# Assessing Pesticide Loading and Concentration with Assistance of Integrated Hydrological Models in Streams of Small to Medium-Sized Watersheds

by

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# Abstract

Pesticides are increasingly used around the world alone with the expansion of intensive crop cultivation and food production. Pesticide residues from agriculture fields being carried to surface and ground water impose a potential threat to the aquatic ecosystem as well as to human health. However, monitoring potential threat of pesticide residuals in river systems is expensive and difficult. Previous studies indicated that traditionally used grab sampling methods could potentially underestimate the maximum concentrations of pesticide residues in streams by 10 to 1000 times. The objective of this study was to assess pesticide loading and concentration with assistance of integrated hydrological models in streams of small to medium- sized watersheds. Soil and Water Assessment Tool (SWAT) was selected for simulating hydrological processes together with pesticide loading and in stream pesticide concentration. Model predicted pesticide loading and pesticide concentration was compared with three years measured data from Black Brook Watershed and two Sub-basins within the same watershed. We found that the model predicted pesticide loading and in stream concentrations of three pesticides had the same seasonal trend with field surveys with some discrepancies. The discrepancies are likely caused by three main factors. 1. Model predicts the daily pesticide loading and daily average pesticide concentration and while actual pesticide concentrations change rapidly during stormflow period. 2. Current field sampling method could not capture the rapid change of pesticide concentration due to mechanical limitations. 3. Input data on exact pesticide application date were not available. In general, the pesticide modelling results indicate that the model is an effective tool in loading and concentration prediction in small agricultural watershed. We also found the model predicted pesticide loading during

baseflow period were relatively high compare with near zero pesticide concentration observed. This suggest there is a need to improve in pesticide routing algorithm in SWAT model and current estimation during based flow period should be manually adjusted.

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# Introduction

Pesticides are widely used to reduce insect damage; control weed competition or prevent diseases in agriculture crop production. Pesticide residues being carried into aquatic system by runoff water or soil erosion could cause damages aquatic ecosystem. For example, pesticide washed off from nearby agricultural field had led to many cases fish kills in Prince Edward Island (Standards and Use 2009). Pesticide residues in surface and groundwater could also threat human health (Nicolopoulou-Stamati et al 2016).

In New Brunswick, agriculture sector is a key part of the provincial economy and agriculture associated pesticide issue is also a raising public concern. According to Xing et al (2013), pesticide residues were detected in 17-22% of the water samples in watersheds that under agricultural operation from 2003-2007. The measured concentrations of pesticide exceeded the Canadian council of Ministers of the Environment (CCME) Environmental Quality guideline with the exceedance rate range from 3.4 to 30%. In fact, the pesticide issue may be more severe than reported due to the inherited limitations of the grab sampling method being used to conduct pesticide surveys in the past (Xing et al. 2013).

As a general principle, the environmental risks of pesticide of a given pesticide in water is related the pesticide concentrations as well as the durations of the residue associated with pesticide pollution events. Pesticide concentrations in streams could be affected by many factors including pesticide properties, pesticide application method, environmental conditions and watershed characters (Wauchope and Leonard 1980). As a consequence, pesticide concentrations in stream are often shown complicated spatial and temporal patterns. For example, high concentrations of the pesticides are often characterized as a short-duration pulse, with variabilities associated with the pesticides properties as well as hydrological characteristics of rain event (Gao et al. 2018). As a result, low sampling frequency such as monthly samples may miss the severe pesticide pollution event (Pinto et al. 2010). However, higher sampling frequencies implies that a large number of water samples need to be collected in the field and analyzed in the laboratory, which is not only time consuming, but also expensive. As such, pesticide estimations based on the traditional grab sampling method with fixed time interval, or at random sampling points may not reflect the true severity of pesticide risks across landscape. A more innovative and economical alternative approach is required to obtain the pesticide pollution information and using model to simulate pesticide concentration or loading is a viable option. Although pesticides can be transported to non-target areas by volatilization, spray drift, the major mechanisms that lead to pesticide pollutions in aquatic ecosystem are closely associated with hydrological processes. For this reason, models that could be used for predicting pesticide concentrations require a robust description of the hydrological processes related to pesticide transport, partitioning and transformation (Kannan et al. 2006). In addition, model-generated data could partially supplement the problem of lacking high frequency field sampling data.

In this study, SWAT was chosen to estimate the pesticide concentration and loading variations. The SWAT model is a physically based, semi-distributed comprehensive hydrological model. The model was developed for assessing of effects of different management practices on hydrological, sediment and agriculture chemicals dynamics and transport at watershed scale. The latest version of SWAT model incorporated several other models, the Groundwater Loading Effects of Agricultural Management System (GLEAMS) model (Leonard et al. 1987) and the Erosion-Productivity Impact Calculator (EPIC) Model (Williams 1990). The SWAT model has been calibrated and validated for the Black Brook Watershed for hydrological and nutrient dynamic simulations in an earlier study (Qi et al. 2016). The general objective of this study is to use the SWAT model to estimate pesticide loading and pesticide concentration in small and medium sized watersheds. Specific objectives include: (1) Estimate event-based pesticide concentrations based on pesticide monitoring records. (2) Use SWAT model to estimate daily mean pesticide concentrations. (3). Assess the feasibility of using SWAT model to predict pesticide risks in agriculture watershed.

## Methods

### Study site

The research was conducted in a nested watershed located in northwestern part of New Brunswick, Canada (47°5′to 47°9′N and 67°43′to 67°48′W). The Black Brook watershed (BBW) is a sub-watershed of the Little River Watershed, and covers an area of 1450 ha. The elevation ranges from 127 to 432 m. Slopes range from 2% to 15% (Anon 2013). The annual precipitation in the BBW is approximately 1134 mm, and about one-third of the precipitation is in the form of snow. Up to 65% of the total area of the watershed is crop land. Forests cover only 21% of the land together with a small proportion pasture and residential areas. In 1990, the BBW was established as an experimental watershed for studying the effectiveness of soil conservation practices on soil erosion water quality. Since then, stream discharge, water level and nutrient concentration in streams have been monitored, thus providing a wealth of hydrological data for this study. In this study, data from monitoring stations 1, 8 (2018, with a total area of 2.98 $km^2$ where 84% is agriculture) and 9 (2006 to 2008, with a total area of 0.8 $km^2$ where 93% is agricultural) were chosen for analysis due to the completeness of their measured streamflow and pesticide loading records (Figure 1.1).

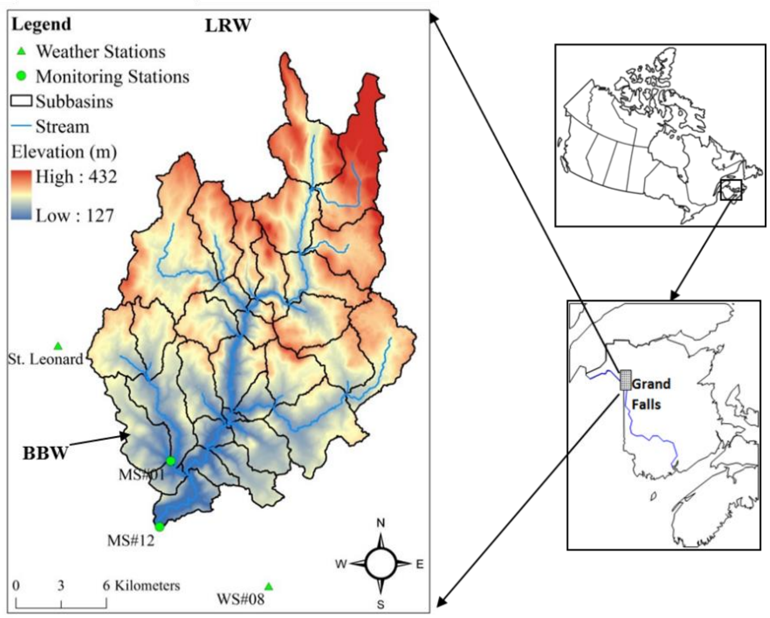


Figure 1. Location map of the Black Brook watershed and the Little River Watershed.

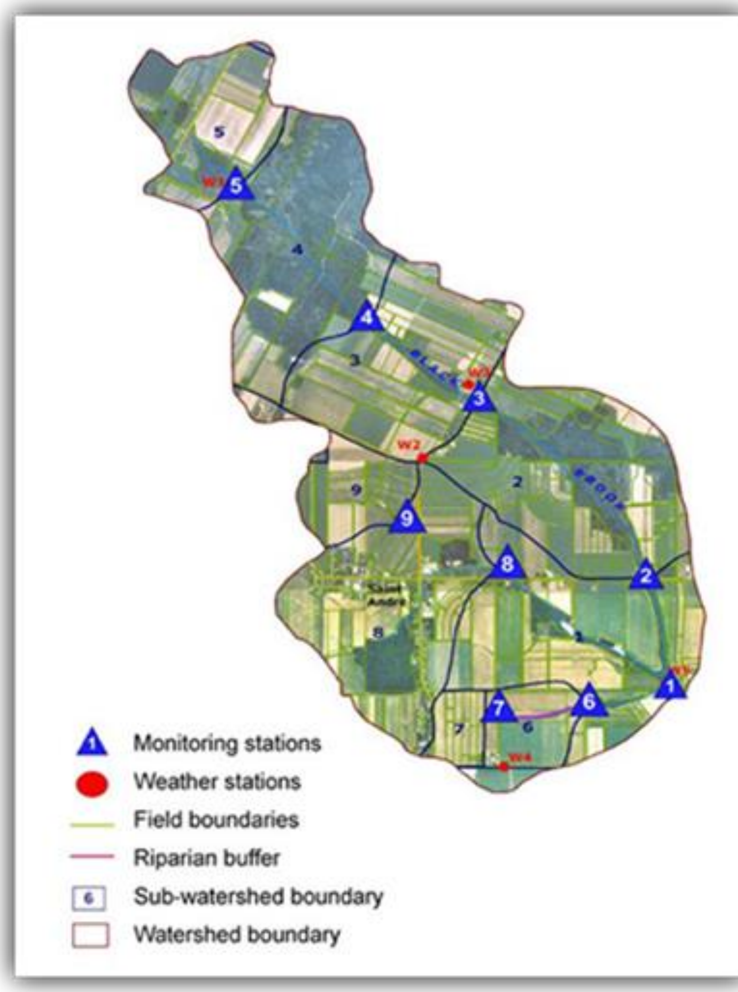


Figure 2. Sub-basins of Black Brook Watershed (BBW) and location of the monitoring stations #01 and SUB#9.

**Input data for SWAT model**

The SWAT model requires topographic, weather, soil, land use, streamflow and pesticide dataset as input files. Topographic data (DEM) for BBW was obtained from Service New Brunswick. The 1-meter DEM derived from high precision Lidar data was used to define flow path, watershed boundary and hydrological response units (HRUs).

The source of weather data was the St Leonard station (47.16°N, 67.83°W), from Environment and Climate Change Canada (1986 to 2015) and Fort Kent station (47.23°N, 68.61°W), Maine United States from the National Oceanic and Atmospheric Administration (2015 to 2018).

Detailed soil information and high-resolution soil map (1:10000) was provided by Agriculture and Agri-Food Canada (AAFC). In BBW, there is one organic soil association (St. Quentin) and six mineral soil associations (Grand Falls, Interval, Siegas, Undine, Muniac and Holmesville) in the BBW. Compared with other soil types, Holmesville soils are the most extensive, accounting for about 45% of the whole watershed. The drainage class for Holmesville varies from imperfectly drained to well-drained, but most poorly drained sites are forested. Siegas soils are the second most predominant soil type in the BBW, occupying approximately 33% of the total land. Similarly, its drainage class varies from very poorly (7.9 ha) to well and moderately well drained (202 ha) (Qi et al. 2017). St. Quentin soil (organic soil) are found in the forested area located in the northern part of the BBW, occupying some 24.9 ha.

Land use information of the BBW has been recorded yearly since 1988. Generated land use classes include Cropland, Forest, Pasture and Residential. The most important cash crop in the BBW is potatoes, in rotation with corn, grain (wheat, oat and barley) and clover. In general, potato planting season starts in late March or April and ends in October, with slight variations depending on climate conditions. For SWAT model, basic crop information is required, such as harvest index, leaf area index and so on. Crop information was obtained from the built-in SWAT database, where appropriate crop parameters were selected for model setup.

