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Pesticide transport simulation in a tropical catchment by SWAT

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ABSTRACT

The application of agrochemicals in Southeast Asia is increasing in rate, variety and toxicity with alarming speed. Understanding the behavior of these different contaminants within the environment require comprehensive monitoring programs as well as accurate simulations with hydrological models. We used the SWAT hydrological model to simulate the fate of three different pesticides, one of each usage type (herbicide, fungicide and insecticide) in a mountainous catchment in Northern Thailand. Three key parameters were identified: the sorption coefficient, the decay coefficient and the coefficient controlling pesticide percolation. We yielded satisfactory results simulating pesticide load dynamics during the calibration period (NSE: 0.92–0.67); the results during the validation period were also acceptable (NSE: 0.61–0.28). The results of this study are an important step in understanding the modeling behavior of these pesticides in SWAT and will help to identify thresholds of worst-case scenarios in order to assess the risk for the environment.

1. Introduction

The mountainous regions of Southeast Asia are undergoing drastic changes in land-use and land-management strategies, including changes in farming practices (Fox and Vogler, 2005; Ziegler et al., 2009). In northern Thailand, for example, market demands have driven intensification in crop production, including the introduction of new, high-value crops (Schipmann and Qaim, 2011; Schreinemachers et al., 2011). As many of these crops are targeted for sale in large, competitive local and regional markets, great efforts are afforded to limit damage from insects, disease, and climatic elements. It is estimated that crop damage/loss by pests and disease would be 50% if agrochemicals were not applied (Oerke and Dehne, 2004). Currently, Thailand ranks third out of 15 Asian countries in mass of pesticides per unit area applied each year (Walter-Echols and Yongfan, 2005). As pesticides pose a risk to human health, it is important to understand how they move through the environment via surface runoff, preferential transport, or vertical leaching (Kruawal et al., 2005; Panuwet et al., 2012).

Losses of pesticides to the environment depend greatly on transport pathways and the physico-chemical properties of the compounds (Duffner et al., 2012; Sangchan et al., 2012). Many hydrological models have been developed that facilitate modeling pesticide movement from sources into catchment surface and groundwater systems (Gevaert et al., 2008). Hydrological models are usually applied to predict runoff within a catchment and to assess water resources management practices (Singh and Frevert, 2006). Not all models used for these assessments were developed specifically for simulating agrochemical transport at all appropriate scales of interest. For example, some models simulate pesticide fate only at the scale of individual fields, while others allow basin-wide simulations. Common field-scale models are the Pesticide Root Zone Model (PRZM, Carsel et al., 1985) or GLEAMS (Groundwater Loading Effects of Agricultural Management Systems, Leonard et al., 1987).

Borah and Bera (2004) presented a summary of several hydrological models at the watershed scale with regard to their strengths and restrictions in terms of pesticide transport modeling. AnnAGNPS (Annualized Agricultural Nonpoint Source Model, Bingner et al., 1997), the Hydrology Simulation Program-FORTRAN (HSPF, Johanson and Kliewer, 1982), and the Soil and Water Assessment Tool (SWAT, Arnold et al., 2011) have been successfully applied to simulate pesticide transport at the catchment scale. Of these models, AnnAGNPS is believed to be a good predictor of

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effects of management practices on watershed scales. HSPF was highlighted for its strength in studying the impact of urbanization, whereas SWAT has been recommended for predominantly agricultural watersheds (Borah and Bera, 2004).

Our study focuses on improving the implementation of the popular SWAT model for studying pesticide fate in agricultural catchments in northern Thailand. Use of the SWAT model is well documented and it is increasingly being used to simulate pesticide transport (Gassman et al., 2007; Holvoet et al., 2008). The processes implemented in SWAT to simulate pesticide transport are largely controlled by specific physicochemical parameters such as sorption coefficient, half-life time, or percolation coefficients (Neitsch et al., 2011). A large physico-chemical parameter database, incorporated in the recent SWAT version, enables the user to simulate the movement of many common compounds at the catchment scale (Arnold et al., 1998). A further advantage of SWAT is the opportunity to include specific land-management operations and crop rotations.

SWAT has been successfully applied for pesticide simulations in temperate regions. For example, Larose et al. (2007) effectively used SWAT to study atrazine in the Cedar Creek Watershed within the St. Joseph River Basin in northeastern Indiana (USA). Catchment-scale simulations reached Nash-Sutcliffe efficiency (NSE) values of 0.43–0.59, and the model satisfactorily captured the dynamics of stream flow and atrazine concentrations in the relatively large (707 km^2) agricultural catchment. Simulations on the transport pattern of isoxaflutole became acceptable after careful model parameterization (Ramanarayanan et al., 2005).

In contrast, Boithias et al. (2011) did not reach the same conclusions for the Save river in south-western France. Trifluralin loads were underestimated or overestimated during a flood, and the coefficient of determination (R^2) between monitored and simulated loads was only 0.38. Similarly, unsatisfactory results were obtained by Parker et al. (2007) in simulations of metolachlor, atrazine, and trifluralin in the Sugar Creek Watershed, Indiana. Trifluralin concentrations were predicted with R^2 values between 0.02 and 0.51. For atrazine, R^2 values ranged between 0.21 and 0.41. metolachlor simulations had R^2 ranging from 0.28 to 0.41.

Luo and Zhang (2009) presented results of a SWAT simulation of the transport of chlorpyrifos and diazinon in a watershed in California. They reached NSEs around 0.55, with variability existing for rainfall periods versus irrigation periods. Ficklin et al. (2012), simulating the transport of chlorpyrifos and diazinon in another large Californian agricultural watershed (Sacramento River watershed 23,300 km^2), reported that the loads of both compounds were only moderately determined by streamflow (chlorpyrifos: $R^2 = 0.44$; diazinon: $R^2 = 0.23$). In recent times, Ahmadi et al. (2013) simulated atrazine loads of Eagle Creek in Indiana, USA, with NSEs between 0.14 and 0.52.

In the past, the SWAT model has been calibrated mostly using the Parasol calibration tool (van Griensven and Meixner, 2007), which is a built-in routine of SWAT. In the Parasol tool within SWAT, most parameters directly related to the fate and transport of pesticides are not selectable and therefore not part of the autocalibration. The same is true for the built-in sensitivity analysis tool of SWAT. Thus, calibration of these parameters in prior studies has been performed almost exclusively manually (Ahmadi et al., 2013; Ramanarayanan et al., 2005; Boithias et al., 2011). Alternatively, default values have often been used (e.g. Luo and Zhang, 2009; Zhang and Zhang, 2011). Only recently, Ficklin et al. (2012) presented an automatic calibration of some of the pesticide-related parameters in SWAT using the SUFI-2 method (Abbaspour et al., 2004).

