

*Rerearch paper*

## Assessing pesticide fate and transport following modeling approach: A case study of fipronil in the Sakura River watershed, Japan

Le Hoang Tu<sup>1\*</sup>, Hirozumi Watanabe<sup>2</sup>

<sup>1</sup> Research Center for Climate Change, Nong Lam University Ho Chi Minh city, Ho Chi Minh city, Vietnam; tu.lehoang@hcmuaf.edu.vn

<sup>2</sup> International Environmental and Agricultural Science, Tokyo University of Agriculture and Technology, Tokyo, Japan; pochi@cc.tuat.ac.jp

\*Corresponding author: tu.lehoang@hcmuaf.edu.vn; Tel.: +84-931844631

Received: 5 February 2022; Accepted: 16 March 2022; Published: 25 April 2022

**Abstract:** Modeling approach has considered as an effective alternative method for environmental risk assessment in recent decades. This work aimed to assess the pesticide fate and transport from rice paddy which has higher potential of pesticide runoff compared to upland fields as reported in previous studies. The study area was the Sakura River watershed, Ibaraki Prefecture, Japan. For modeling rice pesticide, the study applied the PCPF-1@SWAT2012 model. The model was used to simulate concentration of a rice pesticide namely fipronil (C<sub>12</sub>H<sub>4</sub>C<sub>12</sub>F<sub>6</sub>N<sub>4</sub>OS) in 2009. The simulated streamflow and pesticide concentration were calibrated and validated. The results showed that the maximum pesticide concentrations at the monitored point in the watershed was 0.008 µg/L in rice paddy cultivation season of 2009. In conclusion, the modeling of the pesticide was successfully performed in the Sakura River watershed by using the PCPF-1@SWAT2012 model. The fate and transport of the pesticide were assessed. Thus, the modeling can be useful tool for environmental risk assessment.

**Keywords:** The PCPF-1@SWAT2012 model; Pesticide fate and transport; Rice paddy; Rice pesticide; The Sakura River watershed.

---

### 1. Introduction

Rice is main daily meals for nearly half of the world's population especially in Asia [1]. The total global rice consumption is increased from 150 million tons in 1961 to 475 million tons in 2016 and predicted continue to rise in the future [1–2]. Maintaining production of rice is very important task for agriculturists. Due to occurrences of various insects, diseases and weeds, rice farmers have been forced to depend on pesticides [3–4]. However, inappropriate use and management of rice pesticides may adversely affect the aquatic environments. Numerous monitoring studies from Europe and Japan have provided evidence that high pesticide concentrations were usually found in rivers during pesticides application periods of rice cultivation season [5–6]. Because pesticides are applied in the rice paddy where rice is cultivated under the submerged condition, pesticide runoff can occur more frequently via drainage or seepage and percolation [7]. Asian countries produce 90% of rice production in the world [2]. As a result, the aquatic environment of these countries may be at high risk of water contamination due to pesticides loss from rice paddy fields.

Japan is the tenth largest producer of rice in the world. Though pesticides use in Japan has decreased, it is still higher compared to other Asian countries [8]. Some studies reported

that the loss of pesticides from rice paddies is one of the major non-point sources of pesticide pollution of water in streams or rivers in Japan [7, 9–10]. Sakura River watershed is located about 50 km north-east of Tokyo and one of the popularity monitored watershed. Sakura River watershed is an agricultural watershed with 77.6% of the geographical area under forest and agriculture in Ibaraki prefecture, Japan [11]. During the rice cultivation season of the watershed, pesticides loads of the streams which are elevated due to agricultural drainages from rice paddies, have a potential to cause aquatic toxicities. Recent investigations reported that more than 39 kinds of herbicides, insecticides, and fungicides were detected in the watershed [11–12]. Specifically, in 2007 and 2008, concentrations of herbicides such as bromobutide, daimuron, and imazosulfuron were monitored at more than 2 µg/l in early-mid of rice season while simetryn and bentazone were high in mid and late of rice season. The high concentrations of these pesticides may adversely affect aquatic ecosystems by changing water quality and interrupting the aquatic food chain resulting in the loss abundance aquatic species [13]. Due to these reason, pesticides use in the rice production of Sakura River watershed is of great concern. Therefore, the prediction and assessment of their fate and transport in water is required to minimize the adverse impacts in the aquatic environment of the watershed.