Three widely used pesticides (Linuron, Chlorothalonil and Metribuzin) were selected for model simulation. Key physical and chemical properties of these pesticides are shown in Table 1. Water samples used for pesticide testing were collected from the monitoring stations of the BBW and sub-watershed 9 in 2008.

Table 1. Pesticide properties of Linuron (Herbicide), Metribuzin (Herbicide) and Chlorothalonil (Fungicide).

| | Partition coefficient (the concentration ratio between two media) | Soil Half-life (Days) | Solubility (mg/L) | Foliage Half-life (Days) | Wash-off Fraction |
|---|---|---|---|---|---|
| Linuron | 400 | 60 | 75 | 15 | 0.6 |
| Chlorothalonil | 1380 | 30 | 0.6 | 10 | 0.5 |
| Metribuzin | 60 | 40 | 1220 | 5 | 0.8 |

**Pesticide monitoring**

Automatic water sampler (ISCO 2900 sampler) coupled with a flow-monitoring system was installed to collect pesticide samples at outlets 1, 8, and 9 (Figure 1.2). The ISCO 2900 sampler can accommodate twelve 2-L amber bottles for sample collection, and a CR10X data logger (Campbell Scientific, Logan, UT, USA) was installed and programed to trigger water sample collection based on water level changes. Flow rates were measured at 5-min intervals and recorded on an hourly basis during non-rainfall periods when the change of water level was less than 2 cm. Flow rates were recorded more frequently, less than one hour, when water level change was more than 2 cm during heavy rain events. In this study, the event-based sampling method was adopted for pesticide sample collection. Based on the analysis of previous years' water level variations, the auto-sampler was activated by the data logger to take water sample at every 3 cm change in water level in the BBW station in 2006 and 2008, and every 5 cm change in water level in Sub-watershed 9 station in 2006 and 2008 (Xing et al. 2013). In 2018, the sampler was set to take water samples at every 5 cm change in water level in both Sub-watershed 8 station and the BBW station.

Collected water samples were stored in cool and dark places and then forwarded to the Atlantic Laboratory for Environmental Testing (ALET) for analysis. In 2006 and 2008, one insecticide, two fungicides and two herbicides were analyzed. In 2018, one insecticide, one fungicide and two herbicides were analyzed. However, considering the pesticide application amounts and rates, only one fungicide (Chlorothalonil) and two herbicides (Metribuzin and Linuron) were selected for modelling purpose. All pesticides were separated and measured by using gas chromatography- mass spectrometer (GC-MS) analysis. It should be noted that pesticide concentration analysis is supposed to be performed on both filtered and unfiltered extracts of the same water sample. However, only dissolved pesticide concentrations were analyzed and discussed in this study because of the larger proportion of dissolved pesticides in streams (Table 2). Also, attached pesticides were not discussed here because only the amount of dissolved pesticides was analyzed in 2018.

Table 2. Maximum, minimum and average percentages of dissolved pesticide (µg/L) /total pesticide (µg/L) in the Little River watershed

| | 2006 | | | 2007 | | |
|---|---|---|---|---|---|---|
| Pesticide | Max | Min | Average | Max | Min | Average |
| Chlorothalonil | 99.57% | 28.57% | 87.70% | 96.03% | 18.84% | 67.18% |
| Linuron | 99.25% | 40.39% | 83.50% | 92.30% | 38.76% | 69.54% |
| Metribuzin | 98.57% | 87.70% | 94.42% | 99.04% | 86.50% | 92.36% |

### Pesticide loading and concentration calculation

Event-based loading (Le) was calculated according to pesticide concentration and flow rate during rain events:

$$\mathrm{Le} = \sum_{1}^{\mathrm{n}} (\mathrm{c_i} t_i f_i) \tag{1}$$

where $c_i$ is the pesticide concentration of the i$^{\text{th}}$ sample, $t_i$ is the recorded time interval, $f_i$ is the instantaneous flow rate at the time of the i$^{\text{th}}$ sample being sampled and n is the number of samples per rainfall event.

Daily pesticide loadings were also calculated with the same method.

The mean pesticide concentrations during event (MC) was also calculated by event-based pesticide loading and total stream discharge of the event:

$$\mathrm{MC} = \frac{\mathrm{Le}}{\sum_{1}^{n} (t_i * f_i)} \tag{2}$$

where $t_i$ is the recorded time interval, $f_i$ is the instantaneous flow rate at the time of the i$^{\text{th}}$ sample being sampled and n is the number of samples per rainfall event.

Daily mean pesticide concentrations were calculated in the same method.

### Calibration and validation

The SWAT model is a process-based model with some pre-set parameters for hydrological and nutrient simulations. However, considering diverse climate and geological conditions in different watersheds, calibrations are necessary to obtain adequate prediction accuracy.

The hydrological processes of the SWAT model was calibrated with monthly base flow and total discharge for the period 1992 to 2001 in the BBW station (Qi et al. 2017). Then, the model was validated by using monthly streamflow discharge for the period 2002 to 2011. Further detailed information about model calibration and validation can be found in Qi et al. (2017).

The measured event-based pesticide concentration data of 2006 and 2008 were used for calibration and validation of the pesticide module of SWAT model. Pesticide concentration calibration was done by adjusting pesticide property parameters listed in Table 3.

Table 3. Final values of SWAT calibration parameters for pesticide concentration simulation.

| Parameters | Unit | SWAT Name | Chlorothalonil | Linuron | Metribuzin |
|---|---|---|---|---|---|
| Soil Adsorption coefficient | Ratio | SKOC | 1380 | 500 | 80 |
| Wash-off fraction | Ratio | WOF | 0.5 | 0.6 | 0.8 |
| Foliar half-life | Days | HLIFE_F | 5 | 10 | 5 |
| Soil half-life | Days | HLIFE_S | 15 | 20 | 10 |
| Pesticide solubility | mg/L | WSOL | 0.6 | 75 | 1220 |

### Evaluation criteria

The Nash–Sutcliffe efficiency (NSE) and the coefficient of determination ($R^2$) were used for evaluating model performance on hydrological predictions (2006, 2008 and 2018). The NSE is a coefficient that measures how well a model simulation matches the observed data (Scott et al. 2008). The range of NSE lies between -∞ and 1 (perfect fit) (Scott et al. 2008). The $R^2$ is a commonly used statistical measure of the correlation between observed and predicted values. The $R^2$ value ranges between 0 and 1, with a value of 0 indicating no correlation and a value of 1 representing perfect fit. As the measured data was insufficient to obtain a reliable estimation of daily pesticide loading that required to compare with SWAT model prediction, the model performance in pesticide simulation was mainly assessed by visual inspection.

## Results

### Hydrological calibration and validation

Predicted and measured daily flow rate are shown in Figures 1.3-5, and calculated NSE and $R^2$ for model predicted flow rate are listed in Table 1.4. There was a slight overestimation of flow rates during the peak flow period (around April 2006, Figure 1.3). In 2008, however, there were a underestimation of peak flow during the during the same season. These results indicated that model prediction of snow melting could be improved. However, there were no pesticide applications during snow melting season and the small discrepancies would have little impacts on pesticide assessment. In general, the SWAT model predicted flow rate follows the observed trends quite well during the three-year period (Figures 1.3-5). The NSE for stream flow ranged between 0.695 to 0.724 in 2006, 2008 and 2018. The $R^2$ ranged between 0.709 to 0.809 in 2006, 2008 and 2018, which indicated an acceptable model performance. Despite the discrepancies between the measured and simulated streamflow during snow melting seasons, the overall hydrologic performance of SWAT model can be considered as satisfactory for pesticide assessment based on both the statistical and graphical evaluation.

Table 4. SWAT performance statistics for daily discharge in the BBW (2006, 2008 and 2018).

| BBW / Year | NSE | $R^2$ |
|---|---|---|
| 2006 | 0.724 | 0.748 |
| 2008 | 0.695 | 0.709 |
| 2018 | 0.695 | 0.879 |

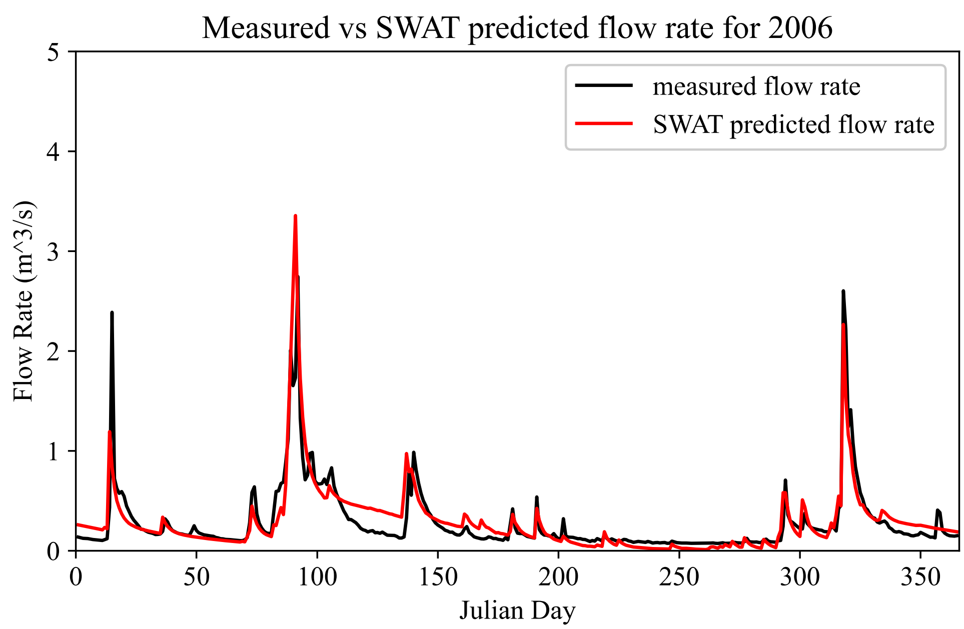


Figure 3. Measured and simulated daily streamflow in the BBW in 2006.

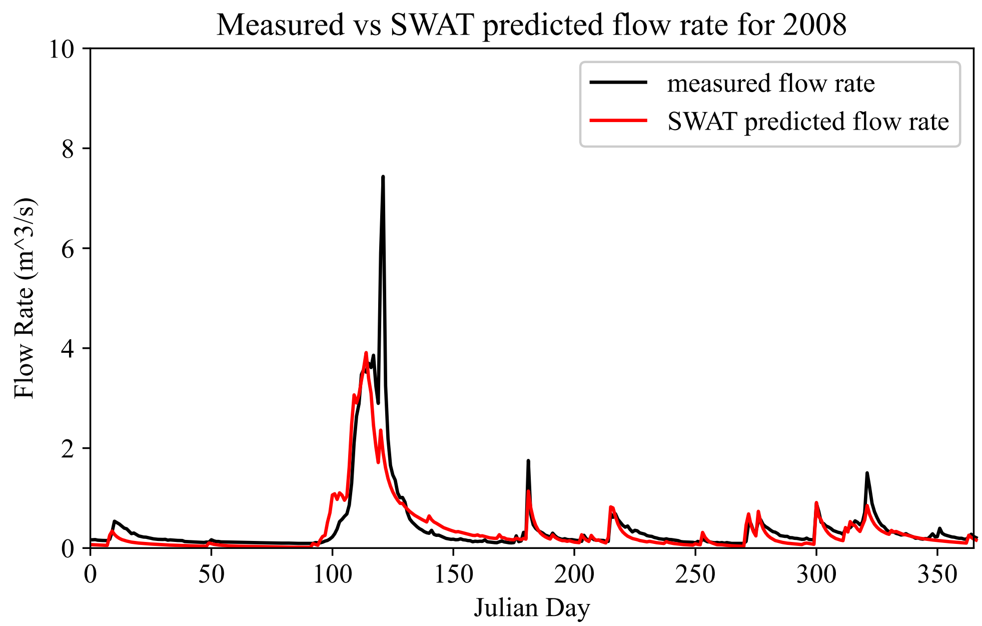


Figure 4. Measured and simulated daily streamflow in the BBW in 2008.