In this study, we apply a new Monte-Carlo-based calibration method, ANSELM, with SWAT to study the transport of three pesticides in a tropical catchment in northern Thailand. We compare modeled daily stream concentrations, loads and applications with measured data. In the modeling process, we perform a Latin-hypercube (LH) sensitivity analysis of all pesticide-related parameters. All these parameters are integrated in the calibration, together with the time of pesticide application as an additional parameter. After model testing, we perform an uncertainty analysis. In addition to the goal of understanding the dynamics of pesticide movement in the catchment, which is rapidly undergoing agricultural changes, we also sought to develop improved methods for such simulations using SWAT, particularly for tropical environments.

2. Material &methods

2.1. Study site

The Mae Sa catchment (18° 54″ N, 98° 54″ E), located 35 km northwest of Chiang Mai in northern Thailand, has a total area of about 77 km^2. In 2006, about 24% of the catchment area was under agricultural use, whereas much of the remaining area was covered by deciduous and evergreen forest characterized by various degrees of disturbance. The catchment spreads over elevations ranging from 325 to 1540 m a.s.l. Many hillslopes are steeper than 100%. The main soil types are Acrisols and Cambisols (FAO, 1998; Schuler, 2008). The underlying geology includes granite and gneiss along with pockets of freshwater limestone and marble. Tropical climatic conditions are dominant, with a mean air temperature of 21 °C and a total annual rainfall of 1250 mm. The rainy season typically begins in May and ends in late October, with the dry season extending from November to April. Typical crops now grown in the Mae Sa catchment are bell pepper, litchi, chayote, cabbage and flowers (Schreinemachers et al., 2011). Most crops are grown in the rainy season. Those grown in the dry season are irrigated. Many farmers in the study area frequently shift from one crop to another between different years (Schreinemachers and Sirijinda, 2008). Among the different categories of pesticides, insecticides were used most frequently (87%), followed by fungicides (68%) and herbicides (29%) (Schreinemachers et al., 2011). Pesticides are applied manually with hand-spraying devices.

2.2. Stream flow and pesticide monitoring

From January 2008 to December 2010 we operated two weather stations (Thies GmbH, Germany; UIT GmbH, Germany) equipped with sensors for monitoring air temperature, solar radiation, relative humidity, wind speed and rainfall. Rainfall data were recorded by 12 automatic tipping bucket gauges (Fischer GmbH, Germany), which were evenly distributed throughout the watershed (Fig. 1). At the main catchment outlet, an automatic water sampler (6712 Portable sampler) coupled with an ultrasonic water level sensor (710 Ultrasonic module, Teledyne ISCO Inc., USA) was installed to collect water samples and to measure stream flow at 10-min intervals. A stage–discharge relation curve was derived by a series of calibration measurements using an acoustic digital current meter (OTT ADC GmbH, Germany) across a wide range of discharges. Water samples were taken discharge-proportionally on a daily basis. In total, 82 and 89 samples were collected in 2008 and 2009, respectively.

Water samples were analyzed for one herbicide, one fungicide and five insecticides (reported by Sangchan et al., 2012). For our modeling study, we selected one pesticide of each usage group: Atrazine (herbicide), chlorothalonil (fungicide) and endosulfan (insecticide). Key physico-chemical properties of these pesticides are presented in Table 1. Water samples were filtered through glass fiber filters (GF/F, 0.7 μm, Whatman Inc., USA). Pesticides were extracted from water samples by solid phase extraction (SPE) (Supelclean™ Envi-carb, Supelco, Germany). Chlorothalonil and endosulfan were analyzed by a gas chromatograph-micro electron capture detector (GC-μECD). Atrazine was analyzed by a gas chromatograph-nitrogen phosphorus detector (GC-NPD). The selected samples with outstanding high peak concentrations were confirmed by a gas chromatograph–mass spectrometer (GC–MS). Limit of detection, recoveries and relative standard deviation (RSD) of the monitored pesticides are shown in Table 2. Pesticide loads in the river were calculated by multiplying measured average daily pesticide concentrations by the corresponding mean daily discharge. Additional information on the sampling and analyzing procedure is reported in Sangchan et al. (2013).

2.3. Modeling

SWAT is a semi-distributed, watershed-scale model that operates at a daily time step. The model requires input data on climate, topography, soil and land use. The basic entities of SWAT are hydrological response units (HRUs). Apart from simulating surface and subsurface hydrological processes, SWAT provides sub-models to simulate different management operations and pesticide fate and transport (Neitsch et al., 2011). SWAT, however, does not simulate stress on plants due to pests or stress relief following pesticide application. Thus, the effect of pesticides on plants is not

