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Modeling the fate of paddy field pesticide in surface water and environmental risk assessment

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Abstract: The risk of drinking water is greatly concerned because of the large amount of pesticide applied to paddy field and the contamination of drinking water sources due to the runoff. A mathematical model is developed, based on the mass balance, to predict the fate of paddy field pesticides from application, runoff and mixing in a river, taking account of the physical-chemical properties and processes of volatilization, degradation, adsorption and desorption. The model is applied to a river basin in Japan to estimate the contaminant level of several popularly used pesticides at the water intakes. The health risk in drinking water induced by each pesticide concerned is estimated and evaluated by comparing with the acceptable daily intake values (ADI) and with that induced by trihalomethanes. An index to evaluate the total risk of all pesticides appearing in water is proposed. The methods for risk management are also discussed.

Key words: modeling; pesticide; paddy field; environmental risk assessment; drinking water

Introduction

Micro-organic compounds have been identified as one of the main risk agent groups in drinking water. In surface water, agricultural chemicals account for a large part of the organic compound contents. In East and Southeast Asia, including China and Japan, cultivating of rice, the main food in the region, depends more and more on the use of pesticides. As a result, the application amount of these chemicals has been increasing. In Japan, about forty percent of agricultural pesticides are applied in paddy fields. During the rice-farming season, especially the period of rice seedling transplant when various kinds of agricultural chemical are intensively used, the residual pesticides are discharged from the paddy fields effluent and runoff with rainwater and then enter the receiving waters. High contaminant levels of pesticides have been monitored in Japan in irrigation canals for paddy field and some rivers that serve as drinking water sources. The health risk induced from the chemicals has become a public concern.

On the other hands, trihalomethane (THM) is also a main risk agent in drinking water. Unlike pesticides, THM is a by-product formed in the chlorinating process of water purification, in which chlorine reacts to the organic substances in the raw water, mainly humic substances. THM could be controlled or reduced within the water purification processes or by changing the traditional way of disinfection by chlorine. Comparing to this, the pollution control of pesticides in a river is difficult.

In this paper a mathematical model is developed to trace the applied pesticides and to examine the impact of the runoff chemicals on river waters. The model is applied to a typical river basin to predict the concentration of popularly used pesticides in the river water. The risk in drinking water is estimated and evaluated based on drinking water standards and compared with the risk of THM.

1 Model description

1.1 Pesticide model

Residual pesticides in paddy field enter the water sources of a river by runoff from the field associated with irrigation water and/or rainwater and then flow down the river to a water intake point. To model the fate in the environment, the behavior and movement of pesticides between the water, soil and atmosphere and the degradation in water and soil must be taken into account. The paddy field model was established based on the mass balance of a pesticide in the water and soil of one unit area of paddy field (Li, 1992b) as shown in Fig. 1.

Paddy field water:

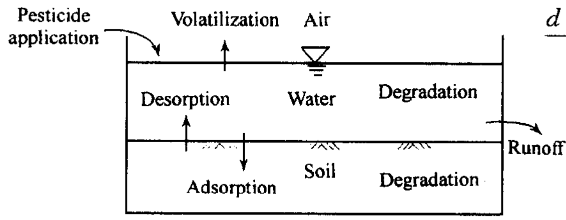

Fig. 1 Concept of pesticide fate in paddy field

$$\frac{d(h_w C_w)}{dt} = p - qC_w - K_w h_w C_w - K_{wa} h_w C_w + K_{sw} h_s \gamma_s C_s - K_{ws} h_w C_w, \quad (1)$$

Paddy field soil:

$$\frac{d(h_s \gamma_s C_s)}{dt} = - K_s h_s \gamma_s C_s - K_{sw} h_s \gamma_s C_s + K_{ws} h_w C_w, \quad (2)$$

where C_w and C_s are the concentration of pesticide in paddy field water and soil(mg/m^3, mg/t), respectively; h_w is the depth of paddy field water(m); h_s is the effective soil depth of adsorption(m); t is time(d); P is the rate of pesticide application (mg/(m^2·d)) ; q is the direct runoff of water from one unit area of paddy field(m/d); r_s is the specific gravity of soil(t/m^3); K_w is the first order degradation rate of pesticide in water (1/d); K_s is the first order degradation rate of pesticide in soil(1/d); K_{wa} is the volatilization rate of pesticide from water to atmosphere(1/d); K_{ws} is the adsorption rate of pesticide from water to soil(1/d), and K_{sw} is the desorption rate of pesticide from soil to water(1/d). At present little information about dynamics of adsorption and desorption of pesticides is available. A third equation has to be introduced to express the exchange of chemicals between the water and soil. Suppose that the adsorption of pesticides in the water onto the soil and the desportion can reach an equilibrium state in a short period of time, the Freundlich's adsorption isotherm is linear, and the adsorbent is the organic carbon of the soil, the following relationship is given:

$$C_s = K_{oc} M_s C_w, \quad (3)$$

where K_{oc} is the adsorption equilibrium constant(m^3/t); and M_s is the organic carbon content of soil. By substituting Equation(2) and (3)into Equation(1), the pesticide model is obtained:

$$(h_w + h_s \gamma_s K_{oc} M_s) \frac{dC_w}{dt} = p - qC_w - C_w \frac{dh_w}{dt} - K_w h_w C_w - K_{wa} h_w C_w - K_s h_s \gamma_s K_{oc} M_s C_w. \quad (4)$$

1.2 Water management

The water management for rice cultivation depends to a great extent on the breed of rice, the texture of the soil and the weather conditions. Farmers usually decide the way of irrigation based on these factors as well as their personal experience. Fig. 2 shows a typical pattern of irrigation practices in Japan. In order to keep the water depth in the field during various stages of rice growth, the consumed water is to be supplemented. The water consumed per day is the water requirement expressed in water depth per day, which reflects the evapotranspiration and the losses due to percolation. Most of the paddy field has a water requirement ranging from 1.5 to 2.0 cm/d. The volume of runoff water from one unit of paddy field can be estimated by:

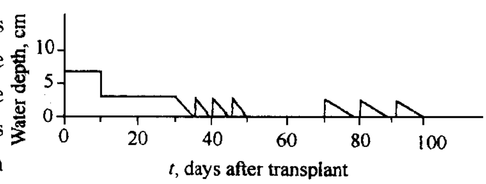

Fig. 2 Typical irrigation pattern

$$q = \begin{cases} f(d - \delta), \text{if } R \leqslant d \\ f(R - \delta), \text{if } R > d, \end{cases} \quad (5)$$

where d is the water requirement(m/d); δ is the evapo-tranpiration (m/d); R is the rainfall (m/d); and f is the runoff coefficient of paddy field.

2 Model application

2.1 Model verification

The pesticide model was verified (Li, 1992b) before application. The experimental site used in the model testing is a 2760 hm^2 watershed located at the upstream basin of Shibuya River in

Kanagawa Prefecture of Japan. The watershed includes 700 hm^2 of paddy field. Three herbicides, chlornitrogen(CNP), thiobencarb and simetryn, were popularly used in the rice transplant period and their concentrations in the river were monitored for seven weeks with a sampling interval of one week(Iizuka, 1982). It was found by comparing the calculated results produced by the model with the observed data that the model simulates the runoff profiles quite well.

2.2 River basin

The pesticide model is applied to the Yodo River Basin, Japan, to predict the pesticide concentrations in the river. The Yodo River is merged by the Kizu River, Uji River and Katsura River at one point and serves as drinking water sources of over ten million people in the Kansai area. Many water intakes are located along the riverbanks. Two main water intakes, Isojima and Kunijima, are located at the left bank, 6.4 km downstream of the junction, and at the right bank, 23.8 km downstream of the junction, respectively. They have capacities of 2000000 and 1500000 m^3/d, respectively, and serve a total population of about 7000000. Due to the difference in water quality of the three confluent tributaries, transverse mixing occurs in the mainstream. Li *et al*. (Li, 1987) introduced a factor called mixing ratio, which is the volumetric share of water contributed by a tributary within one unit of water sampled at an intake, to represent the mixing level at the intake. Therefore, the concentration at the intakes could be expressed as:

$$C_i = \sum_{j=1}^{3} \alpha_{ij} c_j \qquad (i = 1,2), \tag{6}$$

where i represents Isojima($i = 1$) and Kunijima($i = 2$) intake, respectively; j represents the Kizu River($j = 1$), Uji River ($j = 2$) and Katsura River($j = 3$), respectively; C_i is the concentration at the ith intake; c_j is the concentration of the jth tributary; and α_{ij} is the mixing ratio of the jth tributary at the ith intake. The values of mixing ratio could be determined by simulation with a two-dimensional diffusion equation (Li, 1992a). The river's hydraulic data and areas are listed in Table 1.