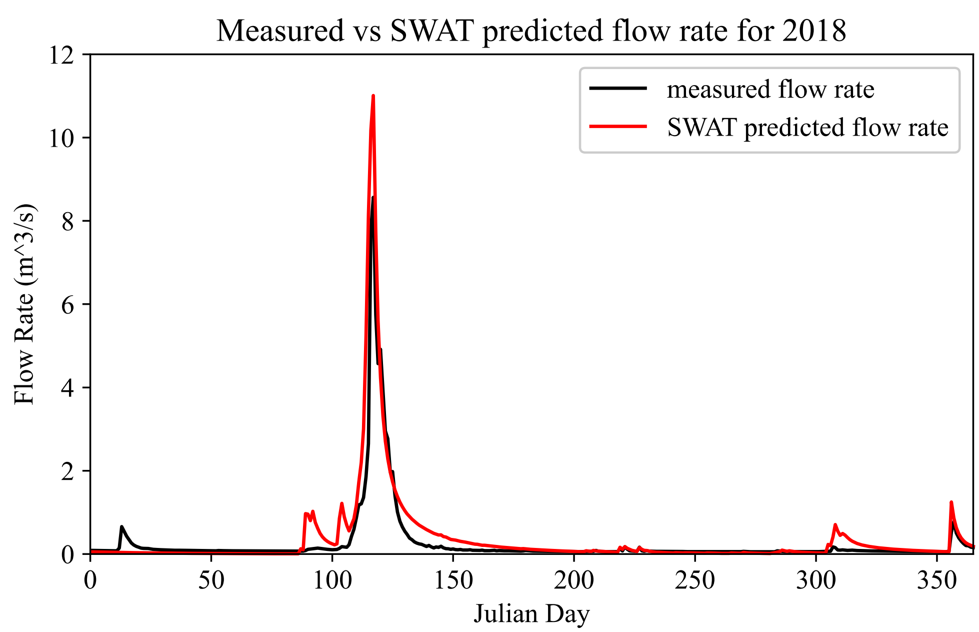


Figure 5. Measured and simulated daily streamflow in the BBW in 2018.

**Pesticide loading**

The measured and SWAT-predicted soluble pesticide loadings, and observed flow rates in the BBW are shown in

Figure 6-Figure 8. Overall, the SWAT-predicted loadings matched well with the measured data during the whole growing season, with few exceptions in heavy storms.

In 2006, the SWAT model showed satisfactory performance in metribuzin and linuron loading predictions in the BBW, while the predicted Chlorothalonil loadings were higher than observed values for some rain events at the beginning of the growing season. For Linuron and Metribuzin, the model successfully simulated peaks for most of the simulation period; the exception was for Linuron at day 180 when the model underestimated Linuron loading compared to the measured data. For Chlorothalonil, the model simulated well in the timing of peak pesticide emission although the magnitude of prediction needs further improvement.

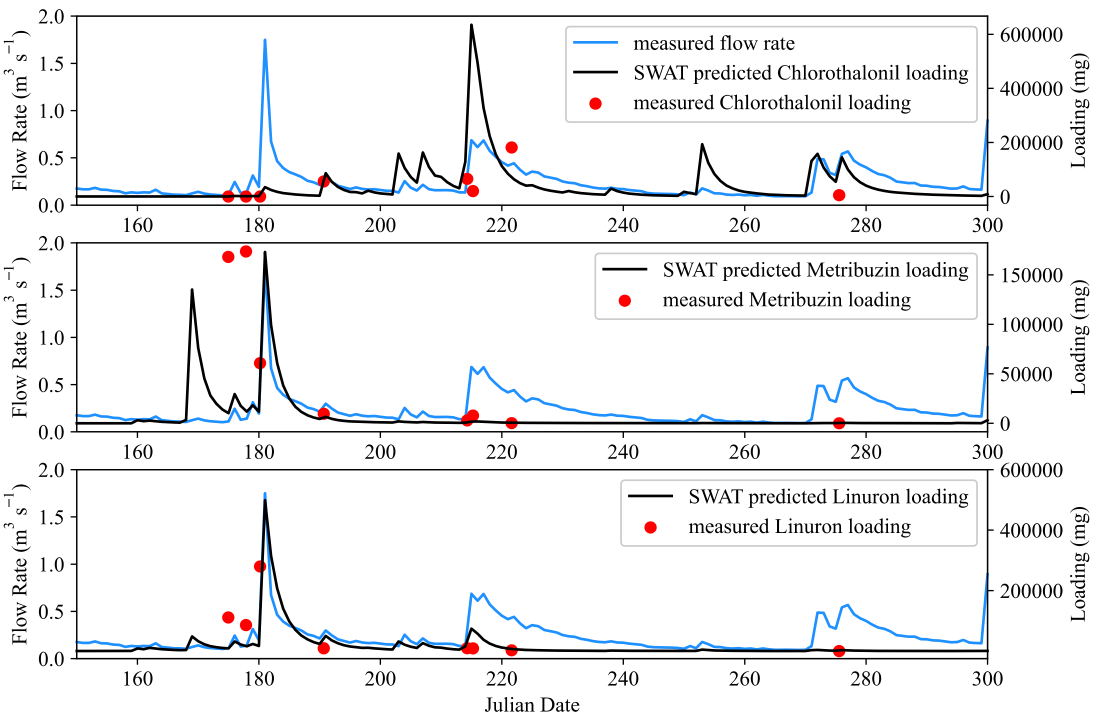


Figure 7 shows a good agreement between measured and SWAT-predicted Chlorothalonil and Linuron loadings in the BBW. However, for Metribuzin, the predicted loadings were three times higher than measured ones at the first two rain events. In 2018, the model predicted pesticide loadings were almost four times higher than measured ones for the three sampled rain events. However, due to the low sample size, we cannot determine whether SWAT model failed in capturing pesticide loading variation pattern for 2018.

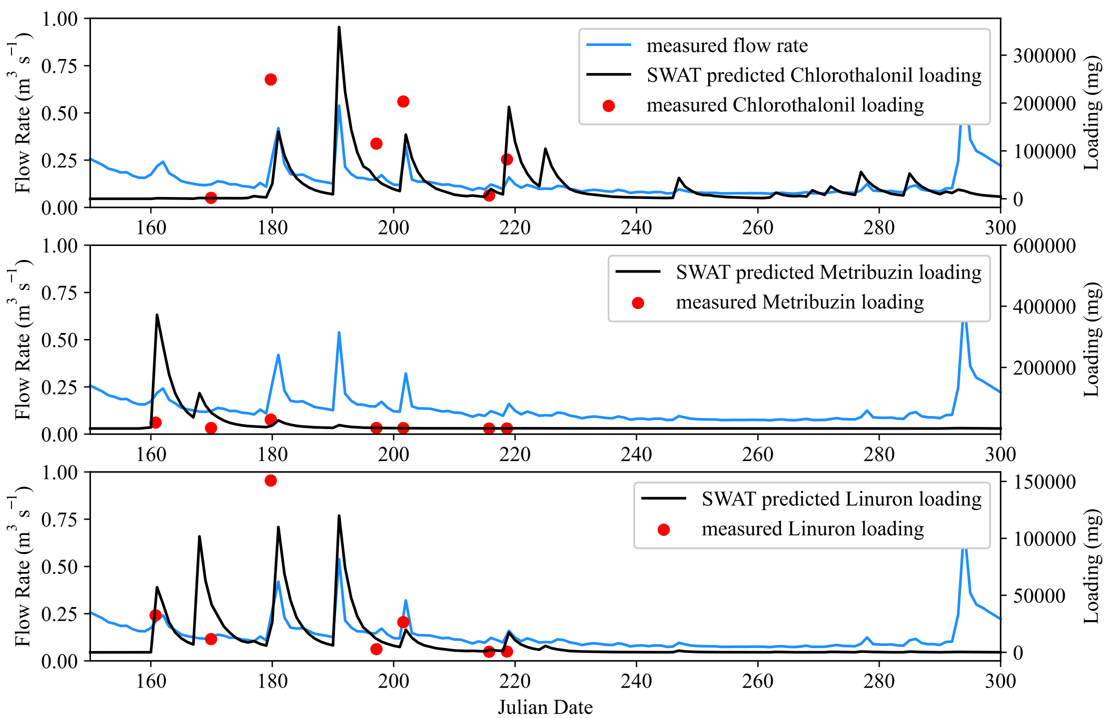


Figure 6. Observed event-based dissolved pesticide loadings and SWAT-predicted dissolved daily pesticide loadings in the BBW for 2006.

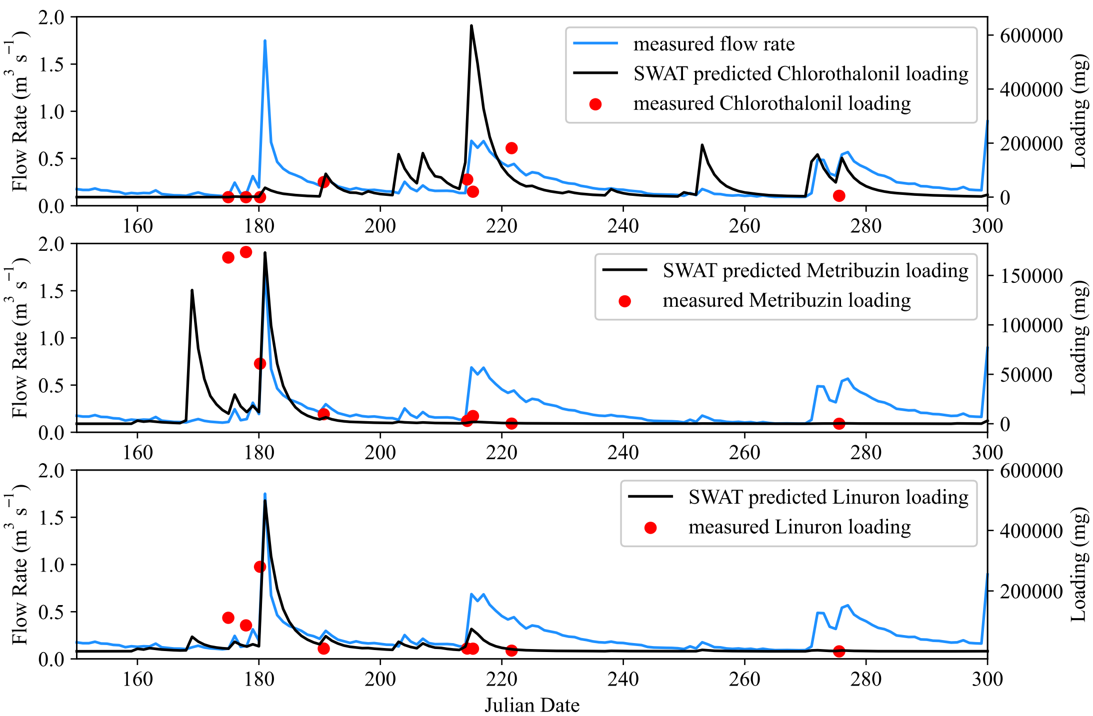


Figure 7. Observed event-based dissolved pesticide loadings and SWAT-predicted dissolved daily pesticide loadings in the BBW for 2008.