In recent decades, computer models have been developed and widely applied in many fields such as graphics, geology, geography, environment and agriculture. For rice paddy, they have become an advantages management tool since the last two decades. Since a rice paddy model in watershed scale has been required for assessing the potential environmental risks in Sakura River watershed, RICEWQ-RIVWQ, PADDY-Large, and PCPF1@SWAT2012 model could be considered as best candidates (REF). However, the RICEWQ-RIVWQ and PADDY-Large algorithms for runoff and pesticide movement have focused only on simulation of paddy hydrology and ignored other types of land uses, which may significantly influence the hydrologic dynamics and pesticide concentrations of river basins [14]. On the other hand, the PCPF-1@SWAT2012 simulates both hydrologic processes and pesticide transports from the watershed at two phases [15]. First, the upland phase controls the amount of surface runoff and pesticide loadings to the main channel from upland fields. Second, the water or routing phase controls the movement of water and pesticide loadings through the channel networks of the watershed into the outlet. Thus, the PCPF-1@SWAT2012 is a more appropriate model for this specific study. Therefore, this study aims to evaluate a rice pesticide transport at the Sakura River watershed by using the PCPF-1@SWAT2012model.

## **2. Materials and Methods**

### *2.1. Study area*

The Sakura River watershed located in Ibaraki Prefecture, Japan (Figure 1). The watershed area is about 335 km<sup>2</sup> and main stream, namely the Sakura River, which flows into Lake Kasumigaura is 53.4 km long [11, 16]. The topography of the watershed is classified into mountain areas in the north, and flat in the west and southeast of the watershed, with average elevation ranging from 8 to 852 m [17]. The land use in the Sakura watershed consists of forest land (32.0%), rice paddies (28.6%), upland agricultural fields (17.0%), residential land (13.9%), and other land use (8.5%) [11, 18]. With respect to soil types, the lower and upper parts of the watershed are mostly Brown forest, Black, and Gray lowland soils while other parts are mostly composed of Gley and Peat soils [19]. The Sakura watershed generally has a temperate climate; with the average annual rainfall of 1,318 mm. The average daily maximum and minimum temperatures are 19.6°C and 10.1°C, respectively [20].

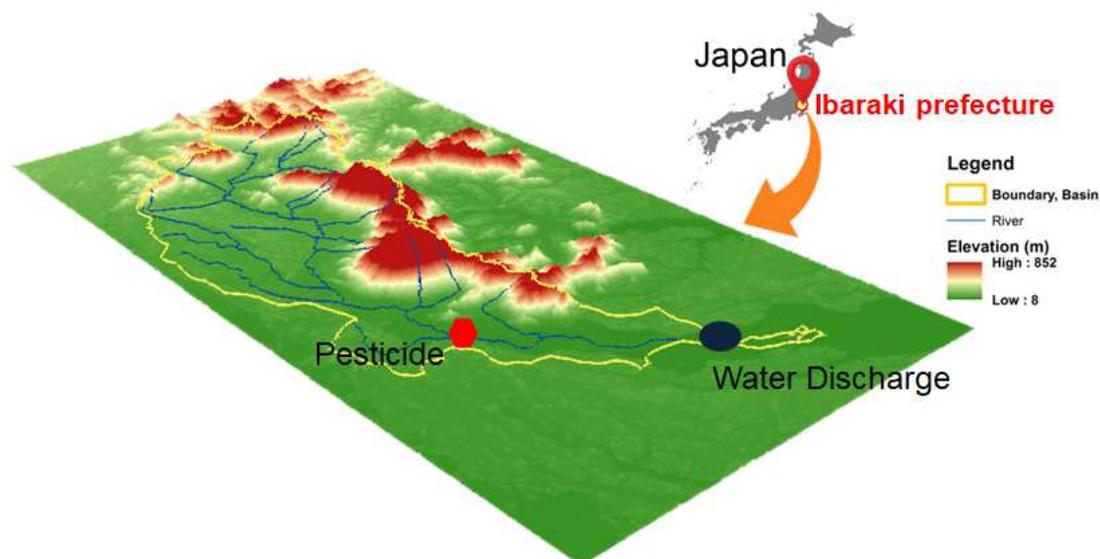


Figure 1. Location and elevation of the Sakura River watershed.