Table 1 Data of the Yodo River Basin

River	Flow rate, m^3/s	Basin area, km^2	Paddy area, km^2	Mixing ratio, % Isojima	Mixing ratio, % Kunijima
Kizu R.	20	1643	164.7	23.12	12.74
Uji R.	104	4334	626.0	68.86	66.24
Katsura R.	33	1172	81.8	8.02	21.02

2.3 Pesticide application

Of the pesticides used for paddy field, six are chosen for simulation, including two insecticides (fenitrothion (MEP) and diazinon), two fungicides (kitazin-p(IBP) and isoprothiolane) and two herbicides (CNP and thiobencarb). The principles to choose these pesticides are: (a) they are popularly used in the basin; (b) their physico-chemical properties and environmental dynamic data are known; and(c) there are drinking water quality standards for them.

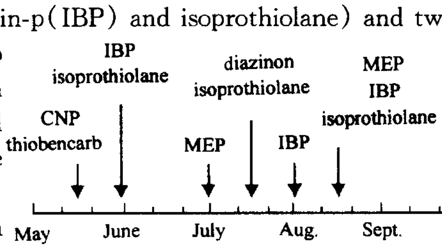

Fig. 3 Typical schedule of pesticide application

Fig. 3 shows a typical schedule of application recommended by the pest and blight prevention and control guidelines proposed by the local government. The situation of paddy field pesticide application in the Yodo River Basin is shown in Table 2.

Table 2 Pesticide application in Yodo River Basin(1991)

Pesticides	Use rate, kg/hm²	Number of time	Area of application, hm² Kizu R.	Uji R.	Katsura R.
MEP	0.70	2	2188	7527	1864
Diazinon	1.05	2	1341	2520	860
IBP	6.80	3	516	460	119
Isoprothiolane	4.80	3	243	832	106
CNP	2.80	1	392	14719	279
Thiobencarb	2.80	1	1610	7662	706

Generally, the season of rice seedling transplant may continue for several weeks. This results in different starting time of irrigation as well as pesticide dusting. In case where the study area is large, it is possible to consider these human activities as random events occurring within a certain length of time. In this study, it is assumed that these events obey a standard normal distribution. The daily use of pesticides is estimated based on this assumption.

2.4 Environmental dynamic data

Several environmental factors in the model have to be determined. However, it is difficult to obtain the environmental data of all the pesticides from experimental results because the number of pesticides in use is huge. Many researches were focused on the relationships between the physico-chemical properties of organic compounds and their environmental dynamics (Kenaga, 1979; Kanazawa, 1987). By using these relationships, the environmental dynamic data of the six pesticides are estimated and shown in Table 3. Other parameters of the model are shown in Table 4. The volatilization rate is estimated by using the following formula(Liss, 1974; Mackay, 1975):

Table 3 Physico-chemical properties and environmental dynamics of pesticides

Pesticide	MW	MS, mg/L	$\log P_{ow}$	VP(20℃), mmHg	K_{oc},	K_w, 1/d	K_s, 1/d
MEP	377.2	14	2.04	6.1×10^{-6}	1022	3.16×10^{-2}	6.32×10^{-2}
Diazinon	304.3	40	3.14	1.4×10^{-4}	574	3.72×10^{-2}	7.44×10^{-2}
IBP	288.3	400	2.08	2.3×10^{-6}	162	1.13×10^{-1}	2.26×10^{-1}
Isoprothiolane	290.4	48	2.81	1.4×10^{-4}	519	4.47×10^{-3}	8.94×10^{-3}
CNP	318.5	0.25	2.67	1.7×10^{-6}	9357	2.51×10^{-3}	5.02×10^{-3}
Thiobencarb	257.8	30	3.42	1.5×10^{-6}	672	8.52×10^{-3}	1.70×10^{-2}

Note: P_{ow} is the octanol/water partition coefficient

$$K_{wa} = 1/L_w[1/K_L + 1/(HK_g)]^{-1}, \tag{7}$$

$$K_L = 4.752(44/MW)^{1/2}, \tag{8}$$

$$K_g = 720(18/MW)^{1/2}, \tag{9}$$

$$H = 16.04VP \cdot MW/(WS \cdot T), \tag{10}$$

where L_w is the depth of liquid (m); H the dimensionless Henry's Law constant; T the absolute temperature (°K); MW the molecular weight; WS the water solubility (mg/L); and VP the vapor pressure(mmHg).