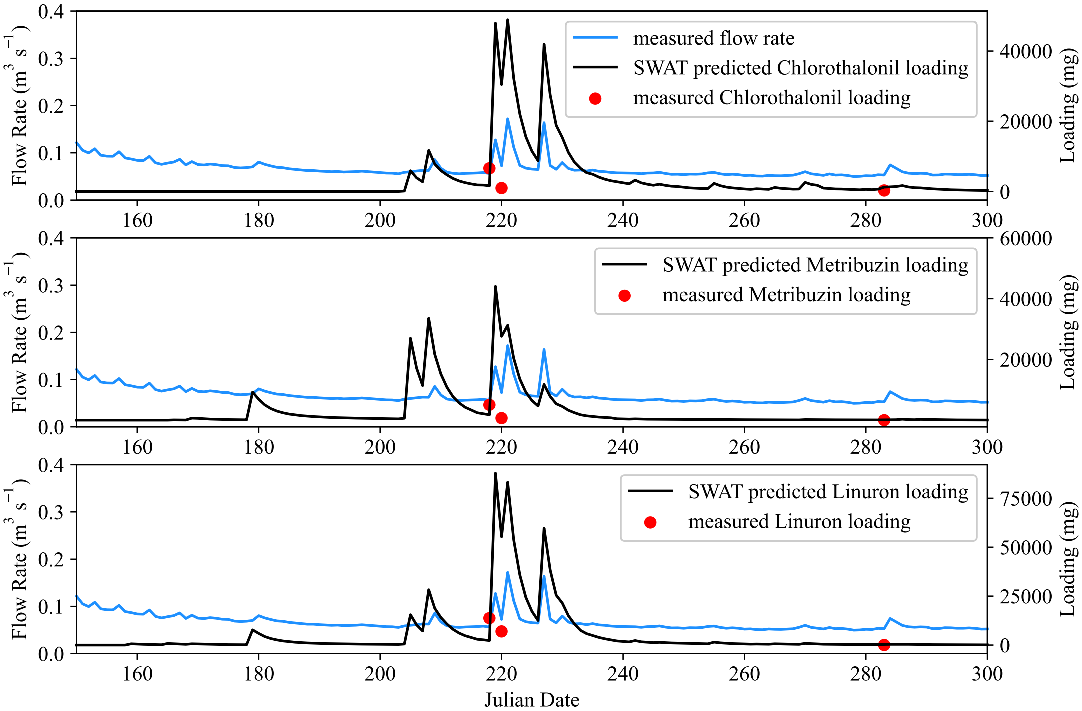


Figure 8. Observed event-based dissolved pesticide loadings and SWAT-predicted dissolved daily pesticide loadings in the BBW for 2018.

Measured and predicted pesticide loadings in Sub-watershed 9 (2006 and 2008) and Sub-watershed 8 (2018) are shown in

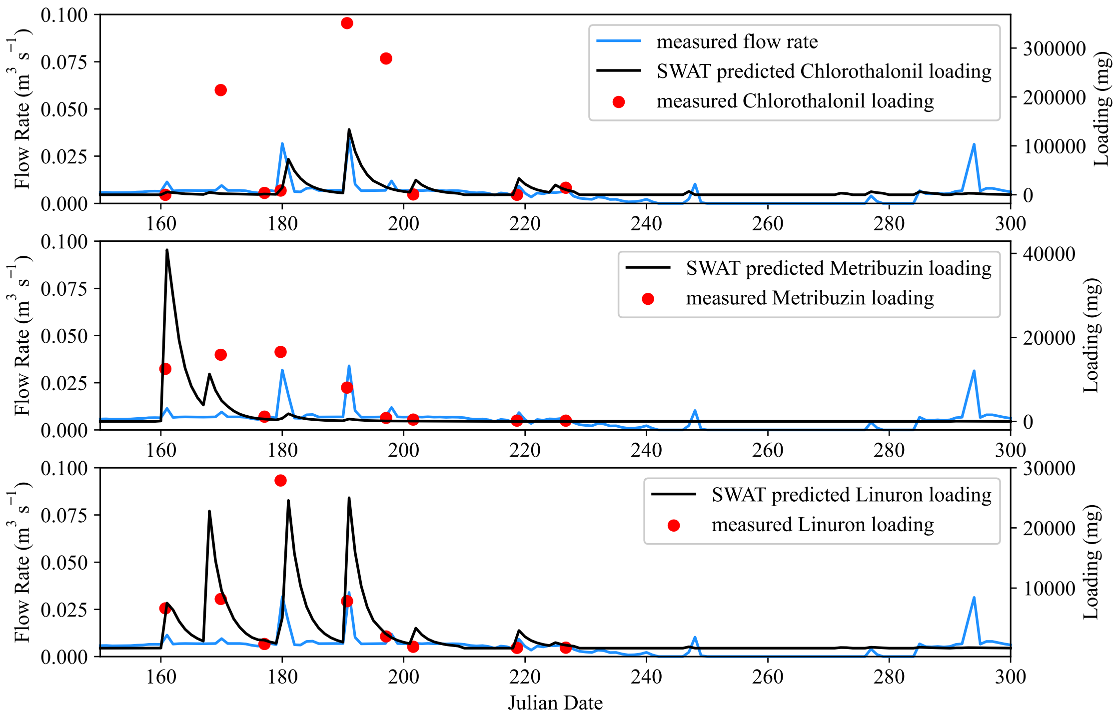


Figure 9-Figure 11. The SWAT model produced pretty good predictions in Metribuzin and Linuron loadings in 2006. As for Chlorothalonil, the SWAT model captured the timing of peak loading while the predicted values were lower than observed ones. Similar phenomenon also occurred in pesticide loading predictions in 2008 and 2018, when model predicted values were much lower than observed ones at the beginning of the growing seasons. In addition, it is interesting to note that measured Chlorothalonil and Metribuzin loadings were much lower than predicted values at day 218 and 220 in 2018 when sharp rise in water levels was recorded. Although poor simulations were obtained for Chlorothalonil in 2006, it might be attributed to potential wrong pesticide application data. Chlorothalonil was frequently used in the field to protect crop from fungi disease, and

sometimes farmers may mistake the application date. According to Boithias et al. (2014), even a small error in pesticide application date can cause significant discrepancies in model simulation results. Generally, pesticides with fewer application times tend to have a better performance in model predictions, like Linuron and Metribuzin. The two pesticides are both herbicides and were applied only one to two times in the entire growing season.

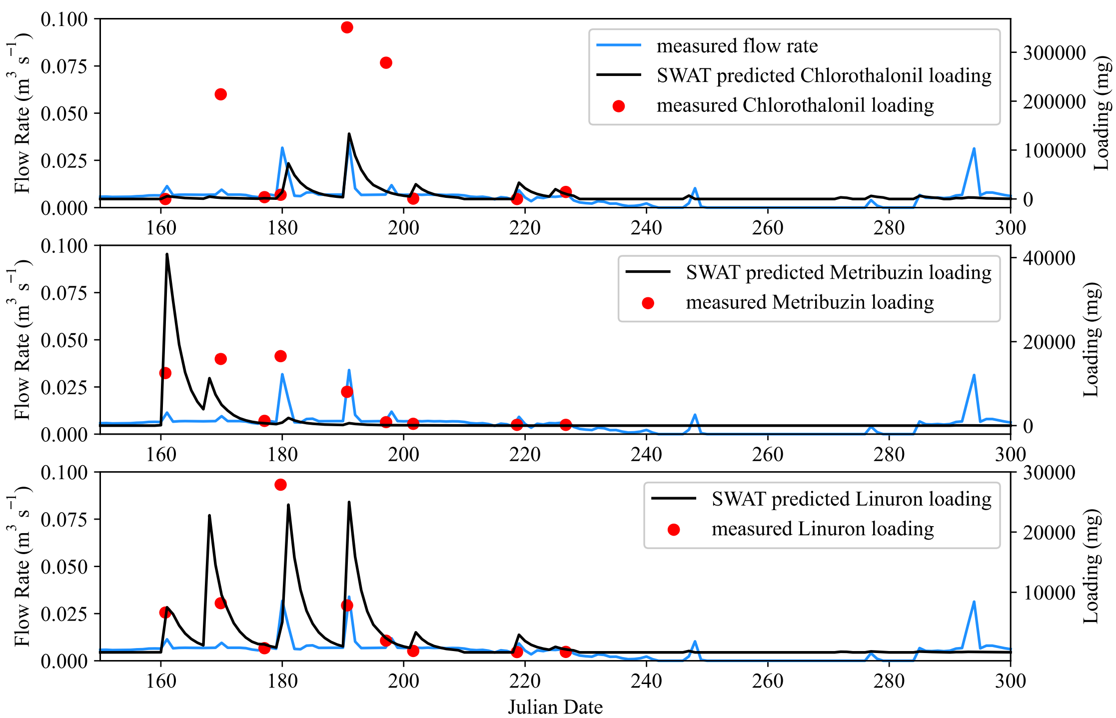


Figure 9. Observed event-based dissolved pesticide loadings and SWAT-predicted dissolved daily pesticide loadings in Sub-watershed 9 for 2006.

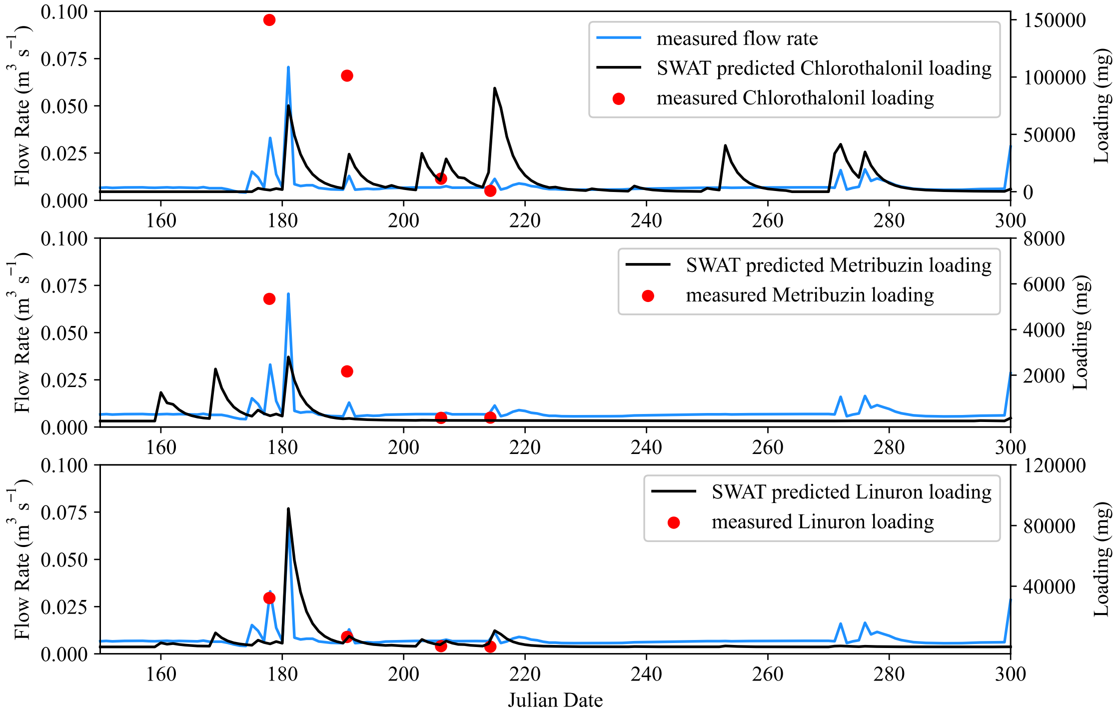


Figure 10. Observed event-based dissolved pesticide loadings and SWAT-predicted dissolved daily pesticide loadings in Sub-watershed 9 for 2008.

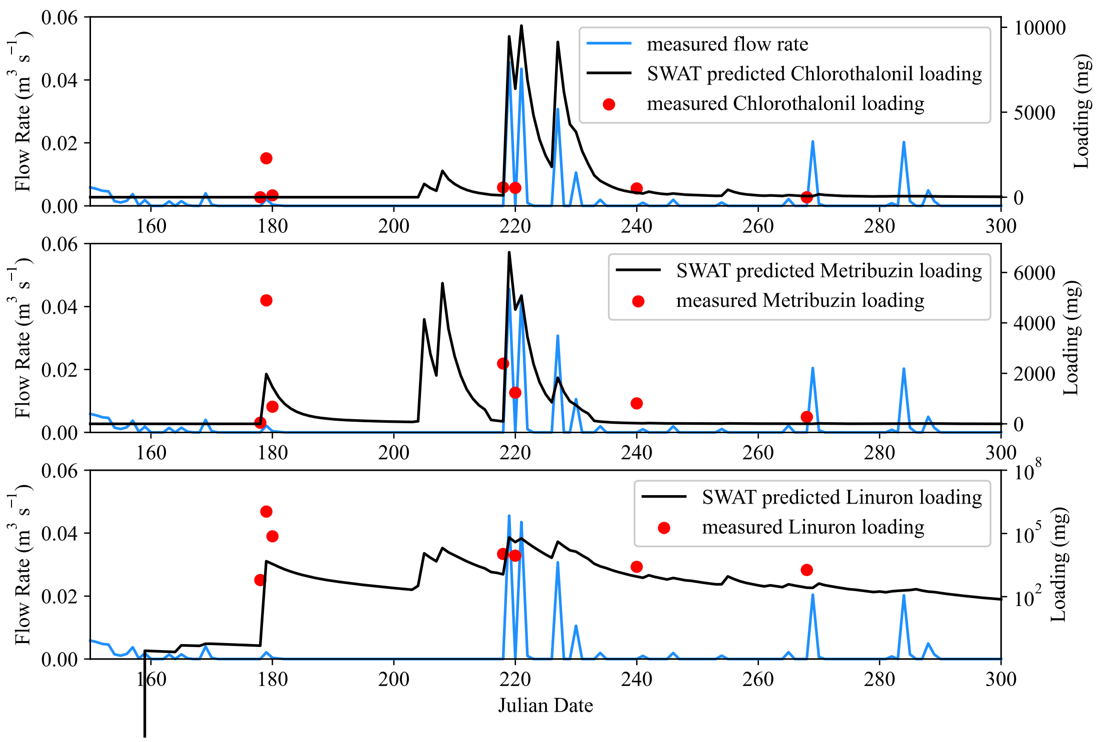


Figure 11. Observed event-based dissolved pesticide loadings and SWAT-predicted dissolved daily pesticide loadings in Sub-watershed 8 for 2018.