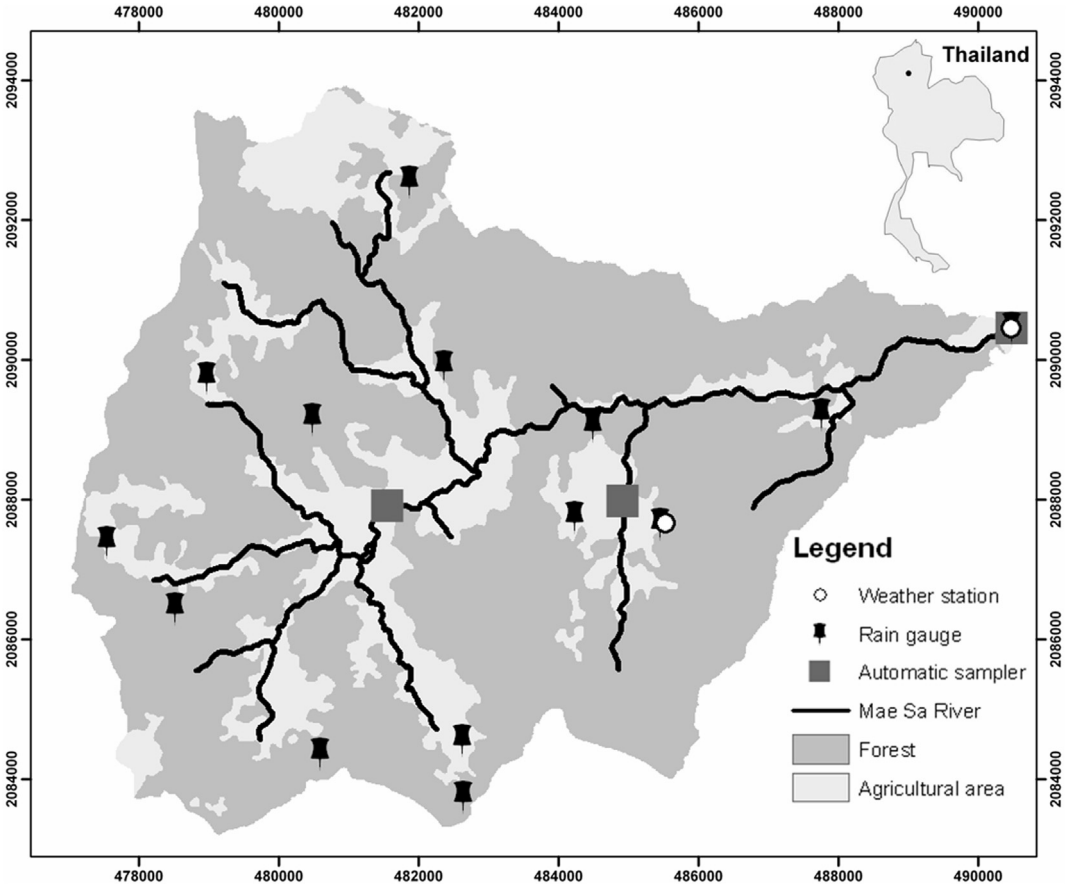


Fig. 1. The 77-km^2 Mae Sa catchment in northern Thailand with locations of monitoring devices (altered after Sangchan et al., 2013).

simulated directly. Nonetheless, the fate and transport of pesticides within a catchment following application can be simulated via process-based equations adopted from the GLEAMS model (Leonard et al., 1987). Briefly, pesticides are transported by water and sediment in surface runoff and by soil water leaching through different soil layers down to a shallow aquifer. Furthermore, pesticides are routed throughout the stream by flowing water and when sorbed to suspended particles. The key processes implemented in SWAT are sorption (linear approach), degradation (first order approach), percolation and wash-off.

As a first step, we set up SWAT to simulate only the discharge dynamics of the Mae Sa catchment. Here, the catchment was divided into five sub-basins. The sub-basins were further divided into 111 HRUs, defined by land use, soil type and slope. Calibration and validation of the model to the observed discharge of the watershed were performed by means of the recently developed ANSELM tool (Bannwarth et al., under revision). Briefly, ANSELM is a Monte-Carlo-based calibration approach that searches within pre-defined ranges using a triangular search strategy around a predefined peak value. It uses the Nash-Sutcliffe modeling efficiency (NSE; Nash and Sutcliffe, 1970) for evaluating the model performance during calibration. Any SWAT input parameter can be calibrated and the calibration of all parameters is simultaneously.

After determining the parameter set with the highest discharge simulation performance, we integrated pesticide applications into the model. We derived pesticide application rates from data supplied by Schreinemachers (pers. comm.) (Table 3). Since the survey data did not include spatial information, we divided the total applied amount of pesticide by the total agricultural area to estimate the application rate in g/ha. After calibration pre-tests designed to reduce simulation time and uncertainties in the calibration, the maximum number of pesticide applications was restricted to five. For each of these application events, the application time and amount was calibrated independently. The starting values of the physico-chemical parameters of the pesticides (Table 3) were set according to published data (e.g., Tomlin, 2003; The Footprint pesticide database, 2013). The pesticide application efficiency parameter artificially reduces the amount of the applied pesticide mass per hectare. As total pesticide application within the catchment was of interest, we kept the application efficiency to unity. The different pesticides were simulated separately because SWAT allows only one pesticide to be routed at a time.

During calibration of pesticide dynamics, those parameters sensitive to discharge were fixed to the values gained from the optimal run in the hydrological optimization. Because parameters exclusively related to pesticides cannot be selected by the built-in sensitivity analysis tool of SWAT, we developed and implemented a Latin-hypercube (LH) analysis following the approach of van Griensven et al. (2006). That approach uses 100 intervals to evaluate the sensitivity of ten parameters (Table 3). Criteria for the sensitivity were the mean simulated pesticide load per day, the maximum simulated pesticide load, and the NSE value of the simulated time series.

The overall relative sensitivity of each parameter was calculated in multiple steps. First, after calculating the separate sensitivities of each parameter in each interval, the mean sensitivities in all intervals for each parameter were calculated. These sensitivities were then normalized by the parameter with the highest sensitivity for each criterion. Lastly, the mean of the sensitivities for all three criteria was taken as an overall relative sensitivity. Minor changes in the application time, which is needed for LH-sensitivity analysis data, were not an input to the model. This is because SWAT runs on a daily basis. Therefore, application time and frequency were not included in the sensitivity analysis.

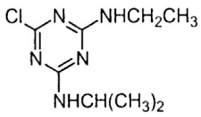
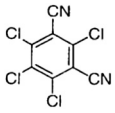
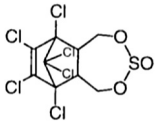
We used the ANSELM approach to calibrate all parameters used in the sensitivity analysis, including the application time. This study shows an automatic calibration approach for the full range of the physico-chemical pesticide parameters of SWAT together with the temporal variability of the application. We used measurements from 2008 to 2010 for calibration and model testing, respectively (Sangchan et al., 2013). Model uncertainties were calculated by means of the generalized likelihood uncertainty estimation (GLUE, Beven and Binley, 1992).

3. Results

3.1. Sensitivity analysis

The results of the LH-sensitivity analysis performed for 10 model parameters using 100 intervals are summarized in Table 4. The sensitivity ranking of the parameters was different for the three pesticides, although some parameters were more dominant than others. The percolation parameter was found to be one of the key

Table 1
Key physico-chemical properties of the selected pesticides used in this study (Tomlin (2003) and The Footprint Pesticides Properties Database (2012)).