Table 4 Parameters used in simulation

hs, m	Ms, %	r_s, t/m³	d, m/d	δ m/d	f
0.03	4.0	1.5	0.015	0.005	0.6

2.5 Results

The pesticide concentrations in the three tributaries of the Yodo River were simulated with the pesticide model under the above mentioned condition. Typical precipitation in the basin of each tributary was used as input data. For the purpose of risk assessment, the annually averaged concentration is given and shown in Table 5, though the model could give dynamic output. The results of simulation reveal that pesticides runoff from paddy field is related to the amount of use, but it is dominated mainly by the physico-chemical properties. Pesticides with high water solubility, such as IBP, runoff relatively easily with irrigation and rainfall water and as a result, it appears in the river in high concentration after the application. As contrast, despite its large amount of use, CNP, which has low water solubility and strong adsorptivity, appears in the river in low concentration and last for a longer time.

Table 5 Pesticide concentration in the river by model simulation

Pesticide	Average concentration, μg/L			Maximum concentration, μg/L		
	Kizu R.	Uji R.	Katsura R.	Kizu R.	Uji R.	Katsura R.
MEP	0.20	0.106	0.09	5.4	3.8	2.5
diazinon	0.04	0.01	0.01	2.9	0.8	0.5
IBP	0.64	0.09	0.09	20.6	3.5	4.4
isoprothiolane	0.64	0.36	0.15	14.3	9.9	3.4
CNP	0.05	0.29	0.02	0.5	5.5	0.2
thiobencarb	0.68	0.59	0.18	10.1	11.9	4.8

3 Risk assessment

3.1 Comparison with the drinking water standard

Comparing the risk agent concentration with the drinking water standard is one of the main methods of risk assessment for water sources. In Japan, the environmental standard and drinking water standard for 15 items of pesticides were set in 1993, including the six items in this study. These chemicals had been used for more than one decade by then without regulation for water. In China, there is no environment or drinking water standard for any pesticide in current use.

Concentrations of paddy field pesticides at Isojima and Kunijima intake are shown in Table 6, associated with the drinking water standard levels. The concentrations were calculated by Equation (6) with annually averaged concentrations in the three tributaries of the Kizu River, Uji River and Katsura River as shown in Table 5, and mixing ratios in Table 1. Because these pesticides are non-carcinogenic chemicals, the standard levels are determined based on the acceptable daily intake values for human being (ADI). The drinking water standards are the ADI value in drinking water (ADId), which is 3% of the ADI for MEP and 10% for the others.

Table 6 Concentration of risk agents at water intake

Chemical	Concentration at intake, μg/L		Drinking water standard, μg/L
	Isojima	Kunijima	
MEP	0.12(4.00%)	0.11(3.67%)	3
diazinon	0.02(0.40%)	0.02(0.40%)	5
IBP	0.22(2.75%)	0.16(2.00%)	8
isoprothiolane	0.40(1.00%)	0.35(0.88%)	40
CNP	0.21(4.20%)	0.20(4.00%)	5
thiobencarb	0.58(2.90%)	0.51(2.55%)	20
THMFP	47.5(47.5%)	59.2(59.2%)	100*

Notes: the data in parentheses represent percentage of drinking water standard; * the standard is set for THM.

The results show that at present the pesticides appear in low concentration in the water, about 0.36% to 4.18% of the ADId's values. Attention must be paid to the tributaries in which some of the maximum concentrations of the pesticides are higher than the standards: MEP in Kizu River, IBP in Kizu River and CNP in Uji River. Therefore, there still exists the possibility that the pesticide concentrations at the intakes exceed the standards.

3.2 Comparison with the THM

The load of THM formation potential (THMFP) in a river includes the contribution from both wastewater discharge and runoff water swept from farm and forest areas. By plotting the surveyed THMFP load data of the Kizu River, Uji River and Katsura River against the flow rates, Li *et al*. (Li, 1996) found that the THMFP loads increase when the flow rates become larger and a power function could be employed to express the relationship:

$$L_T = aQ^b, \tag{11}$$

where L_T is the THMFP load in a river (kg/d); Q is the river flow rate(m^3/s); and a and b are parameters. Regression analysis was conducted with the surveyed data to determine the values of a and b and the correlation coefficient r. The correlation coefficients of the three rivers range from 0.90 to 0.98, which indicate high correlation between L_T and Q.