### Pesticide concentration in streams

The measured dissolved pesticide concentrations are event-based values and were calculated by using the equation (1) and (2) for each rain event. Although SWAT has the capability to simulate both dissolved and attached concentrations of pesticides, only dissolved phased pesticide concentrations were calculated to make the measured and predicted data comparable. The SWAT predicted pesticide concentrations were calculated with the daily pesticide loading (mg) divided by the total daily discharge ($m^3$). As such, the predicted pesticide concentration reflects daily average concentration.

Good agreement between measured and SWAT-predicted Metribuzin and Linuron concentrations was observed in the BBW in 2006. As for Chlorothalonil, the general pesticide concentration variation trend was followed, and the only exception occurred at day 192 when the simulated Chlorothalonil concentration was greatly underestimated compared with measured data.

In 2008, the simulated Chlorothalonil concentrations did not match well with the measured data, especially between day 210 to 225. The simulated Chlorothalonil concentration was higher than observed ones at day 214 and 215, and lower at day 221. Predicted Linuron and Metribuzin concentrations showed a good agreement with the measured data except for day 174. The simulated concentrations of Metribuzin and Linuron were both underestimated in this rain event.

In 2018, pesticide concentration data were not adequate to observe its seasonal trend since only three rain events were successfully monitored in the BBW. Besides, the predicted pesticide concentrations were significantly larger than measured values for all the three pesticides (Chlorothalonil, Metribuzin and Linuron) at day 220, which showed consistency in pesticide loading variation trend in 2018.

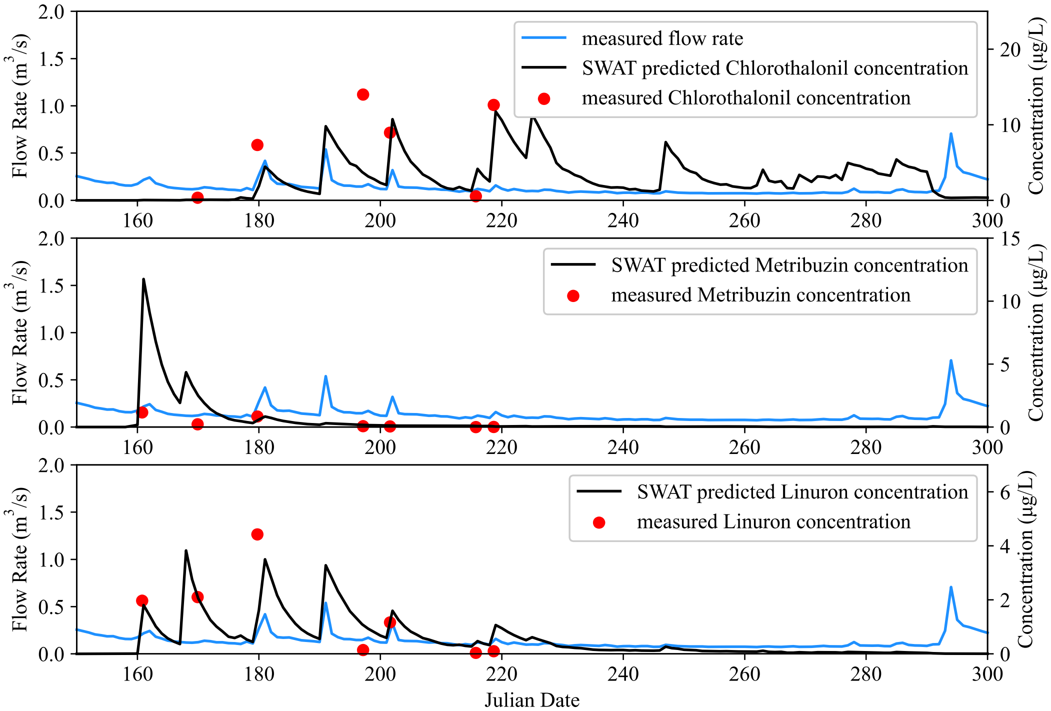


Figure 12. Observed event-based mean pesticide concentrations and SWAT-predicted dissolved daily mean pesticide concentrations in the BBW for 2006.

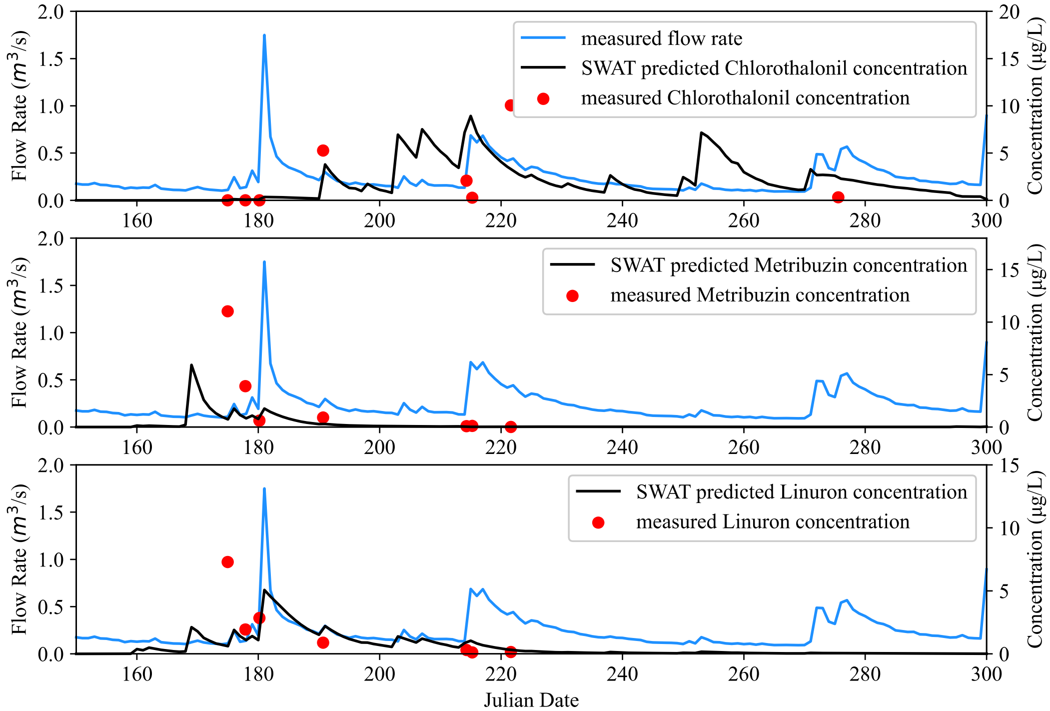


Figure 13. Observed event-based mean pesticide concentrations and SWAT-predicted dissolved daily mean pesticide concentrations in the BBW for 2008.

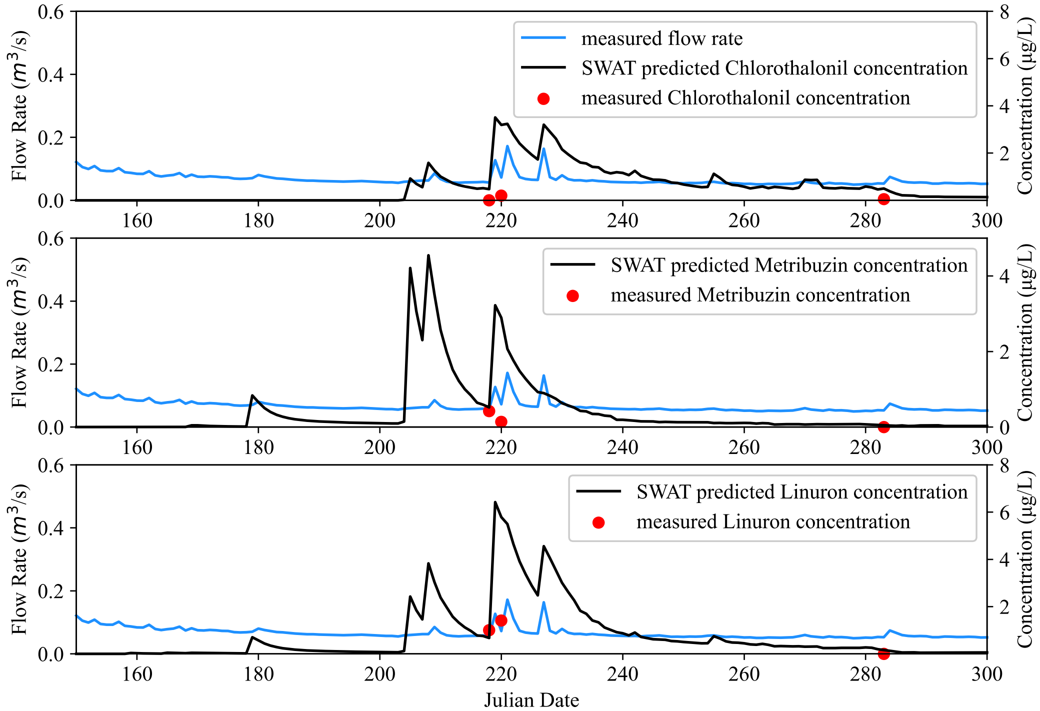


Figure 14. Observed event-based dissolved pesticide concentrations and SWAT-predicted dissolved daily pesticide concentrations in the BBW for 2018.

Sub-watershed 9 monitoring station was not operated in 2018, so Sub-watershed 8 station was selected to continue pesticide monitoring task. Thus, the three graphs below are not strictly comparable because the SWAT model was run for two slightly different watersheds.

In general, there was a good match between observed and simulated pesticide concentrations in Sub-watershed 9 in 2006 for Metribuzin and Linuron. The Chlorothalonil concentrations were greatly underestimated at day 169 and day 190, when the measured concentrations were much higher than predicted ones, up to 200 µg $L^{-1}$ and 189 µg $L^{-1}$ at day 169 and 190, respectively. In the case of Chlorothalonil, the possible reason for the poor result at day 169 may be attributed to wrong model input data. The first model predicted peak loading for Chlorothalonil occurred at day 181, and normally during a rain event, the surface runoff can wash off pesticide residues from soil and foliage into surface runoff (Topaz et al. 2018). Thus, it is almost impossible that with correct application data, the predicted pesticide concentration was almost 200 times lower than measured data after a rain event.

In 2008, the concentrations of Chlorothalonil, Metribuzin and Linuron were all underestimated at day 177. This phenomenon can probably be attributed to the difference between measured and simulated flow rate. There was a spike in measured flow rate at day 177 while no fluctuations shown in SWAT-predicted daily flow rate. The measured flow rate (approximately 0.014 CMS) was threefold higher than the simulated value (approximately 0.004 CMS) at day 177.

