, 1992). These findings clearly indicate that water management in paddy fields in these regions is inappropriate with regard to pesticide runoff.

Many kinds of pesticides are used for rice plantings, and the pesticides used and the application periods differ from region to region, because of the significant climatic differences between the northern and southern regions of Japan. Although many studies

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of pesticide runoff from paddy fields have been conducted, results from cold regions are limited.

In this report, we describe the runoff characteristics of pesticides as determined from weekly river observations in typical rice-planting regions in Hokkaido Prefecture, which is located in the northernmost area of Japan. We also report on changes in herbicide concentrations in paddy waters over time.

Observation areas and methods

River water samples were collected on Monday or Tuesday from early May to late August from 1997 to 1999 from the downstream areas of two tributaries of the Chitose River: the Old-Yubari River (St. 1) and the Horomui-Unga River (St. 2) (Figure 1). The Chitose River is one of the main tributaries of the Ishikari River, which is the largest river in Hokkaido, and supplies tap water to the city of Ebetsu and the town of Nanporo at sites 1 and 2. The Old-Yubari River and the Horomui-Unga River are 18.5 and 9 km in stream length and have 100 and 34.8 km^2 watershed areas, respectively. Rice cultivation areas ranged from 3,690 ha (1997) to 3,220 ha (1999) at St. 1 and from 1,430 ha (1997) to 1,200 ha (1999) at St. 2. In these watersheds, rice seedlings were transplanted from mid to late May, and in particular between 20 and 25 May. Because most farmers in this region are full-time farmers, their farm work is not concentrated at the weekends.

When river water samples were collected, pH, water temperature, and river flow were also measured. River flow was estimated by measuring the cross-sections of the rivers and the water velocity with an electromagnetic current meter.

Changes in the herbicide concentration of paddy water were investigated in three paddies (Figure 2). Paddies A and B had the same dimensions, 176 m × 28.5 m (50 a area); paddy C was 58 m × 29.5 m (17 a). Rice was cultivated by means of a standard method in these paddies. Paddy water samples were collected daily for several days after herbicide applications and thereafter at 2- to 7-day intervals. There were three sampling sites in paddies A and B (A/B-1–3) and four in C paddy (C-1–4).

