Development and validation of a pollutant runoff module in SPEC model

by

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Abstract

The objectives of the study were to (1) improve SPEC (Predicted Environmental Concentrations in agricultural Soils) model for simulating pesticide fate and transport; (2) develop a pollutant runoff module in SPEC for simulating runoff water, sediment concentration and yield in runoff water, and pesticide concentrations in runoff water and in the sediment; and (3) calibrate and validate the model with experimental runoff data using artificial rainfall simulator for assessing pesticide runoff.

The improvements were made for the existing SPEC model for increasing the accuracy in simulating pesticide fate and transport at multiple soil layers and for developing a new module to simulate the pollutant runoff. The improvements allow users to simulate runoff as well as pesticide in soil not only in single event but also continuous simulation. The finer input and output time steps enable model capability to simulate in single rainfall events. The improvement was made not only in the simulation codes but also in output display. It allows displaying dynamically in both tables and graphics. The additional codes integrated in the SPEC model including statistical indexes and Monte Carlo simulation support the users in evaluating the model performance, sensitivity analysis, calibration/ validation, as well as uncertainty analysis.

The improved SPEC model was tested for three applications. The first case study applied to simulate the pollutant runoff for two types of pesticides (clothianidin and imidacloprid) under artificial rainfall event in Sakeacho upland bare soil (Tokyo, Japan) conducted on October 2nd, 2017. The second case study was conducted to simulate the fate and transport of imidacloprid and clothianidin in 4 layers of soils in Sakaecho upland bare soil (Tokyo, Japan) in 65 days from September 26th to November 29th, 2017. The third simulation was applied for the case study of Sakaecho upland bare soil (Tokyo, Japan) with two types of pesticides (atrazine and metolachlor) in 329 days from June 10th, 2013 to May 4th, 2014 under two options which were 2 and 3 soil layers simulations.

The calibration and validation for pollutant runoff module under artificial rainfall condition were conducted for the Sakaecho upland field (Tokyo, Japan) on October 2nd, 2017 for two types of pesticides, imidacloprid and clothianidin. The simulated results of runoff rate using both CN method and Green-Ampt method matched with the observed data at a satisfactory level. The simulated results of cumulative runoff using CN method and Green-Ampt method performed a very

good agreement with the observed data. The simulated time to first runoff matched well with the observed data. The results of sediment yield also performed a very good agreement with the observed data. The results of clothianidin concentrations in sediment and runoff water performed a satisfactory level. The results of imidacloprid concentrations in sediment performed a very good agreement with the observed data.

The second case study for simulating pesticide concentration in multiple soil layers was conducted for imidacloprid and clothianidin in Sakaecho upland field in 65 days. In this application, 4 layers of soils and 10-minute time step were chosen for rainfall input and model output. The simulated results included average water content in 15 cm depth, the concentrations in 4 soil layers as well as the average concentrations in 15 cm of imidacloprid and clothianidin. The water content results had a negative *NSE* indicated an unsatisfactory model performance; however, the *PBIAS* indicated a satisfactory model performance. There were implications of errors in observed water content data. The performance of simulated pesticides in multiple soil layers was not good because of the imprecise observation data. However, the simulated pesticides in the first soil layer (0-1 cm) indicated the potential of the model to predict the pesticides concentration in multiple soil layers.

The third case study for simulating pesticides in multiple soil layers was applied for Sakaecho upland field for atrazine and metolachlor in 329 days. The simulations for the same soil depth of 10 cm, but classified into 2 and 3 layers were performed. It was found that the simulated results from 3 layers simulation performed better than those in 2 layers simulation for both types of studied pesticides. The simulated results of 2 types of pesticides indicated the better model performance in the improved SPEC model as compared to those in the previous study calculated by the previous version of SPEC model (Boulange et al., 2016).

The improvements of SPEC model were tested for runoff pollutant as well as for pesticide concentrations in multiple soil layers case studies. The results implied the potential capability of the improved SPEC model to predict pesticide fate and transport in multiple layers of soil as well as runoff pollutant in upland field.