The 2018 to 2019 hydrological year was dry, and water level was very low at the Sub-watershed 8 station. Recorded stage height was negative for some samples collected at weir station 8, which means that there was no continuous flow over the V-notch during the sample collection process, and only the pool before the weir was filled with water. Therefore, the data collected from weir station 8 were considered error-prone and were not recommended for quantitative analysis, and it is obvious that some extreme values occurred in measured data. For example, the Linuron concentration at day 180 was greatly underestimated in SWAT model by up to two order of magnitude. And for the same rain event (day 180), the observed Metribuzin and Chlorothalonil concentration were much higher than predicted ones as well. Another possible explanation for these extreme values was that the pesticide properties have changed over the ten-year period. In this study, the pesticide data were compared for 2006, 2008 and 2018, and it is most likely that the pesticide manufacturer improved some physical or chemical properties to increase pesticide efficiencies. Thus, the old SWAT dataset might be outdated, and the pre-calibrated model may not perform well in 2018.

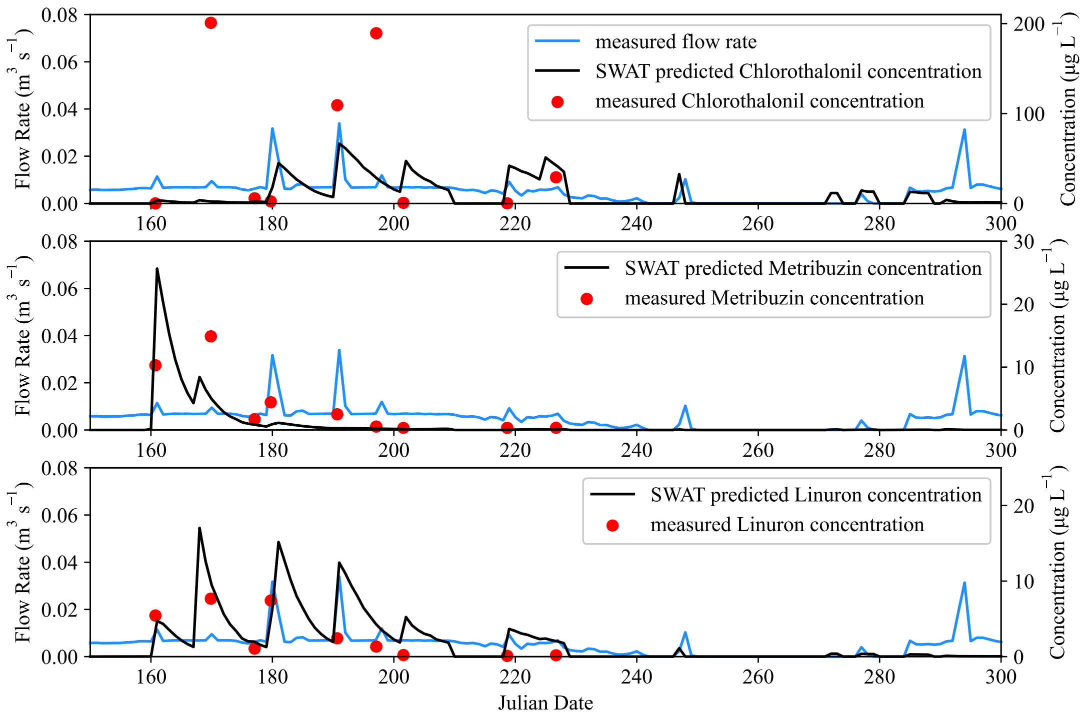


Figure 15. Observed event-based dissolved pesticide concentrations and SWAT-predicted dissolved daily pesticide concentrations in the Sub-watershed 9 for 2006.

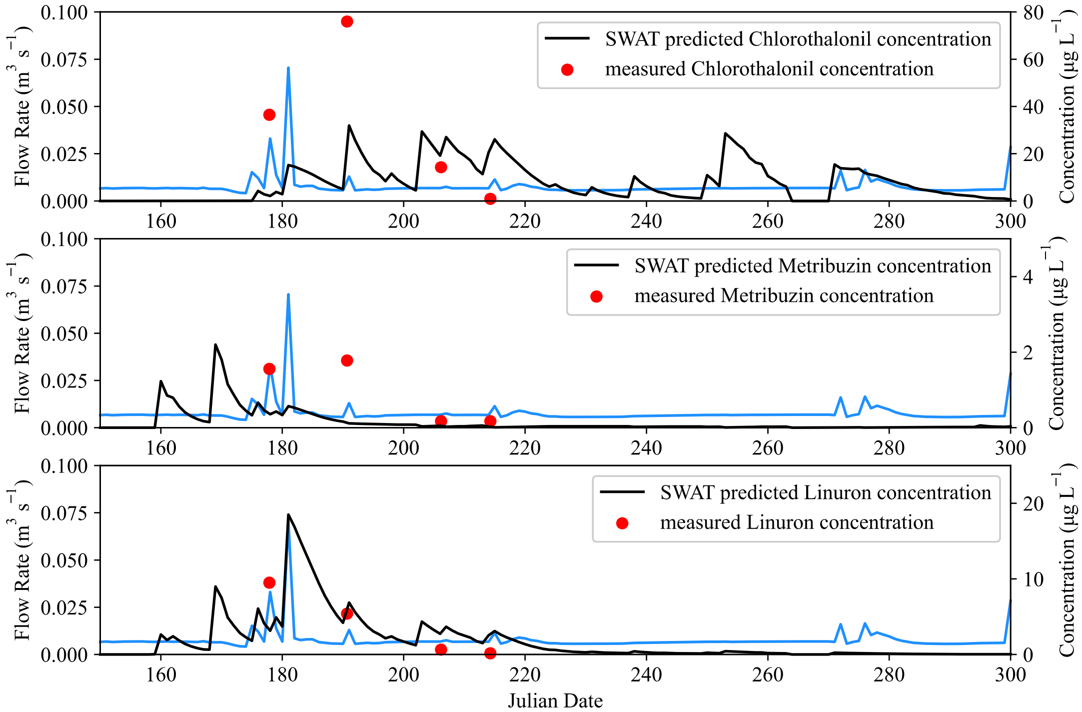


Figure 16. Observed event-based dissolved pesticide concentrations and SWAT-predicted dissolved daily pesticide concentrations in Sub-watershed 9 for 2008.

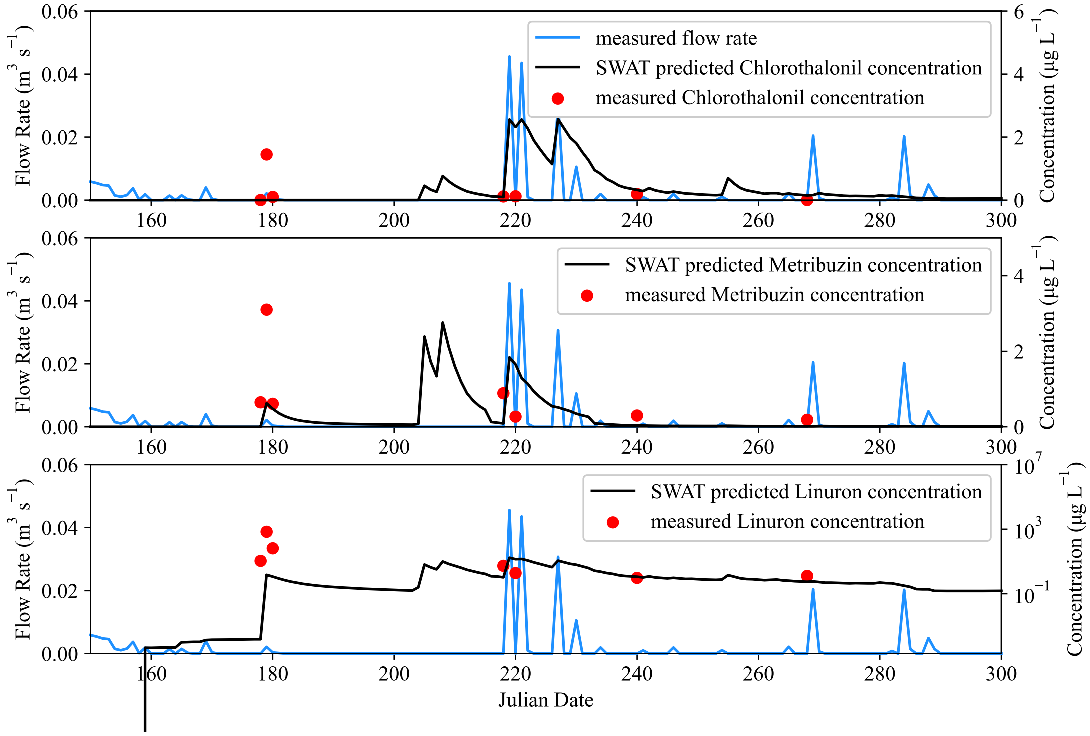


Figure 17. Observed event-based dissolved pesticide concentrations and SWAT-predicted dissolved daily pesticide concentrations in Sub-watershed 8 for 2018.

## Discussion

### Uncertainties of event-based pesticide loading and concentration estimation

Quantification of pesticide concentrations in a rain event plays an important role in water quality assessment and hydrologic model setup (Cha et al. 2010). In reality, although the flow rate can be measured near-continuously, the pesticide concentration data is often derived from discrete sampling method which contains lots of data gaps (Novic et al.

2018). Therefore, it is important to understand the uncertainties associated with pesticide concentration estimation.

### Variations of pesticide concentrations during one rain event

Figure 18**Error! Reference source not found.** shows some typical pesticide concentration distributions on different rain events sampled in 2006, which gives an insight on inter-storm pesticide concentration variability. Flow rate and pesticide concentration were plotted over time to explore their relationships.

Two of the four plots (A and B) show first flush effect, which means the initial storm water received by stream channel is the most polluted (Stenstrom and Kayhanian 2005). It is obvious that in the two graphs, the maximum pesticide concentration occurred earlier than the peak flow rate. Schiff and Sutula (2001) observed similar phenomenon in diazinon in urban southern California watersheds. The occurrence of first flush effect mainly depends on two factors: watershed size and the mobility of pesticide. In large watersheds, the travel time of runoff from various places is quite different. This time lag leads to the mixture of a small amount of pesticide with a significant amount of streamflow, where pesticides are diluted. For pesticides have higher solubility, first flush effect is much more likely to be observed because storm water can move them easily at the beginning of rain event (House and Warwick 1998). Considering this unique phenomenon, it is obvious that if pesticide samples were not collected as quickly as possible to capture the rapid concentration variation, then the total pesticide loading calculated by equation (1) is error-prone to a certain degree. Since the first flush effect is quite common in small-sized watershed (Stenstrom and Kayhanian 2005), the discrepancy between measured and predicted 2008 pesticide loading and concentration (Chlorothalonil, Metribuzin and Linuron) in Sub-watershed 9 may be attributed to it.

In contrast, graph (C) shows a different pesticide concentration distribution pattern. In this case, the Chlorothalonil concentration peaked on the falling limb and then gradually decreased. The maximum flow rate in graph (C) was around 0.4 CMS, which was lower than that in graph (A) and (B) (around 2.5 CMS), indicating that the characteristics of rainfall (amount, intensity and duration) may influence pesticide transport (Leecaster, Schiff, and Tiefenthaler 2002). In other words, pesticides are more prone to wash-off in heavy storm events. The disagreement between measured and predicted 2008 pesticide concentration for the first sampled event in Sub-watershed 9 may also be explained by rainfall property difference. Since daily rainfall intensity data were not available in this study, a built-in storm pattern was used for SWAT simulation. It was reported that runoff and sediment yields were strongly affected by rainfall intensity (Mohamadi and Kavian 2015). Thus, high-intensity rainfall events that yield large quantities of surface runoff over relatively short time periods might result in marked differences between observed and predicted pesticide concentration. This inference can be applied well in the case of rain event at day 178 in Sub-watershed 9 in 2008.

Graph (D) shows that sometimes collected water samples do not adequately represent the original hydrograph, which may result in errors in pesticide concentration estimation. The samples collected in this rain event did not cover the entire hydrograph. In other words, there were some missing periods in the pesticide concentration data while flow rate data were available. Although linear interpolation was applied to treat these data gaps, the missing data may still cause adverse effects on pesticide concentration calculation.

Therefore, it is a challenge for researchers to develop an economic sampling strategy to use as few of samples as possible and still represent the whole hydrograph.