## 2.2. PCPF-1@SWAT2012 model

### 2.2.1. Brief model description

PCPF-1@SWAT2012 was updated from the PCPF-1@SWAT which was developed for assessing the impacts of rice pesticides on aquatic environments in watershed scale [21]. Similar to the Soil and Water Assessment Tool (SWAT) model, the PCPF-1@SWAT2012 model also requires topography, land use, soil, weather, crops management practices and pesticide as input data. Figure 2 shows the implementation of Pesticide Concentration in Paddy Field (PCPF-1) model into SWAT model version 2012. In the PCPF-1@SWAT2012 model, rice paddy has been defined as pothole, which is a kind of water bodies for impoundment function in SWAT model. Hence, all performances of the PCPF-1 model are executed inside the pothole of SWAT model. In the PCPF-1@SWAT2012 model, the subbasin can be divided into one or multi hydrologic response units (HRUs). Each subbasin can be set one or multi potholes. When the water is ponding into the pothole, a water balance algorithm is used to calculate the daily amount of runoff. This water balance includes precipitation, water inflow, surface runoff, evapotranspiration, seepage and discharge. In addition, the calculation of water balance components, irrigation process and the pothole variables were redefined. When integrating PCPF-1 model into SWAT model, a procedure to calculate the concentration of pesticide sorbed on sediment was added in the PCPF-1@SWAT2012 model. Because the sediments dissolved in paddy water are not simulated by the PCPF-1 model, pesticide sorbed on soil could not be predicted by overflow [22]. Moreover, recirculation scheme of water was developed. This option aims to calculate the water loss via surface water drainage and tile drainage, which can be collected and re-injected in the field to reduce fresh water requirement.

The PCPF-1@SWAT2012 model was verified and validated in two phases. In the first phase, the pothole algorithms and pesticide mass balance of the model were checked with single and multiple pesticide applications scenarios. The verified results showed that the algorithms used to simulate paddy field water management and pesticide concentrations for single and multiple applications were also correctly implemented into SWAT, and the PCPF-1 was correctly linked to the SWAT model. For the second phase, the

PCPF-1@SWAT2012 model was applied in Sakura River watershed (Ibaraki, Japan) for simulating four herbicide fate and transport. The simulated water flow rate and pesticides concentrations in the Sakura River watershed were good. The model needs to be checked and verified in other watersheds with various pesticides and pollutants.