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List of Symbols

Term	Unit	Meaning
A	m²	The area of plot (catchment)
alpha	unitless	The ratio of pesticide concentrations in mobile water and static water
beta	unitless	The ratio of pesticide concentrations in runoff water and percolation water
C	unitless	Time step runoff coefficient
C_sed	g/L	Sediment concentration
C_sedD	mg/kg	Daily sediment concentration
C_sedD_cum	mg/kg	Total sediment concentration in a day
C_USLE	unitless	The cover and management factor
C0	mg/kg	Initial pesticide concentration in soil layer
Cds	mg/kg	The pesticide concentration in solid compartment
Cds_spd	mg/kg	Average pesticide concentration in solid compartment at sampling depth (time step value)
Cds_spd_cum	mm*mg/kg	Multiplication of depth with pesticide concentration in solid compartment (time step value)
CdsD	mg/kg	Daily pesticide concentration in solid compartment
CdsD_cum	mg/kg	Total pesticide concentration in solid compartment in a day
CdsD_spd	mg/kg	Average pesticide concentration in solid compartment at sampling depth (daily value)
CFRG	unitless	The coarse fragment factor
Cj	unitless	Runoff coefficient constant
CN1	unitless	Minimum water content Curve number
CN2	unitless	Average water content Curve number
CN2_0	unitless	Initial value of Curve number
CN2s	unitless	Average water content Curve number adjusted for slope different from 5%
CN3	unitless	Maximum water content Curve number
Const_CN		Option for using constant Curve Number
Cper_pst	mg/L	The pesticide concentration in percolation water
Crw_pst	µg/L	The pesticide concentration in runoff water
Crw_pstD	mg/kg	Daily pesticide concentration in runoff water
Crw_pstD_cum	mg/kg	Total pesticide concentration in runoff water in a day
Cs	mg/kg	The pesticide concentration in soil layer (wet soil condition)
Cs_0W	mg/kg	The pesticide concentration in soil layer (dry soil condition)
Cs_op		Option for pesticide concentration simulation

Term	Unit	Meaning
Cs_spd_0W	mg/kg	Average pesticide concentration in soil (dry soil condition) at sampling depth (time step value)
Cs_spd_0W_cum	mm*mg/kg	Multiplication of depth with pesticide concentration in soil (dry soil condition) (time step value)
CsD_0W	mg/kg	Daily pesticide concentration in soil (dry soil condition)
CsD_0W_cum	mg/kg	Total pesticide concentration in soil (dry soil condition) in a day
CsD_0W_spd	mg/kg	Average pesticide concentration in soil (dry soil condition) at sampling depth (daily value)
CsD_0W_spd	mm*mg/kg	Multiplication of depth with pesticide concentration in soil (dry soil condition) (daily value)
Csed_pst	mg/kg	The pesticide concentration in runoff sediment
Csed_pstD	mg/kg	Daily pesticide concentration in sediment
Csed_pstD_cum	mg/kg	Total pesticide concentration in sediment in a day
Csw	mg/L	The pesticide concentration in soil water
Cw	mg/L	The pesticide concentration in solution phase in soil layer
DelWC	mm^3/mm^3	The effective water content
dInf	mm/ts	Infiltration increment (rate)
dInfC	mm/ts	The potential infiltration rate (Green-Ampt method)
dMbio	mg	The increment of pesticide mass loss due to biodegradation
dMper	mg	The increment of pesticide mass loss in percolation water
dMpho	mg	The pesticide mass increment due to photodegradation
dMrw_pst	mg	The increment of pesticide mass loss in runoff water
dMsed_pst	mg	The increment of pesticide mass loss in runoff sediment
dMvol	mg	The increment of pesticide mass loss due to volatilization
dQ	mm/ts	Runoff rate
dQ_hr	mm/h	Output of hourly runoff rate
dRF	mm/ts	Rainfall increment (time step)
dRF_hr	mm/h	Output of hourly rainfall
dSed	mm/ts	Sediment increment
dt1	min	Time difference between the first application time and start time of simulation
dt2	min	Time difference between the second application time and start time of simulation
dt3	min	Time difference between the third application time and start time of simulation
e_coef	unitless	The pesticide enrichment coefficient
e_date		End date of simulation
Energ	$MJ/m^2/d$	Average energy during the experiment
epsilon	unitless	The pesticide enrichment ratio