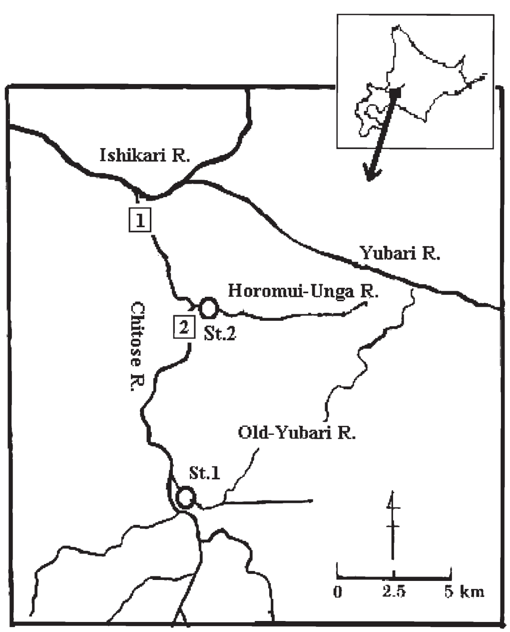

Figure 1 Location of studied watershed

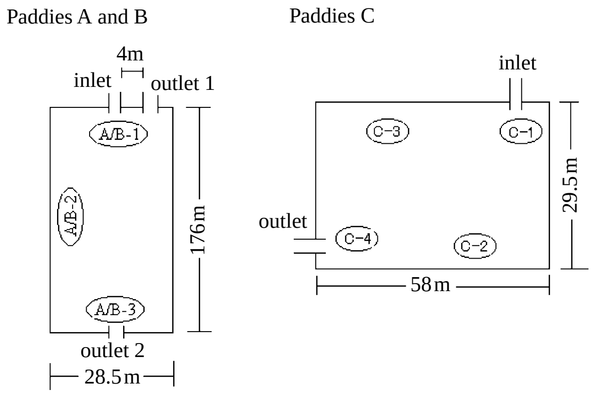

Figure 2 Schematic of observation paddies

The pesticides were analyzed using the methods described previously (Inoue *et al.*, 2002). However, Sep-Pak Plus PS-2 or tC-18 cartridges (Waters) for solid-phase extraction were used, and only the filtrates were analyzed. Twelve herbicides, three insecticides, four fungicides and three oxidation metabolites of pyributicarb (Pyr) and fenthion (MPP) were analyzed. Herbicides comprised pretilachlor (Pre), Pyr, esprocarb (Esp), mefenacet (Mfn), thenylchlor (Tnl), benfuresate (Bnf), thiobencarb (Thio), molinate (Mol), simetryn (Sim), daimuron (Dmr), bensulfuron-methyl (Bnm), and bentazone (Btz); insecticides comprised fenobucarb (BPMC), fenitrothion (MEP), and MPP; fungicides comprised edifenphos (EDDP), fthalide (Ftl), pyroquilon (Prq), and metalaxyl(Mtl); and the oxidation metabolites of Pyr and MPP comprised pyributicarb-oxon (Pry-ox), fenthion-sulfoxide (MPP-sfox), and fenthion-sulfone (MPP-sfon). Three of the herbicides, Dmr, Bnm, and Btz, were analyzed by high-performance liquid chromatography (2690 Separations Module equipped with a 2487 Dual λ Absorbance Detector, Waters). The others were analyzed on a gas chromatograph (HP-6890, Hewlett-Packard) equipped with a mass spectrometer (HP-5973, Hewlett-Packard).

Pesticide application methods

There are two application methods for herbicides: the sequential treatment method and the one-shot treatment method. In the sequential treatment method, the herbicides are applied sequentially in three stages, depending on the growth of weeds.

(1) In the first-stage, the initial herbicides Pre and Pyr are applied until either 4 days before or 7 days after transplantation.
(2) In the second-stage, the mid-term herbicides Mol, Sim, and Thio are applied from 15 to 30 days after transplantation.
(3) In the third-stage, if necessary, the later-term herbicide Btz is applied beginning 30 days after transplantation.

In the one-shot treatment method, a one-shot herbicide is applied once during the period from 3 to 15 days after transplantation. In these watersheds, nine herbicides (not including Mol, Sim, and Btz) of twelve herbicides mentioned above were used as one-shot herbicides.

Pre and Pyr are usually applied both before and after transplantation, and Thio is usually applied as a one-shot herbicide and a mid-term herbicide. However, in these watersheds, Pyr was predominantly applied as an initial herbicide before transplantation, and Thio was applied as a mid-term herbicide.

Insecticides and fungicides were also applied to the paddy water from mid June to early July and to the rice vegetation after the paddy water was discharged from late July to mid August, depending on the forecast and the occurrence of diseases and insect pests. However, one fungicide, Mtl, was applied to the rice seedling box before transplantation and was not directly applied to paddy fields.

The amounts of pesticides applied on the studied watersheds were estimated based on the amounts sold by the agricultural cooperatives, which are the main pesticide distributors in these areas.

Results and discussion

The concentration changes of the main pesticides at St. 2 in 1998 are shown in Figure 3, and the highest concentrations and the detection dates of 19 pesticides and three metabolites are shown in Table 1.

High-concentration runoffs of Pyr and Pre were observed in late May, during the rice-transplantation period. The concentration of Pre then decreased but increased again in early June, and a second concentration peak was observed during early to mid June. In this watershed, less Pre was applied as an initial herbicide before transplantation than was applied as a one-shot herbicide (for example, initial, 128 g/ha; one-shot, 229 g/ha, in 1998). But the highest concentration was observed in late May, before transplantation. The one-shot herbicides Esp and Bnf were detected beginning in late May, with declining concentrations after mid June (similar to the declines in Pre during the same period). The high-concentration runoff period of the mid-term herbicide Mol was found to be mid June to early July, and the late-term herbicide Btz was observed after July.

The runoff periods of the herbicides shifted slightly over the years. The runoff patterns of Pre, Mfn, and Mol after three years' investigation are shown in Figure 4. The highest concentrations of all the pesticides monitored in 1997 were observed later than in the other two years. In particular, the runoff period of Mol in 1997 was about 3 weeks later than in 1998 and 1999. In 1997, the growth of rice seedlings after transplantation was reduced due to low temperatures and lack of sunshine; as a result, it seems that many farmers delayed their herbicide applications.