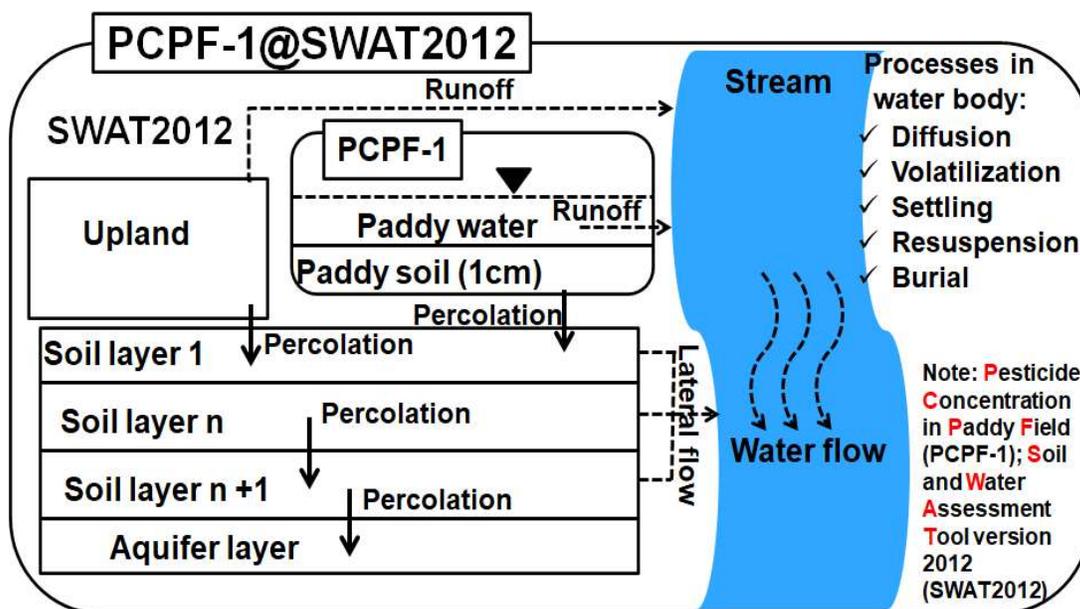


Figure 2. The implementation of PCPF-1 model into SWAT model flowchart [14].

### 2.2.2. Data collections and processing

The topographic data was obtained from the website of the The Terra Advanced Spaceborne Thermal Emission and Reflection Radiometer Global Digital Elevation Model (ASTER-GDEM) at resolution of 30 m [17]. Stream network and subbasin boundaries data were downloaded from the National Land numerical information download service [18]. The land use data of the Sakura River watershed used in this study were created in 2008 [18]. The data were downloaded from National Land numerical information download service. The dominant land use types of the watershed were forest (32.01%), paddy fields (28.55%), upland agricultural (17.04%), and residential land (13.92%). Paddy fields predominantly covered the west and south parts of the watershed. Soil types were identified in the catchment based on a 1:25,000 digital cultivated soil data for Ibaraki prefecture in 2007 [19]. The dominant soil types of the lower and upper parts of the Sakura river watershed were mostly Brown forest, Black and Gray lowland soils. The remaining parts of the Sakura river watershed were mostly composed of Gley and Peat soils. Two of the above listed data were provided in the Japan Profile for Geographic Information Standards format (JPGIS) under Geographic Projection (JGD 2000), which need conversion into spatial vector-type GIS (shapefile) and SWAT attribute format under Universal Transverse Mercator Projection (JGD 2000 UTM Zone 54). The observed daily data of precipitation, minimum and maximum temperatures were also collected. Four years weather data (2006–2009) were downloaded from Japan Meteorological Agency–Radar–AMeDAS–analyzed data base [20]. Water flow rates at the outlet were acquired for 2008 and 2009 from the observation data of the Water Information System of the Ministry of Land, Infrastructure and transport, Japan [18].

Regarding pesticide data, the PCPF-1@SWAT2012 model requires two groups of pesticide data including application and pesticide properties. The model demands pesticide application time, rate, area, and water holding period (WHP) for creating pesticide input table

(Table 1). The application rates of the pesticides were obtained based on shipment amount, usage rate, percentage active ingredient and pesticide product information which were extracted from various literatures especially pesticide database of Japan Plant Protection Association (JPPA) [23]. An insecticide namely fipronil (C<sub>12</sub>H<sub>4</sub>C<sub>12</sub>F<sub>6</sub>N<sub>4</sub>OS) was selected for the model simulation because the required input data of the pesticides were available.

**Table 1.** Required pesticides application data for writing the pesticide input table of the model.

| Parameter         | Unit             | Definition  | Input file |
|-------------------|------------------|---|------------|
| MGT_OP            | none             | Operation code. MGT_OP=19 for rice pesticide application    | .mgt       |
| MONTH/DAY or HUSC | days             | Day and month when the rice pesticide is applied in the HRU | .mgt       |
| pcpfipest         | none             | Integer that identify the pesticide name                    | .mgt       |
| pst_pcpfkg        | g/m <sup>2</sup> | Pesticide application rate                                  | .mgt       |
| pcpfarea          | %                | Percentage of the HRU where the pesticide has been applied  | .mgt       |
| pcpfwhp           | days             | Water holding period  | .mgt       |