Term	Unit	Meaning
Es	mm	The evaporation for soil layer
Es_op		Option for using Es1 or Es2
Es1	mm	The evaporative demand adjusted for water content below field capacity for soil layer
Es2	mm	The final soil water evapotranspiration capacity for soil layer
esco	unitless	Soil evaporation coefficient
ET	mm/d	Daily value of evaporation
ET_const	mm/d	Evaporation constant value
ETj	mm/ts	Simulation time step value of evaporation
Ets		Evaporation time step condition
Ez	mm	The evaporative demand
Facc	mm	The potential cumulative infiltration (Green-Ampt method)
HLbio	d	The biodegradation half-life of the pesticide
HLpho	d	The photochemical degradation half-life of the pesticide
i		subscript for layer order
I30	mm/h	Max rainfall intensity constant
I30j	mm/h	Time step rainfall intensity
Ia	mm	Initial Abstraction
Inf	mm	Cumulative infiltration
InfC	mm	The potential cumulative infiltration (Green-Ampt method)
InfilD	mm/d	Output for daily infiltration
InfilD_cum	mm	Cumulative infiltration in every time step in a day
j, jj		subscript for time order
Kbio_ref	1/ts	The reference first-order rate constant of biodegradation at 25°C
Kbioj	1/ts	The first-order rate constant of biodegradation adjusted for the change of temperature
Kd	L/kg	The partitioning water/organic matter coefficient
Ke	mm/ts	The effective hydraulic conductivity
Koc	L/kg	The adsorption coefficient normalized to the organic carbon content of the soil
Kpho	m^2/kJ	The first-order rate coefficient of photodegradation
Kphoj	1/ts	The coefficient of photodegradation
Ks	mm/h	Saturated hydraulic conductivity
Ks_a	mm/h	Average value of saturated hydraulic conductivity for soil profile
Ksl	mm^2/h	Multiplication of saturated hydraulic conductivity and soil depth
Ksl_acc	mm^2/h	Sum of multiplication of saturated hydraulic conductivity and soil depth for soil profile
kv	unitless	The volatilization coefficient

Term	Unit	Meaning
L	mm	The soil layer depth
l_acc	mm	Soil profile depth
lambda, λ	unitless	Initial abstraction ratio
lastrow_d		Lastrow for "Daily" worksheet
lastrow_h		Lastrow for "Hourly" worksheet
lastrow_o		Lastrow for "Output" worksheet
lastrow_od		Lastrow for "Output_D" worksheet
lastrow_sts		Lastrow for "Small_TS" worksheet
Lplot	m	Plot length
LS_USLE	unitless	The topographic factor
Lslp	m	The slope length in MULSE
m_USLE	unitless	The exponential term in MULSE
M0	mg	The input mass of pesticide in layer 1
Mbio	mg	The cumulative pesticide mass loss due to biodegradation
mc	%	Mass percentage of clay content
mc_a	%	Average value of clay percent for soil profile
mcl	%*mm	Multiplication of clay percent and soil depth
mcl_acc	%*mm	Sum of multiplication of clay percent and soil depth for soil profile
Mds	mg	The pesticide mass in dry soil compartment
Mds0	mg	The residual pesticide masses in dry soil
MEr	%	The pesticide mass error in soil layer
MP	mm	Matric potential at wetting front
Mper	mg	The cumulative pesticide mass loss in percolation received from above layer
Mper_f	mg	The cumulative pesticide mass loss in percolation received from above layer including residual pst mass in that layer
Mpho	mg	The cumulative pesticide mass loss due to photodegradation
Mpst	mg	The total pesticide masses in dry soil and soil water
Mrw_pst	mg	The cumulative pesticide mass loss in runoff water
ms	%	Mass percentage of sand content
ms_a	%	Average value of sand percent for soil profile
Msed_pst	mg	The cumulative pesticide mass loss in runoff sediment
msl	%*mm	Multiplication of sand percent and soil depth
msl_acc	%*mm	Sum of multiplication of sand percent and soil depth for soil profile
Msw	mg	The pesticide mass in soil water compartment
Msw0	mg	The residual pesticide masses in soil water
MUSLE_coef	unitless	The coefficient of MULSE
MUSLE_exp	unitless	The exponent of MULSE
Mvol	mg	The cumulative pesticide mass loss due to volatilization
n	unitless	Numbers of soil layers