Pesticide (common name)	Atrazine	Chlorothalonil	Endosulfan
Usage type	Herbicide	Fungicide	Insecticide
Structure formula			
Substance group	Triazine	Chloronitrile	Organochlorine
Sorption: K_{OC} (linear)	100 ml/g	850 ml/g	11,500 ml/g
Solubility in water (20 °C)	35 mg/l	0.81 mg/l	0.32 mg/l
Soil degradation (aerobic, DT50, lab at 20 °C)	66 days	15.7 days	39 days
Recommended application rate	≤1.5 kg/ha	1–2.5 kg/ha	0.8–2.5 l/ha
WHO classification	III	U	II

parameters. For atrazine, this parameter was the most sensitive, for chlorothalonil it ranked second, and for endosulfan third. Other parameters showed specific sensitivities with respect to each pesticide. The parameter SKOC, for example, demonstrated different sensitivities because of its role in steering the sorption behavior of a particular pesticide – and therefore it was sensitive with atrazine and with chlorothalonil, but not endosulfan. A different picture emerged with HLIFE_S, the half-life time in soil. This parameter was sensitive when simulating the transport of endosulfan and chlorothalonil, but not atrazine (7th most sensitive parameter).

The sensitivity analysis revealed that the parameter application times and rates were important leverage parameters for all three pesticides considered. In the case of each pesticide, one of the five application rate parameters was ranked within the top two parameters with regard to sensitivity.

In the case of endosulfan, only two parameters were identified with a relative sensitivity of more than 0.5. For chlorothalonil, five parameters had high sensitivity. With atrazine, only three parameters showed low sensitivity—and these were for application amounts. The wash-off fraction was marginally important for atrazine and endosulfan, and of low sensitivity for chlorothalonil. The parameter triggering degradation time on the foliage HLIFE_F was minimally important for chlorothalonil and endosulfan and moderately important for atrazine. In general, no parameter showed the same importance level in all three pesticides.

Table 2
Pesticide limit of detection (LOD) and percentage of recovery with relative standard deviation (after Sangchan et al., 2013).

Pesticide	LOD (ng/L)	Recovery (%)
Chlorothalonil	1	58 ± 27
Atrazine	2	113 ± 7
Endosulfan-a	0.1	91 ± 9
Endosulfan-b	0.1	101 ± 7

3.2. Pesticide modeling

3.2.1. Pesticide application

Yearly application rates, calculated from the raw data of Schreinemachers et al. (2011; pers. comm.), were compared with simulated application rates (Table 5). In 2006, no farmer had indicated in the survey to use atrazine (Schreinemachers and Sirijinda, 2008). Application rates of the other two pesticides differed greatly between 2006 and 2010. Regarding chlorothalonil, the application rate in 2006 (2600 g/ha) was almost three-fold higher than in 2010 (1018 g/ha). For endosulfan, the surveyed application rate in 2006 was only 3 g/ha, much lower than 43 g/ha in 2010. As the application rates from the survey may not truly reflect reality, application rates were also subjected to calibration. The simulated application rates of atrazine and chlorothalonil were lower than the survey values. The calibrated application amount of atrazine was almost half that determined in the 2010 survey. For chlorothalonil, however, the calibrated amount (769 g/ha) was less than one third of that in 2006 (2600 g/ha), but in an acceptable range to the value of 2010 (1018 g/ha). The calibrated endosulfan amount was between the 2006 and 2010 survey values. Note that the application rates, fitted by calibration to the measured data in 2006, were used for both the calibration year 2006 and the validation year 2010.

3.2.2. Observation data

Measured concentrations of the three investigated pesticides and the frequency of detection (FD) in the stream at the outlet gauging station in 2008 and 2010 are shown in Fig. 2. Atrazine generally

Table 3
Selected parameters for the sensitivity analysis and calibration of the transport of atrazine (At), chlorothalonil (Ct) and endosulfan (En).

Parameter	Description	Unit	Initial value			Range		
			At	Ct	En	At	Ct	En
Pst_KG1	1st application rate	g/ha	4	204	9	2–30	100–2500	2–20
Pst_KG2	2nd application rate	g/ha	4	204	9	2–30	100–2500	2–20
Pst_KG3	3rd application rate	g/ha	4	204	9	2–30	100–2500	2–20
Pst_KG4	4th application rate	g/ha	4	204	9	2–30	100–2500	2–20
Pst_KG5	5th application rate	g/ha	4	204	9	2–30	100–2500	2–20
SKOC	K_{OC}: Soil adsorption coefficient normalized for soil organic carbon content	ml/g	100	1380	12,400	50–150	1000–1500	10,000–15,000
HLIFE_F	Degradation half-life of the chemical on the foliage	days	5	5	3	1–20	1–20	1–20
HLIFE_S	Degradation half-life of the chemical in the soil	days	60	30	50	20–120	5–60	10–100
PERCOP	Pesticide percolation coefficient	–	0.5	0.5	0.5	0.1–0.9	0.1–0.9	0.1–0.9
WOF	Wash-off fraction	–	0.45	0.5	0.05	0.1–0.9	0.1–0.9	0.1–0.9

Table 4
Relative sensitivity of the calibrated pesticide parameters for atrazine (At), chlorothalonil (Ct) and endosulfan (En). The font size in the cells in the "Rank" column indicates the sensitivity.

Examples: **1:** Very high sensitivity (>0.8)
3: High sensitivity (>0.5)
6: Medium sensitivity (>0.2)
9: Low sensitivity (<0.2)

Para-meter	Description	Unit	Relative Sensitivity			Rank			Calibrated value‡		
			At	Ct	En	At	Ct	En	At	Ct	En
Pst_KG1	1st application rate	g/ha	0.167	0.114	0.227	8	7	6	0.01 (2.3.)	45 (15.3.)	6.51 (12.3.)
Pst_KG2	2nd application rate	g/ha	0.603	0.305	0.202	2	6	7	9.43 (18.4.)	181 (22.4.)	5.78 (1.5.)
Pst_KG3	3rd application rate	g/ha	0.053	0.034	0.268	10	10	5	0.01 (29.7.)	0.01 (3.5.)	7.13 (16.5.)
Pst_KG4	4th application rate	g/ha	0.069	0.679	0.678	9	4	2	0.01 (11.8.)	543 (17.5.)	14.2 (19.6.)
Pst_KG5	5th application rate	g/ha	0.235	1	0.024	6	1	10	0.04 (4.9.)	0.01 (1.9.)	0.17 (24.8.)
SKOC	K_{OC}: Soil adsorption coefficient normalized for soil organic carbon content	ml/g	0.588	0.652	0.127	3	5	8	80.1	1172	7762
HLIFE_F	Degradation half-life of the chemical on the foliage	days	0.377	0.053	0.094	5	9	9	8.7	6.1	5.2
HLIFE_S	Degradation half-life of the chemical in the soil	days	0.214	0.773	1	7	3	1	96	10	19
PERCOP	Pesticide percolation coefficient	-	1	0.854	0.370	1	2	3	0.77	0.68	0.69
WOF	Wash-off fraction	-	0.400	0.058	0.307	4	8	4	0.62	0.61	0.65

‡ values in brackets give the application date (day.month.)

showed the highest mean and maximum daily concentration in both study years. The mean observed concentration in 2008 was only half that of 2010. The maximum concentration in 2008 was lower than in 2010. The 2008 value (0.2 μg/l) was about 20 times higher than the mean, while the 2010 maximum was about 15 times higher. Chlorothalonil showed the second highest mean concentrations; the 2010 mean value was slightly lower than in 2008. The maximum observed concentration in 2008, however, was more than 30-fold greater than the mean. Endosulfan had the lowest values: the mean daily concentrations of 2008 were slightly lower than in 2010. This trend was also present for the daily maxima.