### 2.2.3. The model evaluation

The study used the Nash–Sutcliffe model efficiency coefficient (NSE), the Root Mean Square Error (RMSE) and Percent bias (PBIAS) to evaluate the prediction performance, tendency and model accuracy [24–27]. NSE can range from  $-\infty$  to 1 and an NSE of 1 corresponds to a perfect match between estimation and observations. An NSE of 0 indicates that the model estimations are as accurate as the mean of the observed data, whereas an NSE less than zero ( $-\infty < \text{NSE} < 0$ ) occurs when the model prediction of observed mean is not accurate. Similar to NSE, RMSE is also one criterion most widely used for assessment of model output against observed data. The RMSE values can range from 0 to  $+\infty$  with 0 being a perfect prediction. Because NSE is related normalization of the mean squared error (MSE) and RMSE [28] the PBIAS was additionally calculated. The optical value of PBIAS is 0.0, positive and negative PBIAS values indicate model underestimation and overestimation bias, respectively [26, 29].

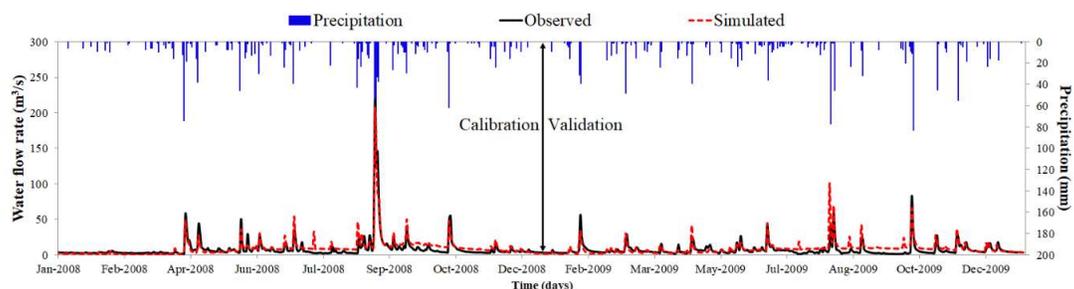
## 3. Results and Discussions

### 3.1. The model calibration and validation

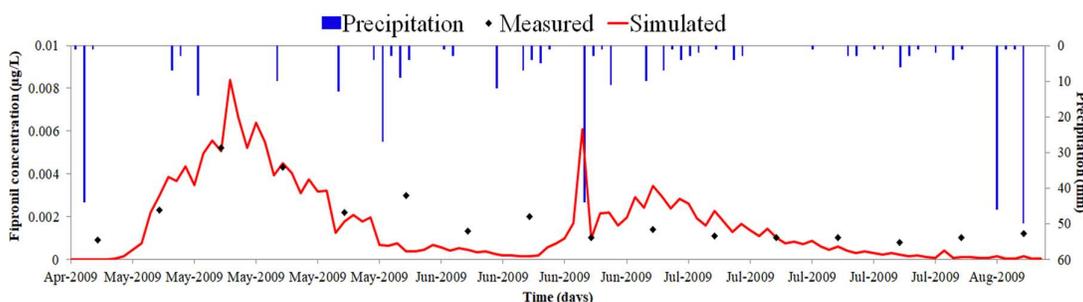
The Sakura River watershed is divided into 36 subbasins based on hydrological characteristics of the watershed. Simulations have been done for the calibration (2008) and validation (2009) of water discharge in daily time step (Figure 3). Since the rice paddy accounted to 28.5% of the Sakura River watershed area, the water management practices in the paddy field have significant effect on the water flow simulation. However, according to [22] no reliable data regarding that kind of activities in the watershed were available. Therefore, the input data related to the water management practices in the paddy field of the watershed were generated based on assumptions, and those data were extracted from the study [14]. The water management input data include (i) the water holding period, which was 7 days after the pesticides application, (ii) the tile flow rate to channel from paddy fields, which was 0.12 cm/day, and (iii) the percolation rate in the paddy fields, which was 1 cm/day. In addition, the study could only calibrate parameters of pesticide simulation in 2009 due to the observed pesticide data limitation. The selected parameters for calibration of the water discharge and pesticide simulations in the Sakura River watershed are shown in Table 2.