Ebise *et al.* reported that the largest loadings of one-shot herbicides in Ibaraki Prefecture were found between 1 and 2 weeks after transplantation (Ebise *et al.*, 1993). In our observations, the high-concentration period was observed between 2 and 3 weeks after transplantation. It appears that herbicides in our observation areas were applied later than in Ibaraki Prefecture as a result of reduced rice seedling growth after transplantation, due to low (10–15 °C) irrigation water temperature.

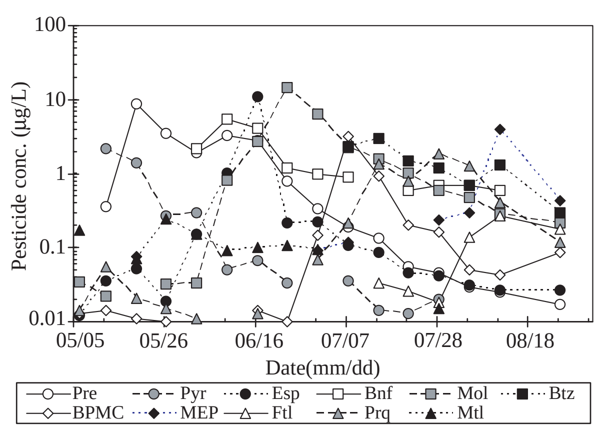

Figure 3 Changes in pesticide concentration at St. 2 in 1998

Table 1 Maximum pesticide concentrations (ng/ml) in river water and detection dates (in parentheses)

	Year	Herbicides												
		Pre	Pyr	Pyr-ox	Esp	Mfn	Dmr	Tnl	Bnf	Bnm	Thio	Mol	Sim	Btz
St. 1	1998	6.84 (5/19)	1.46 (5/19)	0.17 (5/19)	0.35 (6/16)	0.57 (6/16)	3.4 (6/16)	0.17 (6/09)	7.6 (6/16)	0.6 (6/16)	0.08 (6/23·30)	2.78 (6/23)	0.46 (6/23)	6.7 (8/04)
	1999	7.75 (5/25)	0.59 (5/25)	0.24 (5/25)	0.34 (6/15)	0.35 (6/22)		0.26 (6/15)	5.65 (6/15)		0.05 (6/22)	1.62 (6/22)	0.55 (6/08)	
St. 2	1997	6.73 (5/26)	0.62 (5/19)	0.23 (5/19)	1.10 (6/16)	1.04 (6/23·30)	1.6 (6/23)		5.0 (6/16)	0.2 (6/16·23·00)	1.48 (6/30)	11.3 (6/30)	2.66 (6/30)	
	1998	8.77 (5/19)	2.17 (5/12)	0.27 (5/19)	11.1 (6/16)	0.46 (6/16)	0.7 (6/02)	0.07 (6/02)	5.4 (6/09)	0.3 (6/02)	0.27 (6/23)	14.6 (6/23)	1.53 (6/23)	9.5 (7/14)
	1999	5.48 (5/25)	0.56 (5/18)	0.19 (5/25)	0.53 (6/08)	0.24 (6/15)		0.13 (6/01)	4.55 (6/15)		0.27 (6/22)	8.30 (6/15)	1.61 (6/22)	3.0 (7/14)

		Insecticides					Fungicides			
		BPMC	MEP	MPP	MPP-sfon	MPP-sfox	EDDP	Ftl	Prg	Mtl
St. 1	1998	2.58 (7/07)	0.34 (8/04)	0.31 (8/04)	0.71 (8/25)	1.45 (8/04)	1.52 (8/04)	0.17 (8/04)	1.37 (7/14)	0.18 (5/26)
	1999	1.96 (7/06)	0.19 (8/10)	0.75 (7/21)	0.09 (7/27)	0.43 (8/10)	0.93 (7/27)	0.16 (8/03)	0.77 (7/27)	0.08 (6/08)
St. 2	1997	6.10 (7/07)	1.22 (8/11)	0.22 (8/11)			0.63 (8/11)	0.23 (8/11)	7.77 (7/14)	0.15 (5/26)
	1998	3.21 (7/07)	4.00 (8/11)	0.15 (8/11)	0.20 (8/25)	1.66 (8/25)	0.73 (8/25)	0.27 (8/11)	1.87 (7/28)	0.24 (5/26)
	1999	3.36 (7/06)	0/19 (8/10)	0.25 (7/27)	0.10 (7/27)	0.31 (7/27)	0.25 (8/10)	0.29 (8/10)	2.59 (7/21)	0.11 (5/25·6/01)