3.2.3. Simulations

After calibrating the SWAT model using the ANSELM tool, the measured and simulated temporal dynamics of pesticide loads agree acceptably well (Fig. 3). With atrazine, the pattern is matched best over the entire rainy season, as reflected in the highest NSE value in both the calibration and validation period. In the calibration period (2008), the pattern of chlorothalonil is well reproduced early in the rainy season. Larger deviations between observed and simulated loads occur at the end of the dry season and during the rainy season, when the predicted load drops to zero. The situation is similar with endosulfan, but the overall agreement with the observed loads is better than with chlorothalonil. In the validation period (2010), the NSE of the atrazine simulations is still in an acceptable range (NSE = 0.61). In the case of chlorothalonil and endosulfan, however, the predictive power of the model is distinctly lower, with NSE dropping to about 0.3.

The simulated yearly loads of atrazine were the highest among the investigated pesticides. Between 2008 and 2010, values decreased from 0.175 to 0.128 g/ha (Table 5). Chlorothalonil showed the second largest concentration in 2008, dropping to third in 2010, although it was nearly the same as in 2008. Endosulfan was the only pesticide to show an increase between 2008 and 2010. The simulated loss shows the same relations for all pesticides between 2008 and 2010, but the atrazine losses are about 5–13 times higher than those of endosulfan and more than 100 times higher than those of chlorothalonil.

Table 5
Yearly total application rate along with observed and predicted pesticide loads and loss of dissolved pesticides in the Mae Sa watershed in 2008 and 2010.

Pesticide	Yearly mean application[a] (g/ha)		Application (simulated) (g/ha)	Yearly accumulated load (simulated) (g/ha)		Yearly loss (simulated) (%)	
	2006	2010	2008, 2010	2008	2010	2008	2010
Atrazine	n.a.	22	12	0.175	0.128	1.94	1.43
Chlorothalonil	2600	1018	769	0.076	0.072	0.01	0.01
Endosulfan	3	43	34	0.050	0.102	0.15	0.30

[a] Based on the surveys by Schreinemachers and Sirijinda, 2008 and Schreinemachers et al. (2011), n.a.: non-available data.

The simulated loads were converted into concentrations by multiplying by the corresponding mean daily discharge (Fig. 2). The simulated mean atrazine concentration of 2008 matched the observed value of 0.01 μg/l. The simulated mean of 2010, however, underestimated the observed value by 45%. In both years the simulated and observed maxima were similar, although the former were lower than the latter.

As in the observations, the simulated mean concentration of chlorothalonil in 2008 was slightly higher than in 2010, although the variability of the simulation values was higher than the observed values. The simulated maxima were reasonable estimates of the measurements, but did underestimate the values. The simulated endosulfan means of 2008 slightly overestimate the observed values; the same holds true for the 2008 maximum, whereas the 2010 maximum was in line with the observations.

3.2.4. Specific parameter analysis

In the sensitivity analysis, the sorption coefficient and the decay coefficient were identified as two of the most sensitive physical parameters with respect to all pesticides. While the K_{oc} value of the three pesticides differ vastly (Table 1), the half-life is within the same magnitude. However, under anaerobic conditions the half-life time could be considerably higher. In Fig. 4 it is shown by example how the highest daily concentration or the yearly accumulated load of atrazine would be hypothetically affected if the K_{OC} value or Half-Life would be different. Here, the K_{OC} value has the largest impact, values of 50 or result in very high concentrations, the half-life coefficient is only of minor importance.

Since the application time was not part of the sensitivity analysis, it is also of interest, how a variation in application time would affect the peak concentration and yearly accumulated loads. Since atrazine and endosulfan represent the two ends of the K_{OC} value range in this study, these two pesticides have been chosen by example. Both pesticides show a calibrated pesticide application time in mid-march (Fig. 3). This day was shifted to max. 5 days to the future and to the past. Fig. 5 shows the effect of the application timing on peak concentrations and accumulated loads. While with endosulfan a delay of the application time would in general result in higher concentrations, a change of the application time of atrazine would mostly result in lower concentrations.

3.2.5. Uncertainties

The uncertainty bands of the pesticide loads bracket the measurements well (Fig. 6). The pattern of these bands mostly follows the discharge dynamics and is overlaid by the pesticide applications. In atrazine, the band is broad, indicating significant model uncertainty, especially after application. For example, the highest observed atrazine load was 11 g ha^{-1}, but the upper limit of the prediction uncertainty band peaked at 30 g ha^{-1}. The uncertainty band of endosulfan, in contrast, shows the largest uncertainties during high discharge events. The GLUE analysis helps assess the highest possible loads per day. The upper limits of the uncertainty bands of all pesticides are below the threshold of 35 g day^{-1}.

4. Discussion

4.1. Sensitivity analysis

The different parameter sensitivities of the three pesticides can be explained by their properties. Atrazine has a lower K_{OC} value than chlorothalonil and endosulfan. Therefore, the SKOC and PERCOP parameters, which trigger leaching, are among the most sensitive parameters in the atrazine simulation. The different sensitivities of the SKOC parameter within the three pesticides