THMFP loads in the three rivers are predicted by Equation(11), and the concentrations at the intakes are calculated by Equation(6), respectively. The results are shown in Table 6. Assuming that all THMFP transforms into THM after chlorination in the water purification processes, the THM content is about 50% of the standard value. The predicted peak concentrations of THMFP in Isojima and Kunijima would be 109 and 91 μg/L, higher than or close to the standard level. Obviously, the risk of pesticide pollution is much lower than that of THM in the water sources of the Yodo River. At present, the priority of health risk management for drinking water could be given to THM control. However, this does not mean that the contamination of pesticides could be ignored.

3.3 The problem of standard for pesticides

The drinking water standards are set with targets for individual pesticides. It has clear meaning when only one pesticide in water is considered and it is easy to judge if the water is suitable for drinking based on information of water quality monitoring. For carcinogenic substances, the standard values are set with a carcinogenic rate in the lifetime of 100000 people who are exposed to the chemicals. For non-carcinogenic substances, they are set with an ADId value that mainly reflects the chronic effects on human. If the concentration of a non-carcinogenic pesticide is lower than the standard value, however, it is difficult to employ the ADId value to estimate the potential risk because little information is provided by the standard. When multiple pesticides appear in water simultaneously and each of their concentrations is lower than the corresponding ADId value, it may even have problem to judge if the water is safe for drinking with the standard. From the viewpoint of risk assessment, since these organic compounds are toxic and may cause adverse health effects on human, the sum of them should be more dangerous than a single one. Unfortunately, no well-developed method is available at present to evaluate this kind of risk of multiple non-carcinogenic chemicals whose concentrations are lower than the standards. Nakanishi (Nakanishi, 1994) proposed a provisional index by the sum of ratios of each concentration to its standard value:

$$R_T = \sum_{i=1}^{n} c_i / ADId_i , \tag{12}$$

where R_T is the total risk index, n is the number of risk agents, and c_i and $ADId_i$ are the concentration and drinking water standard of the ith risk agent (μm/L), respectively. If $R_T > 1$, then the water is considered as unsafe.

The R_T values are calculated for the six pesticides in the water at Isojima and Kunijima with Equation(12) and the results are 0.1516 and 0.1330, respectively. Although the values are still smaller than 1, they are much bigger than that of a single substance.

It must be noticed that pesticides regulated by the drinking water standard are only a small part of the total number of agricultural chemicals in use. In Japan, over 100 items of pesticides have been registered for use. Most of them are toxic to human, animal and the ecosystems and should be regulated as risk agents. The total risk of pesticides would be much higher when all of them are taken into account.

4 Risk management

4.1 Pesticide use control

Controling the use of pesticides is essential to manage the risk induced by the chemicals in drinking water. Pesticides should be refrained from use and in fact this could be done in many cases. When it is a necessity, they should be applied in proper manner, in terms of the use rate, the dusting method and timing. Low toxic pesticides are recommended.

4.2 Irrigation management

After the application of pesticides, irrigation is the most important human activity affecting the runoff of the chemicals from paddy fields. Simulation of CNP and thiobencarb was done with the model for two cases of irrigation management. Case 1 is the traditional irrigation pattern while case 2 has a three days stop of irrigation water after the application of the pesticides. The results showed that runoff rates of pesticides could be reduced by 12% to 17% in case 2. Other methods of water management such as repeatedly using the irrigation water can also be utilized to protect the runoff of pesticides from paddy field by extending the retention time and cutting down the volume of runoff water.

5 Conclusion

Residual pesticide in surface water is one of the main sources of environmental risk in drinking water. A mathematical model has been developed to predict the runoff of pesticide from paddy field in which various kinds of pesticide are intensively applied during the rice-farming season. The simulation results provide daily variation of pesticide concentration in a river and the amount of runoff. The model is applied to the Yodo River Basin. The health risk caused by the pesticide in the water sources are estimated and evaluated by comparing the concentration with the drinking water standard and by comparing with the risk caused by THM. It is indicated that controlling the use of pesticide and employing appropriate irrigation pattern are important ways to manage the risk.

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