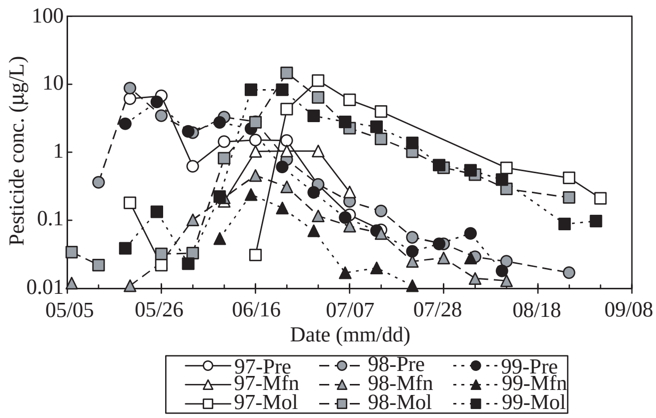

Figure 4 Comparison of herbicide runoff periods, 1997–1999

The insecticide BPMC began to appear in mid June, with a runoff peak in early July. MEP was detected beginning in late July, with a runoff peak observed in August.

Initial detection of the fungicide Prq occurred 1 week later than that of BPMC; the high-concentration period for Prq was from mid July to mid August. The runoff behavior of Ftl was similar to that of MEP. The fungicide Mtl, which was applied to the seedling boxes, was detected from the transplantation period until late June. It appears that Mtl was transported to the paddy field through transplantation of the rice seedlings. The detection of the investigated metabolites was delayed with respect to the detection of the parent compounds.

The relationship between solubility and the runoff rate is shown in Figure 5. The runoff rates of herbicides, insecticides, and fungicides ranged from 1.8% for Esp to 42% for Bnf, 0.3% for MPP to 9% for BPMC and 0.4% for Ftl to 25% for Prq, respectively. Large variations were recorded in the range of runoff rates of each pesticide; greater water solubility resulted in a larger runoff rate. Among the pesticides shown in Figure 5,

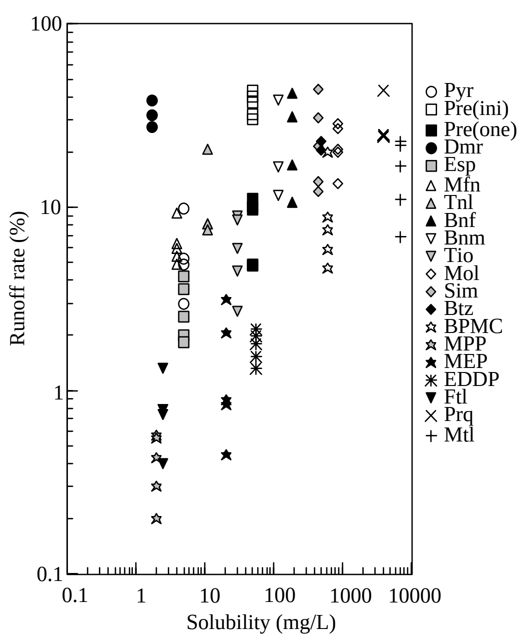

Figure 5 Relationship between solubility and runoff rate. ini: initial herbicide; one: one-shot herbicide

all herbicides, the insecticide BPMC, and the fungicide Prq were applied to paddy water. The other insecticides and fungicides (except for Mtl) were applied to the rice vegetation. The runoff rates of pesticides applied to paddy water were larger than those of insecticides and fungicides applied to the rice vegetation after the paddy water was discharged.

The application dates, amounts, and forms of herbicides; the maximum concentrations; the initial concentrations (extrapolated values); the half-lives and 1/10-lives (the number of days required for the concentrations of herbicides applied to paddy water to decrease to 1/10 of initial concentration) are shown in Table 2. During the observation period, paddy waters were not artificially discharged except before transplantation.

The highest concentrations of herbicides in paddy water were detected on the day of application or 1–2 days later, and herbicide concentrations in paddy water subsequently decreased according to the following equation:

$$C = C_0 \cdot e^{-kt}$$

where C is the pesticide concentration in paddy water; k is a constant; t is the elapsed time in days; and C_0 is the initial concentration of pesticide.