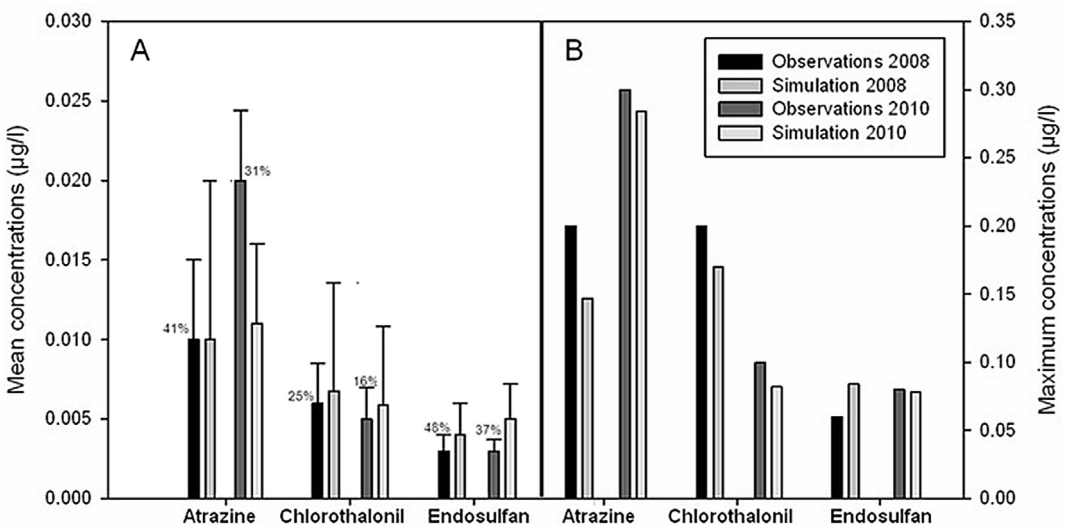


Fig. 2. Mean daily pesticide concentration in stream at the outlet of the Mae Sa watershed in 2008 and 2010. Panel A shows the mean of all daily concentrations, panel B the maximum daily concentrations. Error bars indicate the standard deviation, the percentage numbers the frequency of detection.

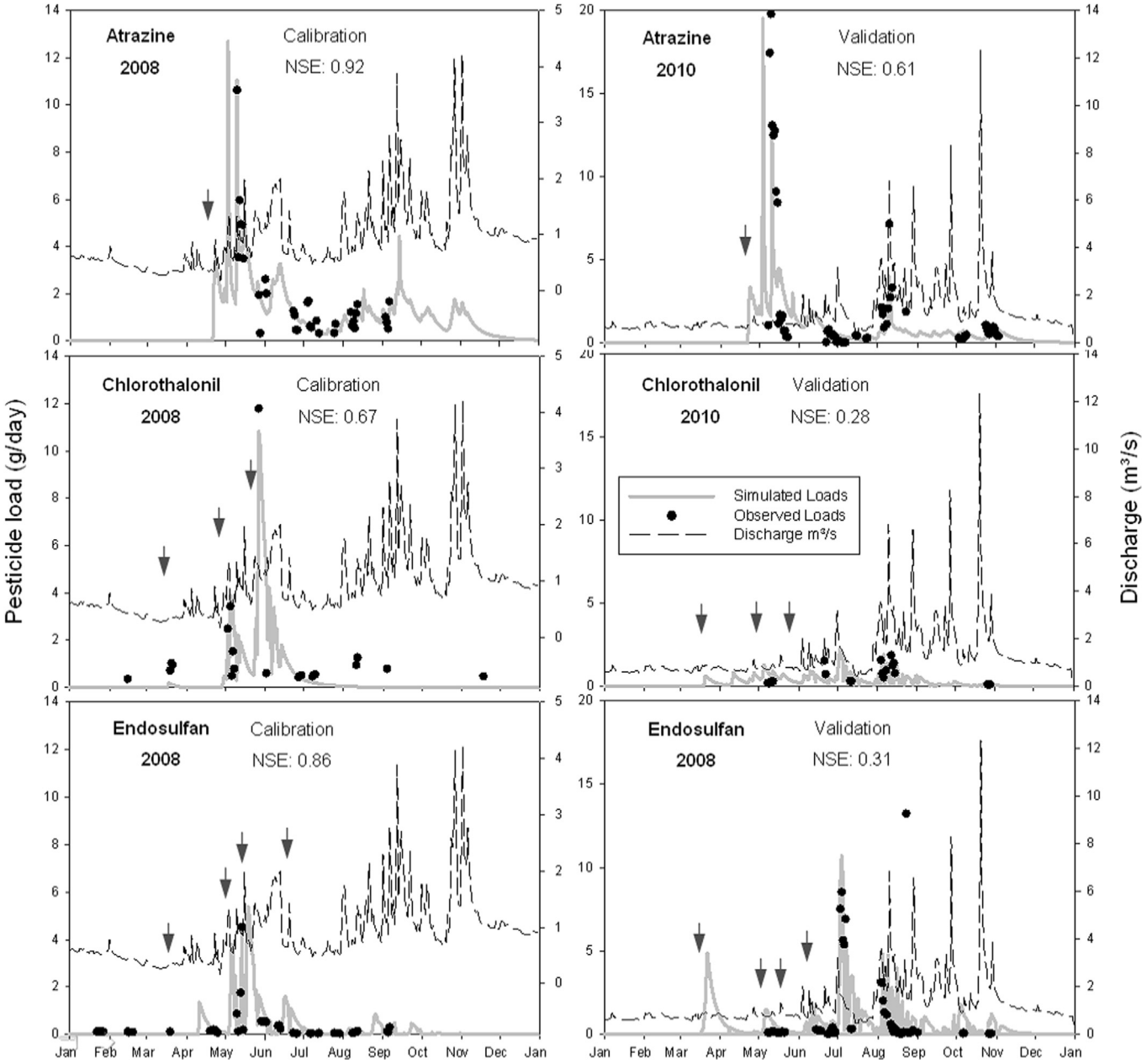


Fig. 3. Observed and SWAT-simulated pesticide loads at the outlet of the Mae Sa watershed. Dark arrows indicate simulated pesticide application rates over 5 g/ha. Note the different scales of the right and left *y*-axes.

match the magnitude of its value. The lower K_{OC} value was the more sensitive. Atrazine is furthermore rather persistent, at least compared with the other two pesticides. Therefore, HLIFE_S, the parameter steering soil degradation, is only moderately important for atrazine. In contrast, this parameter was highly sensitive during simulations of chlorothalonil and endosulfan. The PERCOP parameter was sensitive for all pesticides, although with the lightly degradable endosulfan its relative sensitivity was somewhat lower.

Atrazine is a herbicide, which is most likely applied only once or twice a year, whereas the fungicides and insecticides are often applied repeatedly, whenever needed. Therefore, only one application rate was found to be highly sensitive with atrazine, while with endosulfan, up to four applications had a relative sensitivity exceeding 0.2. Accordingly, usage seems to be highly correlated with the number of applications needed for the simulation.