Term	Unit	Meaning
n_GA		Numbers of loops in solving Trial-and-error for Green-Ampt method
n1	unitless	Maximum numbers of soil layers that can be displayed in charts
Oc	%	Mass percentage of organic carbon
Opts	min	Output time step (value)
OPtsText		Output time step condition
order	unitless	the order of soil layer that contains the bottom of sampling depth
order_s	unitless	the order of soil layer that contains the bottom of sampling depth (in case same soil properties)
P_USLE	unitless	The support practice factor
PD1		The first date of pesticide application
PD2		The second date of pesticide application
PD3		The third date of pesticide application
Per	mm	The actual percolation discharged from soil layer
PestType		Pesticide name
PM1	mg	Pesticide mass applied at the first time
PM2	mg	Pesticide mass applied at the second time
PM3	mg	Pesticide mass applied at the third time
por	unitless	The soil porosity
PR1	g/ha	Pesticide rate applied at the first time
PR2	g/ha	Pesticide rate applied at the second time
PR3	g/ha	Pesticide rate applied at the third time
Q	mm	Cumulative runoff
q_peakj	m^3/s	Max discharge rate
Q10	unitless	Q10
RainD	mm/d	Output for daily rainfall
RainD_cum	mm	Cumulative rainfall in every time step in a day
Rb	g/cm^3	Soil bulk density
RC		Runoff control (allow runoff or not)
RF	mm	Cumulative rainfall
RF_const	mm/d	Rainfall constant value
RF_D	mm/d	Daily value of rainfall data
RF_H	mm/h	Hourly value of rainfall data
RF_t	mm/RF ts	Small time step value of rainfall data
RFts	min	Rainfall time step (value)
RFtsText		Rainfall time step condition
RO_method		Method for runoff simulation
RunoffD	mm/d	Daily runoff
RunoffD_cum	mm	Cumulative runoff in a day
S	mm	Retention parameter

Term	Unit	Meaning
s_date		Start date of simulation
S0	mm	Initial value of retention parameter
S3	mm	Minimum retention parameter, coressponding to CN3
Same_op		Option for using the same properties fro all soil layers
Sed	mm	Sediment yeild (time step)
SedD	g	Daily sediment yield
SedD_cum	g	Cumulative sediment in every time step in a day
SLE_coef		The overall coefficient of MUSLE
slp	unitless	The slope of plot (catchment)
Smax	mm	Maximum retention parameter, coressponding to CN1
spd	mm	soil sampling depth
SR	mm/d	Daily value of solar radiation
SR_const	MJ/m²/d	Solar radiation constant value
SRj	mm/ts	Simulation time step value of solar radiation
SRts		Solar radiation time step condition
T	°C	The temperature at which the half-life of the pesticide must be calculated
T_travel,	h	Travel time
T_ts	unitless	Numbers of simulation steps in whole simulation period
T_ts_D	unitless	Numbers of simulation steps in a day
T1	°C	Average temperature in May to September
T2	°C	Average temperature in October to April
Tempts		Temperature time step condition
Theta, θ	rad	The angle between slope and horizontal line in MULSE
Time	small ts	Small time value
TimeD	date	Daily time value
ts	min	Simulation time interval (time step)
TT	h	Travel time
w1	unitless	The first shape coefficient
w2	unitless	The second shape coefficient
WC	mm³/mm³	Soil water content
WC_a	mm³/mm³	Average value of water content for soil profile
WC_acc_mm	mm	Total soil water content for soil profile
WC_spd	mm³/mm³	Average water content at sampling depth (time step value)
WC_spd_mm	mm	Cumulative value of water content at sampling depth (time step value)
WC0	mm³/mm³	Initial water content
WC0_acc_mm	mm	Total initial water content for soil profile
WC0_mm	mm	Initial water content
WCc	mm³/mm³	Water capacity for soil layer
WCD	mm³/mm³	Output for daily average water content