**Table 2.** The calibrated values of the parameters used for the water flow rate simulation.

| Parameter | Description  | Unit              | Calibrated range | Output variables |
|-----------|--|-------------------|------------------|------------------|
| GWQMN     | Threshold depth of water in the shallow aquifer                      | mm                | 0–5000           | Water discharge  |
| GW_DELAY  | Groundwater delay  | day               | 0–500            |                  |
| GW_REVAP  | Groundwater "revap" coefficient                                      | none              | 0.02–0.2         |                  |
| REVAPMN   | Threshold depth of water in the shallow aquifer for "revap" to occur | mm                | 0–500            |                  |
| LAT_TTIME | Lateral flow travel time   | day               | 0–180            | Pesticide        |
| CN2       | Initial SCS CN II value  | none              | –0.2–0.2         |                  |
| PERCOP    | Pesticide percolation coefficient                                    | none              | 0–1              |                  |
| CHPST_REA | Pesticide reaction coefficient in reach                              | 1/day             | 0–0.1            |                  |
| CHPST_KOC | Pesticide partition coefficient between water and sediment in reach  | m <sup>3</sup> /g | 0–0.1            |                  |



**Figure 3.** The simulated water flow rate at the outlet of the Sakura River watershed during the 2008–2009 period.



**Figure 4.** The predicted fipronil concentration for rice season during 2009 at the pesticide monitoring point in the watershed.

Although the simulated baseflow was fluctuated more than that of the observed data, the simulated flow rate showed good response with the observed data and precipitation. Specifically, when the rain came, peak of predicted water flow rate was achieved and vice versa; and the tendency between the predicted flow rate and the observed data was found similar. Table 3 shows the calculated statistical indices for evaluating the model performance of water discharge simulation. The calculated RMSE and PBIAS values, respectively, showed that the predicted water discharge rate had large errors and they were overestimated. Meanwhile, the NSE values indicated that the water discharge rate simulation of the model was good in the calibration year and acceptable in the validation year.

The predicted concentrations of the insecticides were lower compared to the measured insecticides concentrations. The statistical evaluation results of the predicted values of the insecticides concentrations are summarized in Table 3. The NSE and RMSE values were very close to zero. However, the values of PBIAS index indicated that the predicted concentrations of the insecticide in the reach were underestimated possibly because of the insecticide application timing and rate, which did not match with the corresponding actual application timing and rate. In conclusion, the predicted insecticides concentrations were found acceptable.

**Table 3.** The computed values of model evaluation indices values for the simulated concentrations of the two insecticides.

| Variables       | Period      | NSE  | RMSE  | PBIAS  |
|-----------------|-------------|------|-------|--------|
| Water discharge | Calibration | 0.85 | 6.52  | -15.68 |
|                 | Validation  | 0.22 | 7.03  | -26.24 |
| Fipronil        | Calibration | 0.19 | 0.001 | 19.12  |

### 3.2. Assessment of Fipronil transport

In the Sakura River watershed, the paddy fields are allocated a long with the river in low-land area. So, the applied pesticides in paddy fields are likely to spread to the surrounding aquatic environment. The simulated fipronil concentrations at the monitoring point are displayed in figures 4. The maximum values of the predicted and monitored insecticides concentrations were 0.008 and 0.005 µg/L in 2009 for fipronil. Since insecticides are applied to protect rice against insects throughout the whole growing season, their concentrations in reach increased two times in the 2009 rice season. However, the predicted insecticides concentrations occurred at the beginning of May, rose up in the middle of May, and then decreased.

The pesticides concentrations, which were simulated by the PCPF-1@SWAT2012 model, showed that the rice treated area, application timing, rate and water solubility have strongly affected the prediction. Specifically, the peaks of the insecticides in the middle of May were probably due to nursery-box application upon transplanting. Although fipronil had large rice treated area its peak concentrations of fipronil were low. That can be explained by the application rate of 0.0101 kg/ha, and water solubility values of 3.78 mg/L for fipronil. In addition, the simulated concentrations of the insecticides were low might because of the high Koc (803 ml/g for fipronil) and expected to be mainly applied following the pest forecasting. In other words, the differences in the application rates and methods for the insecticides probably explain why they were detected and simulated at low concentrations. In addition, the pesticide transport was associated with rainfall. When rainfall exceeded certain amount, it caused loss of the applied pesticide from rice paddy. On the other hand, high rainfall also diluted the pesticide concentration in water bodies.