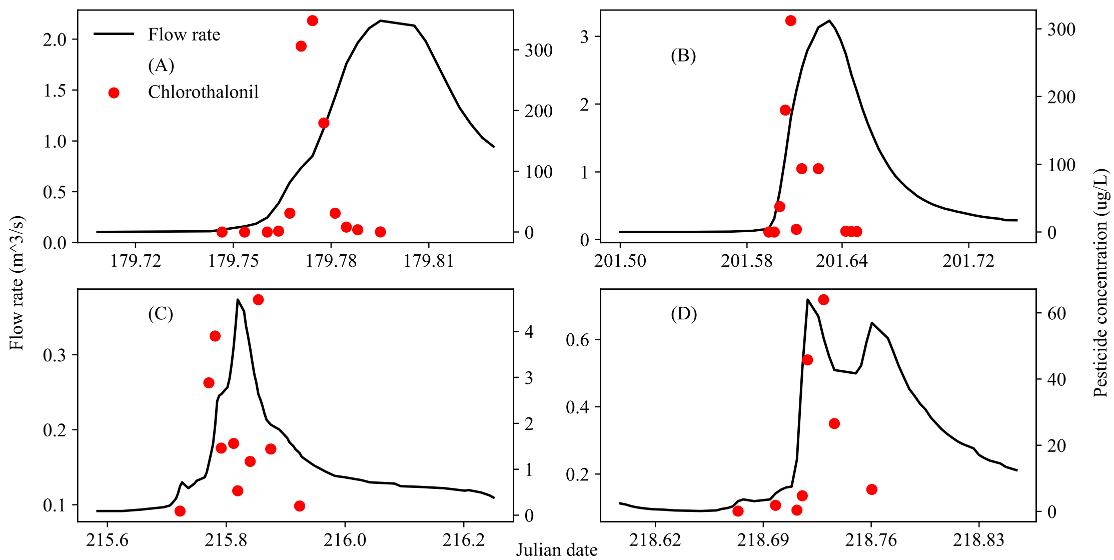


Figure 18. Time–concentration series of Chlorothalonil distribution patterns during different storm events in the BBW in 2006.

**Potential impacts of pesticide properties on pesticide distribution pattern**

Pesticide properties (toxicity, persistence, volatility, solubility and soil adsorption) can affect a pesticide's potential to pollute water. The water solubility of a pesticide determines how easily it goes into solution with water. However, simply being water soluble does not mean that a pesticide will be washed off into surface water because the concentration of pesticide in streams depends on many factors, such as pesticide application method, rainfall intensity and pesticide half-life (Haith and Duffany 2007). Some pesticides must be somewhat soluble in order to work properly. The solubilities for Chlorothalonil, Linuron and Metribuzin are 0.6, 75, 1220 mg/L, respectively. As discussed before, generally, the first flush effect is more likely to occur for those pesticides with large solubility. However, the situation varies from case to case. As shown in Figure 19, the Metribuzin did not show the first flush effect at day 160 (graph A) while the first flush effect occurred at day 179 (graph B) and day 201 (C). Figure 20. showed that there was no obvious first flush effect at day 160 (graph A) and day 215 (graph D) for Linuron. A reasonable explanation for this phenomenon is that the flow rate may have great impacts on pesticide concentration distribution. It is noteworthy that the peak flow rates for Metribuzin and Linuron in graph B and C were both at least four times larger than that of graph A. Namely, the first flush effect can easily occur when soluble pesticides were washed off into surface flow with large quantities of rainfall. Based on this assumption, the distribution pattern for Chlorothalonil (graph A and B) can be well explained. In other words, if the flow rate is large enough with large quantities pesticides being transported into surface water, even the insoluble pesticides can show the first flush effect. Overall, pesticide properties do have effects on in-stream pesticide distribution, but the actual pesticide distribution pattern is results resulting from combined effects of various environmental factors.

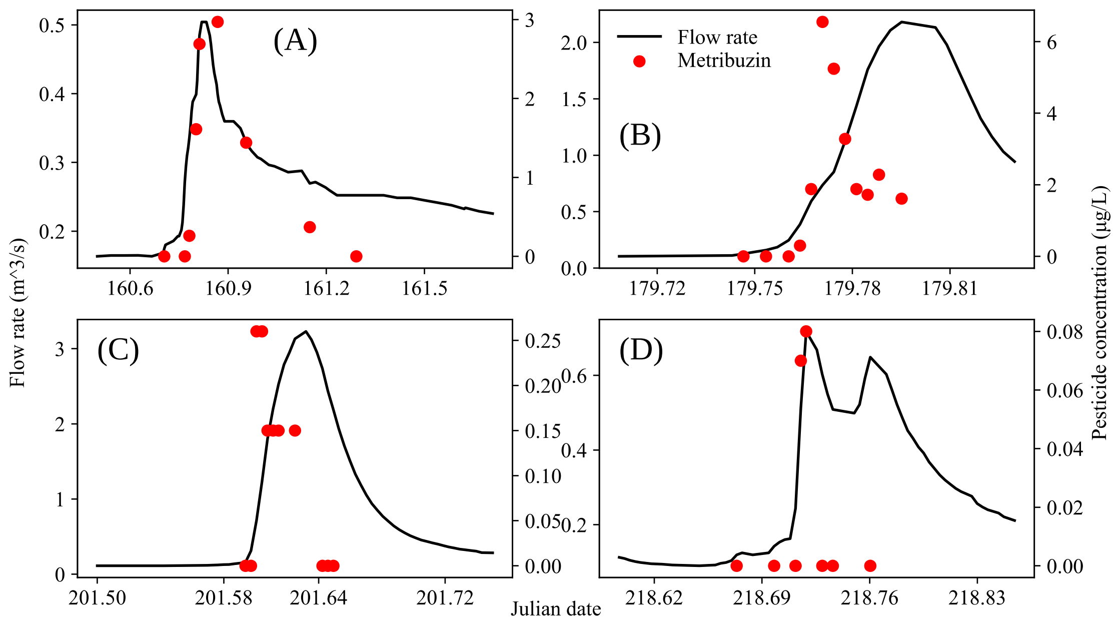


Figure 19. Time–concentration series of Metribuzin distribution patterns during different storm events in the BBW in 2006.

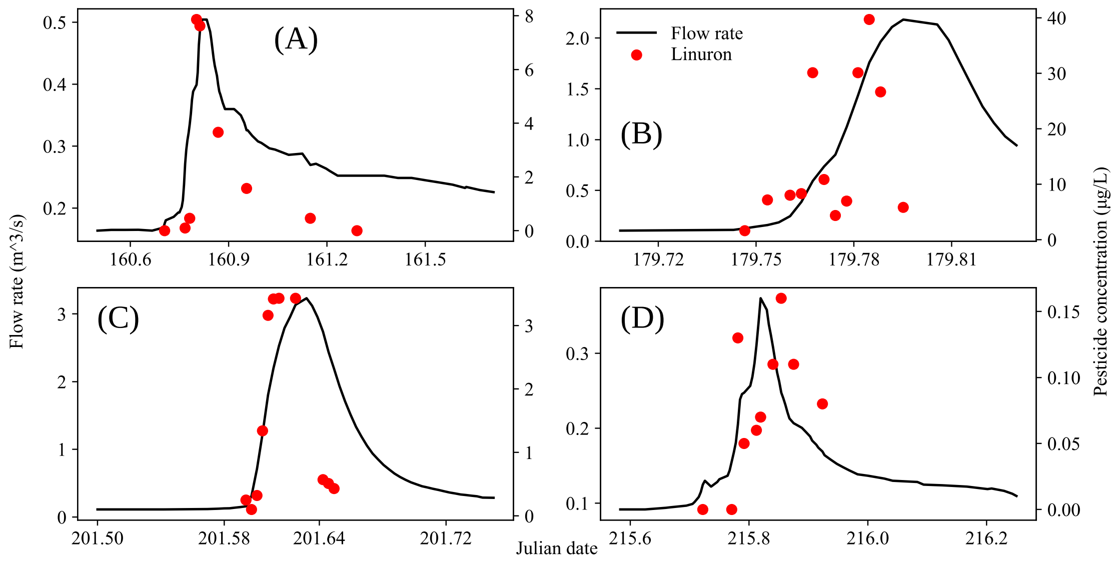


Figure 20. Time–concentration series of Linuron distribution patterns during different storm events in the BBW in 2006.

Overall, the pesticide load and concentration dynamics during a single rain event can be influenced by various factors, such as pesticide properties, rainfall intensity and hydrologic characteristics (Pinto et al. 2010); (Lefrancq et al. 2017a). Unfortunately, it is still not clear that how each controlling factor contributes to the pesticide chemo graph, which may cause uncertainties in load and concentration estimation. Therefore, the reliability of measured pesticide loading and concentration data needs to be taken into account when comparing SWAT-predicted data with observed ones.

**Limitations in pesticide sampling strategy**

Periods of high flow can deliver significant portions of pesticides to streams (Jordan et al. 2012). In this case, the stream receives large quantities of water discharge and a quick rise of water level will trigger the auto-sampler to take samples via the pre-installed pipe. For those small to medium-sized watersheds, since the stage height tends to rise very quickly after rainfall, auto-sampler is unable to respond to the quick change of water levels and some high data points might be missing from sample collections. We used hydrograph-based sampling method for sample collections in the three monitoring sites. However, for Sub-watershed 9 and 8, although the datalogger was set to trigger sample collection at every 5 cm stage height change, the recorded stage height data shows that most samples were taken at every 7 or 8 cm stage height change. In other words, due to technical issues, the current sampling strategy failed to cover the whole hydrograph in some rain events, especially those extreme rain events.

Sampling methods also have great effects on pesticide concentration estimation. In this study, some samples were collected by using the cost-effective composite sampling approach in 2018. The composite samples were made by thoroughly mixing several discrete samples collected during one single rain event, and then the whole composite samples were delivered for laboratory analysis. The composite sampling approach is a powerful option to increase sampling capacity when facing the budget constraint. However, the composite samples represented an average of several pesticide concentration measurements and no information about the concentration variability among the original samples was obtained. Reduced information on the distribution of inner-event pesticide behavior may limit the study of pesticide transport mechanisms and add uncertainties to concentration estimation (Farkas et al. 2014). Another concern about the composite sampling is that subsamples were manually composited to create a new composite sample, which may introduce errors due to operational errors during the combination process. Some extreme pesticide concentration values occurred in 2018 sampling dataset, such as the concentration of Linuron (695 μg $L^{-1}$) at day 179 in Sub-watershed 8, which might be explained by human error in sample collection.

### Limitations in concentration and loading calculation method

While continuous measurement of stream discharge can be achieved for the entire rain event, there were still some missing periods in the pesticide sample collection. Linear interpolation was adopted to treat these missing sampling points. The potential errors caused by this method should be taken into account when compared with the observed data.

### Input data accuracy

It is noteworthy that compared with Metribuzin and Linuron, the variation trends of Chlorothalonil concentration and loading were relatively hard for SWAT model to capture, especially in the middle of growing season. The main reason is Chlorothalonil is a broad-spectrum organochlorine pesticide and was applied 8 times on average in the whole growing season in the BBW and sometimes the application dates on pesticide survey were simply recorded as 8 times, instead of their accurate application dates. In this case, the application dates were evenly assigned throughout the growing season, which can introduce errors to the model. As noted in Cambien (2017) and Boithias et al. (2014), knowing accurate pesticide application dates plays an important role in concentration and loading prediction. Since the impact of pesticide application data on pesticide transport and concentration estimation is not negligible (Watanabe and Takagi 2000) (Malone et al. 2004), inaccurate input data may lead to some unreasonable simulation results as shown in Chlorothalonil modelling results. Considering this limitation, SWAT predictions might be improved if more accurate information on application dates can be obtained from farmers.

### Potential SWAT algorithmic problem

Models are used by scientists to explain and predict the behavior of real objects. However, sometimes the reality is too complex to be perfectly simulated. In this case, a model is a simplified representation of a system that may have slight discrepancies with the real world. Xing et al. (2013) reported that pesticide concentrations analyzed in base-flow detections were generally zero or below detection limits. However, it is obvious that the SWAT-simulated pesticide concentrations usually reached the peak concentration during rain events and then gradually decreased, and the predicted concentration was much higher than detection limits during the whole base-flow period for all the three pesticides (Chlorothalonil, Metribuzin and Linuron). The gradual decrease of predicted pesticide concentration curve was generated in SWAT by using a continuous smooth function, which leads to concentration and loading overestimation in those non-rain events. Therefore, we have enough reasons to doubt whether the SWAT model can be applied for pesticide estimation in non-rainfall days.