Term	**Unit**	**Meaning**
WCD_cum	mm^3/mm^3	Cumulative water content in every time step in a day
WCD_spd	mm^3/mm^3	Average water content at sampling depth (daily value)
WCD_spd_cum	mm	Cumulative value of water content at sampling depth (daily value)
WCf	mm^3/mm^3	Saturated water content at field capacity
WCf_a	mm^3/mm^3	Average value of field capacity for soil profile
WCr	mm^3/mm^3	Residual water content
WCr_a	mm^3/mm^3	Average value of residual water content for soil profile
WCs	mm^3/mm^3	Saturated water content
WCu	mm^3/mm^3	Updated water content
WCX	mm	the available water for soil layer
ws_d	unitless	"Daily" worksheet
ws_gr	unitless	"Graph" worksheet
ws_h	unitless	"Hourly" worksheet
ws_i	unitless	"RUN" worksheet
ws_o	unitless	"Output" worksheet
ws_obs	unitless	"Obs_Data" worksheet
ws_od	unitless	"Output_D" worksheet
ws_rp	unitless	"Report" worksheet
ws_sts	unitless	"Small_TS" worksheet
z	mm	The bottom depth of soil layer

Chapter 1. Introduction

Pesticide has been used for agriculture to improve yield and quality of agricultural products. However, its application and discharge into environment could adversely affect the soil and water as well as plants, animals, and human (Damalas and Eleftherohorinos, 2011; National Research Council, 1993; World Health Organization, 2008). The negative effects of pesticide are needed to be controlled to ensure the health of environment as well as plant, animals and human. Quantifying the pesticide residue in the environment is required to suggest measures to protect environment, especially in Environmental Impact Assessment (EIA). This can be done by pesticide monitoring or pesticide prediction using modeling. However, pesticide monitoring is often expensive and time-consuming thus the use of numerical models is considered to be more efficient to achieve environmental assessment of pesticide fate (Inao and Kitamura, 1999; Williams et al., 2012; Zhang et al., 2000). Water quality models have been widely used as supporting tools for EIA in recent years (Varis, 1996).

In Japan, cultivated lands in agriculture including paddy fields and upland fields accounted for 12.2% of total land area in average in the years 2009 to 2017 (Statistics Bureau of Japan, 2019). The average upland fields occupied for 2.1 million hectares which was 45.6% agricultural land in that period (Statistics Bureau of Japan, 2019). The release of pesticides from agricultural land has been considered to be the non-point source of pollution to the environment (Dowd et al., 2008; U.S. EPA). It is needed to control from the plot scale field for both paddy and upland fields. Many models for simulating pesticides in catchment as well as plot scales for paddy fields were developed (Boulange et al., 2016, 2014; Hoang Tu et al., 2018; Inao et al., 2008; Inao and Kitamura, 1999; Neitsch et al., 2011; Numabe and Nagahora, 2006; Sharpley and Williams, 1990; Watanabe and Takagi, 2000) and thus to achieve the EIA goal, but very few models in Japan were developed for simulating the pesticides fate in upland fields (Boulange et al., 2016).

The application of a numerical model for EIA purpose is valid only when the model was calibrated and validated. These two procedures help the model to find out the validated parameters associated with the properties of soil, soil water, as well as pesticides. They require observed data of hydrology, pesticides, properties of soil, as well as the initial conditions and the weather data. However, some properties of soil, soil water, as well as pesticides are difficult to obtain. Therefore, the use of models required less input of parameters is preferable. SPEC (Predicted Environmental

Concentrations in agricultural soils), which is one of the models developed to simulate pesticide fate and transport in upland field, has been validated for bare soil condition in Japan (Boulange et al., 2016). The advantages of the SPEC model are that, it requires less input parameters and it is easy to use (in input and output as well as post processing of the results) because it was coded in Excel Visual Basic Application (Excel VBA). However, the model still has some shortcomings. The model simulates the pesticide in soil at only two depths (two soil layers). In runoff simulation, there were inappropriate codes developed for simulating runoff water as well as the pesticide concentration in runoff water. In addition, the simulation of sediment concentration and yield as well as pesticide concentration in sediment were not available.