4.2. Pesticide simulations

Coupling ANSELM and SWAT proved to be a useful and reasonable means of calibrating the simulation of pesticide movement in the Mae Sa catchment. The simulation of the three pesticides reasonably matched the observations at both study periods. In the calibration period, high NSEs (0.67–0.92) were achieved for all three pesticides; these values were within the range or higher than those in previous studies (Ramanarayanan et al., 2005; Luo and Zhang, 2009; Boithias et al., 2011; Zhang and Zhang, 2011). Model performance significantly declined in the validation period (NSEs = 0.28–0.61), particularly for chlorothalonil and endosulfan. This decline might be an artifact of using the same application scheme as in the calibration period, owing to limited input data.

Two important factors controlling pesticide dynamics in river water were rainfall and application practices. While rainfall data

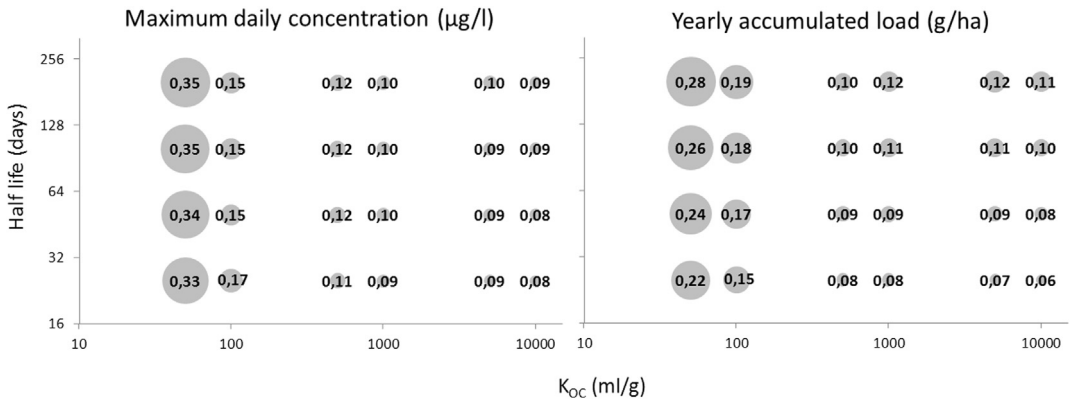


Fig. 4. Simulated maximum daily concentrations (µg/l) and yearly accumulated loads (g/ha) of pesticides with different half-life and K_{OC}-values in the Mae Sa stream water in 2008. All other parameters of the pesticides have been set by example like atrazine (Table 4).

are relatively easy to measure, it is practically impossible to obtain accurate application times and rates of all farmers, except in very small catchments (Doppler et al., 2012). A farmer's decision to apply a pesticide is driven by a variety of factors such as crop development, pest pressure, weather, workload and individual appraisal. The more complex the application scheme, the larger the uncertainty in the model simulation. This probably explains why the decline of the NSE in the atrazine simulation was less than that of the two other pesticides.

The differences between simulated and observed maximum daily concentrations may also be explained by application complexity. Among the investigated pesticides, large discrepancies in application were observed. Atrazine seems to have a quite simple and reproducible application scheme. Only one application, at the beginning of the rainy season, was sufficient, whereas three to four applications of chlorothalonil and endosulfan, distributed over the entire rainy season, were needed to achieve satisfactory simulation results.

Our results of Fig. 4 suggest that when pesticides with very low K_{OC} values are used, high pesticide peak concentrations can be anticipated. In addition, the timing of pesticide application can have a big impact on the magnitude of such events. The first step would be to transfer this information to the farmers and if a pesticide application in the rainy season is absolutely inevitable, weirs and dams could be a measure to ease this problem.

The time series uncertainty bands often show large peaks during periods when no data were available. To judge the model performance of the calibrated model for each pesticide, the efficiencies were calculated only for time steps where observed data were available. Furthermore, the observed concentrations were converted into loads by multiplication with observed discharge and vice-versa, yielding more uncertainties in both observations and simulations. Although the uncertainty bands are quite wide, the upper limit of the prediction uncertainty band was of the same order of magnitude as the observed data. The broad uncertainty band for endosulfan is strongly correlated with the discharge peaks.

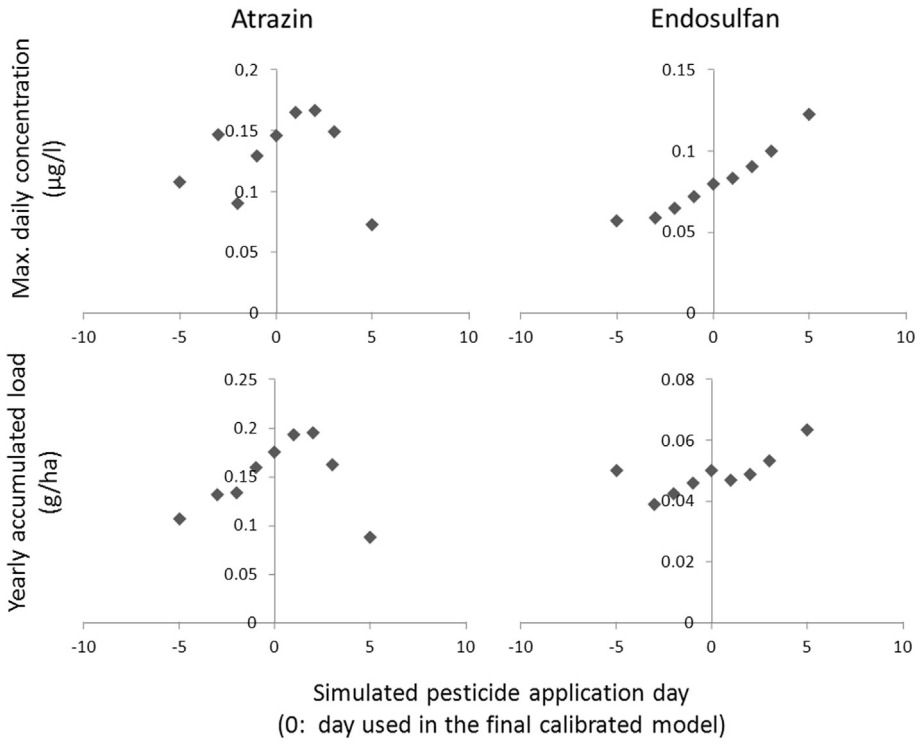


Fig. 5. Simulated maximum daily concentrations (µg/l) and yearly accumulated loads (g/ha) of Atrazine and Endosulfan with changing time of application.