## 4. Conclusions

The PCPF-1@SWAT2012 model was applied for predicting transport of a rice insecticide namely fipronil in the Sakura River watershed during 2008–2009 period. The model simulated the observed data with acceptable tendency. The fipronil concentration was increase during rice seasons in the watershed. Strong relationship existed between the increase in the simulated pesticide concentration in the rivers and pesticide application timing and rainfall. However, the model needs to be verified with other pesticides in this watershed as well as in other watersheds. Furthermore, to improve the model accuracy,

detailed information regarding water management and pesticide use in the watershed are required.

**Author contribution statement:** Collected data: L.H.T., H.W.; Analyzed and processed the data: L.H.T.; Model performing: L.H.T.; wrote the draft manuscript: L.H.T., H.W.; Manuscript editing: L.H.T., H.W.

**Acknowledgments:** Authors are thankful to MEXT scholarship for support during the study. Authors are also thankful to the Ministry of Economy, Trade, and Industry (METI) of Japan, the United States National Aeronautics and Space Administration (NASA), The Ministry of Land, Infrastructure and Transport (MLIT) of Japan, National Institute for Agro-Environmental Sciences (NIAES) of Japan, Japan Meteorological Agency (JMA) and Japan Plant Protection Association (JPPA) for providing required data for this study.

**Competing interest statement:** The authors declare no conflict of interest.

## References

1. Mohanty, S.. Trends in global rice consumption. *Rice today* 2, 2013.
2. FAOSTAT. Global Rice consumption. Food Agric. Organ. 2016. URL <<http://www.fao.org/faostat/en/#data>> (accessed Apr.10.2017).
3. Gianessi, L. Importance of Pesticides for Growing Rice in South and South East Asia. *Crop. Int.* 2014, pp. 4.
4. Savary, S.; Willocquet, L.; Elazegui, F.A.; Teng, P.S.; Du, P.; Van, Zhu, D.; Tang, Q.; Huang, S.; Lin, X.; Singh, H.M.; Srivastava, R.K. Rice pest constraints in tropical Asia: characterization of injury profiles in relation to production situations. *Am. Phytopathol. Soc.* **2000**, *84*, 341–356.
5. Lamers, M.; Anyusheva, M.; La, N.; Nguyen, V.V.; Streck, T. Pesticide Pollution in Surface- and Groundwater by Paddy Rice Cultivation: A Case Study from Northern Vietnam. *Clean Soil, Air, Water* **2011**, *39*, 356–361.
6. Numabe, A.; Nagahora, S. Estimation of pesticide runoff from paddy fields to rural rivers. *Water Sci. Technol.* **2006**, *53*, 139–146.
7. Nakano, Y.; Miyazaki, A.; Yoshida, T.; Ono, K.; Inoue, T. 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 Res.* **2004**, *38*, 3017–3022.
8. FAOSTAT. Rice Production Quantity. Food Agric. Organ. 2014. URL <<http://www.fao.org/faostat/en/#data/QC>> (accessed Apr.10.2017).
9. Inao, K.; Watanabe, H.; Karpouzias, D.G. Simulation Models of Pesticide Fate and Transport in Paddy Environment for Ecological Risk Assessment and Management. *Jpn. Agric. Res. Q.* **2008**, *42*, 13–21.
10. Kawata, K.; Kose, T. Behavior of Pesticides and Their Transformation Products in River Water in Japan. 2012.
11. Iwafune, T.; Inao, K.; Horio, T.; Iwasaki, N.; Yokoyama, A.; Nagai, T. Behavior of paddy pesticides and major metabolites in the Sakura River, Ibaraki, Japan. *Pestic. Sci.* **2010**, *35*, 114–123.
12. Vu, S.H.; Watanabe, H.; Ishihara, S. Probabilistic risk assessment through pesticide fate modeling for evaluating management practices to prevent pesticide runoff from paddy fields. In: The 11th IUPAC International Congress on the Chemistry of Crop Protection. Kobe, Japan, 2006, pp. 263.
13. Uddin, H.; Amin, A.K.M.R.; Haque, M.; Islam, A.; Azim, M.E. Impacts of organophosphate pesticide, sumithion on water quality and benthic invertebrates in aquaculture ponds. *Aquac. Reports.* **2016**, *3*, 88–92.