The half-lives of herbicides in paddy water ranged from 1.2 days for Pre and Esp to 5 days for Sim, and the concentrations of most pesticides in the paddy water had decreased to less than 1/10 of their initial concentrations by about 7 days after application.

The flooding water in the paddy fields should not be usually discharged for 4–5 days after pesticide application. Therefore, if paddy water discharge is managed rationally, the amount of pesticide runoff from paddy fields can probably be controlled. High concentrations of many pesticides were observed in river and lake water immediately after application, however, and the runoff rates of pesticides applied to paddy water obtained in our study were also large. These results suggested that the discharge of irrigation water after pesticide application is not being managed appropriately.

Moreover, initial herbicides, applied before rice is transplanted, were detected at relatively high concentrations in rivers, and the runoff rates of these pesticides were large

Table 2 Concentrations and persistence of herbicides in paddy water

Herbicide	Date:Paddy	Form	Amount g/a	Max-conc. mg/ml	Ini-conc. mg/ml	1/2-life days	1/10-life days
Pyr	97/5/19:B	E	360	89.1 (0)	143	1.81	6.02
	97/6/16:B	F	600	366 (0)	290	1.38	4.57
	98/5/18:C	E	350	123 (0)	125	1.91	6.33
Pre	97/5/19:B	E	240	168 (1)	200	4.32	14.4
	98/5/18:C	E	240	167 (0)	146	3.44	11.4
	98/6/16:A	G	240	104 (1)	176	1.23	4.08
	99/6/15:A	G	u	82.6 (0)	66	1.21	4.03
Esp	97/6/16:A	G	2,100	1,650 (1)	2,075	1.21	4.02
Bnf	98/6/16:A	G	240	390 (1)	499	2.20	7.30
Bnm	97/6/16:A	G	75	127 (1)	145	4.07	13.5
	97/6/16:B	F	70	190 (0)	174	2.01	6.67
Mol	98/6/17:C	G	282	1,940 (1)	2,312	2.47	8.20
	99/6/15:A	G	240	1,950 (1)	2,541	2.05	6.80
	99/6/15:C	G	282	2,650 (1)	4,656	1.64	5.46
Sim	98/6/17:C	G	530	154 (2)	168	4.93	16.39
	99/6/15:A	G	450	437 (0)	647	1.86	6.17
	99/6/15:C	G	530	720 (1)	1,094	2.32	7.69
Mfn	97/6/16:A	G	u	11.2 (1)	18	2.18	7.25

Max-conc. = detected maximum concentration of herbicide (duration of maximum concentration in days)
Ini-conc. = extrapolated initial concentration of herbicide
E = emulsion, F = flowable, G = granule, u = unknown

because paddy waters were discharged immediately before transplanting the rice. For example, the half-life of the initial herbicide Pre is about 4 days. If paddy waters are discharged 4 days after Pre application, the high-concentration runoff of Pre cannot be prevented. Therefore, the application of an initial herbicide having a long half-life before transplanting rice should be discontinued, or the herbicide should be applied 7 days or more before transplantation. Our results indicate that appropriate irrigation-water management is necessary for the conservation of an optimum water environment with regard to pesticide contamination.

Conclusion

Pesticides applied to paddy fields were observed at high concentrations in rivers during pesticide application periods. In particular, initial herbicides, applied before rice was transplanted, were detected at high concentrations in rivers during the transplantation period; runoff rates were large as well. When rice seedling growth after transplantation was reduced, due to low temperatures and lack of sunshine, many farmers delayed herbicide application. As a result, the high-concentration runoff periods of herbicides in rivers were 1–3 weeks later in the year with poorer weather than in average years.

The runoff rates of pesticides applied to paddy fields post-flood were larger, and runoff rates of insecticides and fungicides applied to rice vegetation after paddy water was discharged were smaller. In addition, the larger the water solubility of the pesticide, the larger the runoff rate.

The highest concentrations of herbicides in paddy water were detected on the day of application or 1–2 days later, and the concentrations decreased exponentially after that time. The concentrations of many herbicides in paddy waters had decreased to less than 1/10 of the initial concentrations by about 7 days after application. Therefore, high-concentration runoffs can be controlled by improving the management of irrigation, and appropriate irrigation-water management is necessary to conserve an optimum water environment.

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