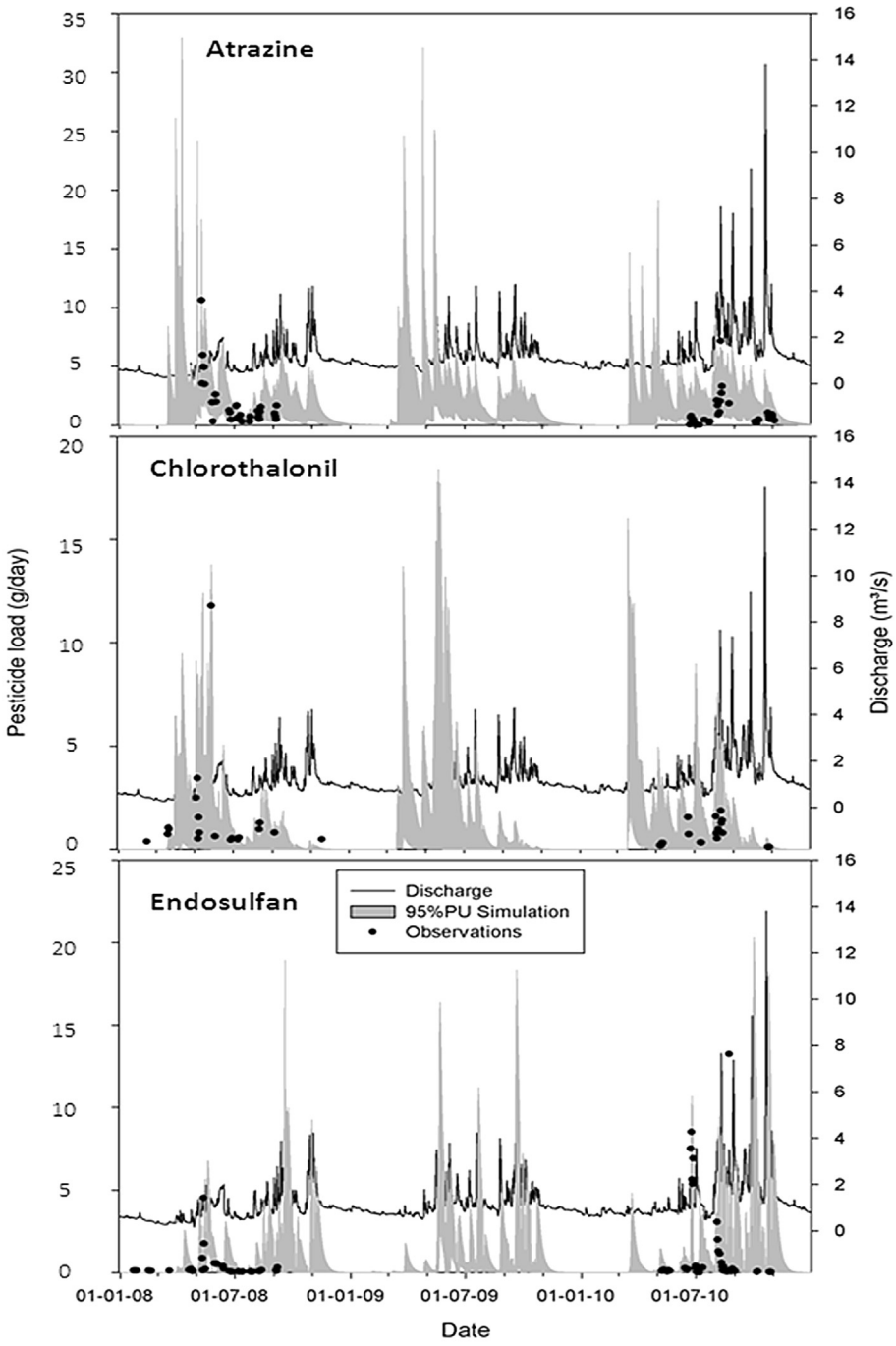


Fig. 6. Predicted uncertainty bands (PU) of the pesticide loads for the years 2008–2010.

In contrast, those of atrazine and chlorothalonil are not strongly correlated, probably because other factors, such as the application amount, more strongly affect uncertainty.

5. Conclusion & outlook

The simulation of pesticide fate using SWAT coupled with ANSELM was successful in different ways. Firstly, all pesticide-related parameters were subjected to both a LH-sensitivity analysis and later auto-calibration. Secondly, we calibrated not only physico-chemical pesticide parameters and the absolute pesticide amount, but also integrated the application time and the necessary number of application events in the auto-calibration. We compared the simulation behavior of three pesticides – each one of a different usage type (herbicide, fungicide, insecticide) – and their sensitivities within SWAT simulations. We found large differences in the sensitivities of different parameters; nonetheless, the percolation parameter seems to be the key parameter in each SWAT simulation. In particular, atrazine and endosulfan differed considerably both in response to the number of applications and application timing, as well as in the sensitivity to parameters concerning degradation and adsorption. Here, the ability of ANSELM to select and use any parameter of SWAT for a LH-sensitivity analysis was very useful.

Because we achieved high model efficiencies during calibration (NSE: 0.67–0.92 for all three pesticides) and reasonable ones during validation (NSE: 0.28–0.61), we largely fulfilled our goal of

simulating the temporal pattern of the pesticide transport to the stream. Simulated mean and maximum daily concentrations matched observations sufficiently. Better results could probably be achieved if reliable data on pesticide application rate and timing were available. A survey of farmers can be a good starting point, but this alone is insufficient. Also, exact spatial information of pesticide application within the catchment should improve simulations. Despite this lack of information, it is encouraging to see that coupling SWAT with ANSELM created realistic simulations.

Nevertheless, unless the external factors of pesticide application can be captured, SWAT and other models cannot be used for exact daily forecasts of pesticide concentrations or loads. For most management applications and ecotoxicological risk assessments, however, yearly or seasonable forecasts are likely sufficient. Our simulation results and the GLUE uncertainty analysis performed with ANSELM indicate that loads on these time scales can be assessed with SWAT.

In future studies, when more complex data would be available, it would be useful to generate predictions at sub-daily intervals – at least for periods with high pesticide peaks. We additionally wish to test the coupling of SWAT and ANSELM for other pesticides in the catchment, especially insecticides. It will be interesting to determine whether the differences we found between the different pesticides are representative for their respective usage types, or whether large discrepancies exist even within these groups. We further plan to couple SWAT with an economical model to assess the effect of pesticide dosage reductions on stream water concentrations, land use and household income.

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