14. Boulange, J.; Watanabe, H.; Inao, K.; Iwafune, T.; Zhang, M.; Luo, Y.; Arnold, J. Development and validation of a basin scale model PCPF-1@SWAT for simulating fate and transport of rice pesticides. *J. Hydrol.* **2014**, *517*, 146–156.
15. Neitsch, S.; Arnold, J.; Kiniry, J.; Williams, J. Soil & Water Assessment Tool Theoretical Documentation Version 2009. Texas Water Resour. Institute, TR-406. 2011.
16. Karpouzias, D.G.; Ribarbelli, C.; Pastori, M.; Capri E. Landscape risk analysis for pesticides applied to rice paddies. *Agron. Sustain. Dev.* **2006**, *26(3)*, 167–177.
17. METI and NASA. The ASTER Global Digital Elevation Model (ASTER GDEM). The Ministry of Economy, Trade, and Industry (METI) of Japan The United States National Aeronautics and Space Administration (NASA). 2012. URL<<http://www.jspacesystems.or.jp/ersdac/GDEM/E/4.html>> [accessed 16 May 2012].
18. MLIT. Digital national Land Information. Ministry of Land, Infrastructure and Transport, Japan; 2012. URL<[http://nlftp.mlit.go.jp/ksj-e/jpgis/jpgis\\_datalist.html](http://nlftp.mlit.go.jp/ksj-e/jpgis/jpgis_datalist.html)> [accessed 16 May 2012].
19. NIAES. Cultivated soil information system. National Institute for Agro-Environmental Sciences. 2009.
20. Agency, J.M. Japan Meteorological Agency. Japan Meteorological Agency. Japan Meteorological Agency, 2012. URL<<http://www.jma.go.jp/jma/index.html>> [accessed 28 May 2012].
21. Tu, L.H.; Boulange, J.; Iwafune, T.; Yadav, I.C.; Watanabe, H. Improvement and application of the PCPF-1@SWAT2012 model for predicting pesticide transport: A case study of the Sakura River watershed. *Pest Manage. Sci.* **2018**, *74*, 2520–2529. doi:10.1002/ps.4934.
22. Boulange, J. Development and application of the PCPF-1@SWAT model for simulating the fate and transport of rice pesticides in watersheds containing paddy fields. Tokyo University of Agriculture and Technology. 2013.
23. JPPA . Pesticide database. Japan Plant Protection Association, Tokyo, Japan. 2009.
24. Chai, T.; Draxler, R.R. Root mean square error (RMSE) or mean absolute error (MAE)? –Arguments against avoiding RMSE in the literature. *Geosci. Model Dev.* **2014**, *7*, 1247–1250.
25. Gassmann, M.; Stamm, C.; Olsson, O.; Lange, J.; Kümmerer, K.; Weiler, M. Model-based estimation of pesticides and transformation products and their export pathways in a headwater catchment. *Hydrol. Earth Syst. Sci.* **2013**, *17*, 5213–5228.
26. Moriasi, D.N.; Arnold, J.G.; Van Liew, M.W.; Bingner, R.L.; Harmel, R.D.; Veith, T.L. Model Evaluation Guidelines for Systematic Quantification of Accuracy in Watershed Simulations. *Trans. ASABE.* **2007**, *50*, 885–900.
27. Nash, J.E.; Sutcliffe, J.V. River flow forecasting through conceptual models part I – A discussion of principles. *J. Hydrol.* **1970**, *10*, 282–290.
28. Gupta, H.V.; Kling, H.; Yilmaz, K.K.; Martinez, G.F. Decomposition of the mean squared error and NSE performance criteria: Implications for improving hydrological modelling. *J. Hydrol.* **2009**, *377*, 80–91.
29. Gupta, H.V.; Sorooshian, S.; Yapo, P.O. Status of Automatic Calibration for Hydrologic Models: Comparison with Multilevel Expert Calibration. *J. Hydrol. Eng.* **1999**, *4*, 135–143.