## Conclusions and Recommendations

In this study, the SWAT model hydrologic and pesticide routines were assessed for their effectiveness in predicting stream discharge and in-stream pesticide concentrations in the BBW. The hydrologic module was calibrated and validated against the best available data by Qi et al. (2017). The satisfactory statistical results and visual inspection of the flow time series graph indicated that the SWAT hydrologic prediction were reasonable. Pesticide module calibration was conducted for 2006, and validation was conducted for 2008 and 2018. In general, the variation patterns of pesticide loading and concentration were well simulated compared to the measured data though some discrepancies were observed for baseflow monitoring days. Pesticides with high application rate (Chlorothalonil) tended to have a more complex variation pattern and sometimes were hard for the model to simulate. Overall, the simulated result indicated that the model was capable of producing satisfactory predictions of pesticide loading and concentration in small watersheds. Our study has also highlighted the variability of pesticide chemo graph patterns and the extent to which this variability can affect pesticide loading and concentration estimation. The fate of pesticides is a complex process and the mechanism of in-stream pesticide dynamics is still not clear. In the future, by improving pesticide monitoring strategies and model optimization, we can gain a better understanding of how pesticides are transported in runoff and corresponding influence factors during this process.

This study compared the event-based measured pesticide data with SWAT-predicted daily loading and concentration data, and showed that rain event can lead to high fluxes of pesticides exported to the outlet of watersheds. It has been proved that the majority of pesticides exhibited rapid concentration variations during the flood event (Lefrancq et al. 2017b). However, in this study pesticide transport was studied on the scale of daily modelling, and further study needs to be done to better understand the contribution of runoff, interflow and groundwater in pesticide transport process. By using high frequency sampling method, inner-event pesticide concentration data can be obtained. Based on solid measured data, hydrograph separation technique might be a solution for pesticide dynamic hydrological characterisation.

## Reference

A. Leonard, R., W. G. Knisel, and D. A. Still. 1987. "GLEAMS: Groundwater Loading Effects of Agricultural Management Systems." *Transactions of the ASAE* 30(5):1403–18.

Anon. 2013. *Watershed Evaluation of Beneficial Management Practices WEBs Managing Our Land and Protecting Our Water*.

Boithias, Laurie, Sabine Sauvage, Raghavan Srinivasan, Odile Leccia, and José Miguel Sánchez-Pérez. 2014. "Application Date as a Controlling Factor of Pesticide Transfers to Surface Water during Runoff Events." *Catena* 119:97–103.

Cambien, Naomi. 2017. "Evaluation of the Soil and Water Assessment Tool ( Swat ) To Simulate Pesticide Dynamics in the Guayas River Basin ( Ecuador )." 2016–17.

Cha, Yoon Kyung, Craig A. Stow, Kenneth H. Reckhow, Carlo DeMarchi, and Thomas H. Johengen. 2010. "Phosphorus Load Estimation in the Saginaw River, MI Using a Bayesian Hierarchical/Multilevel Model." *Water Research* 44(10):3270–82.

D. Wauchope, R., and R. A. Leonard. 1980. *Maximum Pesticide Concentrations in Agricultural Runoff: A Semiempirical Prediction Formula1*. Vol. 9.

Farkas, Zsuzsa, Zsuzsanna Horváth, Kata Kerekes, Árpád Ambrus, András Hámos, and Mária Szeitzné Szabó. 2014. "Estimation of Sampling Uncertainty for Pesticide Residues in Root Vegetable Crops." *Journal of Environmental Science and Health - Part B Pesticides, Food Contaminants, and Agricultural Wastes* 49(1):1–14.

Haith, D., and M. Duffany. 2007. "Pesticide Runoff Loads from Lawns and Golf Courses." *Journal of Environmental Engineering* 133(4):435–46.

House, W. A., and M. S. Warwick. 1998. "Hysteresis of the Solute Concentration/Discharge Relationship in Rivers during Storms." *Water Research* 32(8):2279–90.

Jordan, P., A. R. Melland, P. E. Mellander, G. Shortle, and D. Wall. 2012. "The Seasonality of Phosphorus Transfers from Land to Water: Implications for Trophic Impacts and Policy Evaluation." *Science of the Total Environment* 434:101–9.

Kannan, Narayanan, Sue M. White, Fred Worrall, and Mick J. Whelan. 2006. "Pesticide Modelling for a Small Catchment Using SWAT-2000." *Journal of Environmental Science and Health - Part B Pesticides, Food Contaminants, and Agricultural Wastes* 41(7):1049–70.

Leecaster, Molly K., Kenneth Schiff, and Liesl L. Tiefenthaler. 2002. "Assessment of Efficient Sampling Designs for Urban Stormwater Monitoring." *Water Research* 36(6):1556–64.

Lefrancq, Marie, Alain Jadas-Hécart, Isabelle La Jeunesse, David Landry, and Sylvain Payraudeau. 2017a. "High Frequency Monitoring of Pesticides in Runoff Water to Improve Understanding of Their Transport and Environmental Impacts." *Science of* *the Total Environment* 587–588:75–86.

Lefrancq, Marie, Alain Jadas-Hécart, Isabelle La Jeunesse, David Landry, and Sylvain Payraudeau. 2017b. "High Frequency Monitoring of Pesticides in Runoff Water to Improve Understanding of Their Transport and Environmental Impacts." *Science of the Total Environment* 587–588:75–86.

Malone, Robert W., Lajpat R. Ahuja, Liwang Ma, R. Don Wauchope, Qingli Ma, and Kenneth W. Rojas. 2004. "Application of the Root Zone Water Quality Model (RZWQM), to Pesticide Fate and Transport: An Overview." *Pest Management Science* 60(3):205–21.

Mohamadi, Mohamad Ayob, and Ataollah Kavian. 2015. "Effects of Rainfall Patterns on Runoff and Soil Erosion in Field Plots." *International Soil and Water Conservation Research* 3(4):273–81.

Novic, Andrew Joseph, Christoph Ort, Dominique S. O'Brien, Stephen E. Lewis, Aaron M. Davis, and Jochen F. Mueller. 2018. "Understanding the Uncertainty of Estimating Herbicide and Nutrient Mass Loads in a Flood Event with Guidance on Estimator Selection." *Water Research* 132:99–110.

Pinto, Alicio A., Wulf Amelung, Wolfgang Zech, Carolina J. da Silva, Volker Laabs, and Matthias Wantzen. 2010. "Pesticides in Surface Water, Sediment, and Rainfall of the Northeastern Pantanal Basin, Brazil." *Journal of Environment Quality* 31(5):1636.

Qi, Junyu, Sheng Li, Qiang Li, Zisheng Xing, Charles P. A. Bourque, and Fan Rui Meng. 2016. "A New Soil-Temperature Module for SWAT Application in Regions with Seasonal Snow Cover." *Journal of Hydrology* 538(June):863–77.

Qi, Junyu, Sheng Li, Qi Yang, Zisheng Xing, and Fan Rui Meng. 2017. "SWAT Setup with Long-Term Detailed Landuse and Management Records and Modification for a Micro-Watershed Influenced by Freeze-Thaw Cycles." *Water Resources Management* 31(12):3953–74.

Schiff, Kenneth C., and Martha Sutula. 2001. "Organphosphorous Pesticides in Stormwater Runoff from Southern California." *Annual Report. Southern California Coastal Water Research Project [Annu. Rep. South. Calif. Coast. Water. Res. Proj.]. No.* 23(8):1815–21.

Scott, Robert, Scott W. Woods, and Hans R. Zuuring. 2008. "Hydrologic Calibration and Validation of Swat in A." *Journal Of The American Water Resources Association* 44(6):1411–30.

Standards, Environmental Risk-based, and Pesticide Use. 2009. *National Agri-Environmental Standards Initiative ( NAESI ) Synthesis Report No . 7 Environmental Risk-Based Standards for Pesticide Use in Canada.*

Stenstrom, MK, and Masoud Kayhanian. 2005. "First Flush Phenomenon Characterization. CTSW-RT-05-73-02.6." (August):69.

Topaz, Tom, Roey Egozi, Gil Eshel, and Benny Chefetz. 2018. "Pesticide Load Dynamics during Stormwater Flow Events in Mediterranean Coastal Streams: Alexander

Stream Case Study.” *Science of the Total Environment* 625:168–77.

Watanabe, H., and K. Takagi. 2000. “A Simulation Model for Predicting Pesticide Concentrations in Paddy Water and Surface Soil Ii. Model Validation and Application.” *Environmental Technology (United Kingdom)* 21(12):1393–1404.

Williams, J. R. 1990. “The Erosion-Productivity Impact Calculator (EPIC) Model: A Case History.” *Philosophical Transactions of the Royal Society B: Biological Sciences* 329(1255):421–28.

Xing, Zisheng, Lien Chow, Herb Rees, Fanrui Meng, Sheng Li, Bill Ernst, Glenn Benoy, Tianshan Zha, and L. Mark Hewitt. 2013. “Influences of Sampling Methodologies on Pesticide-Residue Detection in Stream Water.” *Archives of Environmental Contamination and Toxicology* 64(2):208–18.

# Appendixes

### Appendix A. Example of raw hydrological and pesticide sampling dataset

The hydrology and pesticide data in this study were obtained by using automatic water samplers and dataloggers to monitor water level changes and trigger sampling process. Table 5. is a supplementary table that shows how autosampler was set to collect pesticide samples based on changing water levels. The first two columns show the water monitoring system recorded real time (Julian date) and corresponding recorded flow rates (CMS), respectively. The third column shows the time interval between two consecutive recorded flow rates, where we can see that the time interval was nearly one hour when there was no precipitation and it reduced to five minutes or so when flow rates start increasing during a rain event. As stated before, flow rates were recorded at a five-minute interval when water level change is more than 2 cm. And autosampler was set to be triggered by a fixed water level change, which depends on specific watersheds. The potential problem of this sampling method is that autosampler may fail in capturing the peak pesticide concentration during a heavy rain event when the water level changes rapidly during a relatively short period since the minimum sampling time interval is five minutes. Besides, these is a delay between the timing of pesticide collections and recorded flow rate since drawing water from the river takes time.

Table 5. An example of raw hydrological and pesticide sampling data for the BBW in 2006.

| Julian date | Flow rate (CMS) | Time interval between recorded flow rates (minutes) | Measured Pesticide Concentration (ug/L) | | |
|---|---|---|---|---|---|
| | | | Chlorothalonil | Metribuzin | Linuron |
| 179.583 | 0.103 | 59.990 | | | |
| 179.625 | 0.103 | 60.005 | | | |
| 179.667 | 0.103 | 60.005 | | | |
| 179.708 | 0.103 | 59.990 | | | |
| 179.743 | 0.111 | 50.011 | | | |
| 179.747 | 0.125 | 4.997 | 0 | 0 | 1.62 |
| 179.750 | 0.143 | 4.997 | | | |
| 179.753 | 0.158 | 4.997 | 0 | 0 | 7.16 |
| 179.757 | 0.185 | 4.997 | | | |
| 179.760 | 0.246 | 5.011 | 0 | 0 | 8.02 |
| 179.764 | 0.387 | 4.997 | 1.62 | 0.3 | 8.3 |
| 179.767 | 0.592 | 4.997 | 30.94 | 1.88 | 30.1 |
| 179.771 | 0.735 | 4.997 | 306 | 6.55 | 10.86 |
| 179.774 | 0.852 | 5.011 | 348 | 5.24 | 4.35 |
| 179.778 | 1.124 | 4.997 | 179.5 | 3.28 | 6.95 |
| 179.781 | 1.434 | 4.997 | 30.94 | 1.88 | 30.1 |
| 179.785 | 1.760 | 4.997 | 8.08 | 1.72 | 39.7 |
| 179.788 | 1.965 | 4.997 | 3.74 | 2.28 | 26.63 |
| 179.792 | 2.109 | 5.011 | | | |
| 179.795 | 2.182 | 4.997 | 0.13 | 1.61 | 5.83 |

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