To simulate the pesticide from upland fields, the SPEC model should be a candidate. However, it should be modified to satisfy the requirement of pesticide transport in runoff as well as pesticide fate and transport in multiple soil layers. The following issues should be considered in the modification of the SPEC model.

For runoff simulation, two popular methods have been used which are Curve Number (CN) and Green-Ampt methods. The CN method developed by Soil Conservation Service (SCS) which now becomes National Resources Conservation Service (NRCS) of the United States (USDA Natural Resources Conservation Service, 2015, 2004, 1999). The Green-Ampt method (Green and Ampt, 1911) was developed by Green and Ampt in 1911.

The CN method has been successfully applied to simulate runoff in many soil types and regions (Franco and Bonuma, 2017; Kannan et al., 2007; King et al., 1999; Kowalik and Walega, 2015; Nearing et al., 1996; Oliveira et al., 2016; Rawls and Brakensiek, 1986; Soulis and Valiantzas, 2012; Williams et al., 2012). However, some authors reported that the default initial abstraction ratio in CN method was not appropriate for runoff simulation applied for soils in some countries (Ahmad et al., 2015; Hawkins et al., 2010; Lim et al., 2006; Rajbanshi, 2016; Satheeshkumar et al., 2017; Shi et al., 2009; Woodward et al., 2003; Yuan et al., 2012).

The Green-Ampt method has also been successfully applied to simulate runoff in previous studies (King et al., 1999; Nearing et al., 1996; Rawls and Brakensiek, 1986). This method was often used in combination with CN method in the same model to compare between two methods. In the study to find the relationship between the effective hydraulic conductivity (used in Green-Ampt method) and curve number (used in CN method), Nearing reported that the runoff volume predicted by Green-Ampt method performed as well as or better than that predicted in CN method (Nearing et al., 1996). Rawls and Brakensiek (1986) also reported that the Green-Ampt method predicted runoff volumes with less bias and slightly more accurately than those simulated in CN method. Thus, developing runoff simulation using both mentioned methods would be reasonable.

For sediment simulation, the Modified Universal Soil Loss Equation (MUSLE) (Williams, 1995) was applied successfully by previous studies (Sharpley and Williams, 1990; Smith et al., 1984; Vigiak et al., 2015). However, to simulate sediment in small time step, it needs some modifications.

For pesticide simulation, the mass balance method was applied by most of the modelers (Boulange et al., 2016; Chen et al., 2004; Inao and Kitamura, 1999; Okumura et al., 2013; Takahashi et al., 1999; Watanabe and Takagi, 2000). In simulation of pesticide runoff, additional parameters should be included to give better predicted results.

The runoff in the SPEC model was not validated due to a lack of runoff data. This problem can be solved by using rainfall simulators to generate observed runoff data. The benefits of a rainfall simulator are that it helps to carry out the experiment quickly without waiting for the natural rain (Hudson, 1993) and generates flexible constant rainfall intensity. It also allows obtaining pollutant runoff data in small time steps. To cope with the lack of data, especially in runoff, the use of previous studies in Japan if it was available or the field experiment under a rainfall simulator condition could be reasonable.

From all the reasons above, the objectives of the research were to (1) develop a pollutant runoff module in SPEC that simulates runoff water, sediment concentration and yield in runoff water, and pesticide concentrations in runoff water and in the sediment; (2); improve SPEC model for simulating pesticide fate and transport in multiple soil layers and (3) calibrate and validate the model with experimental runoff data using the rainfall simulator for assessing pesticide runoff.

Chapter 2. Literature review

2.1 Modeling

2.1.1 Hydrology model

The Soil Conservation Service Curve Number (SCS CN) method developed by Soil Conservation Service (which now called National Resources Conservation Service, NRCS) is used to simulate runoff (USDA Natural Resources Conservation Service, 2015, 2004, 1999). The runoff, Q, occurs only when the rainfall, P, exceeds a threshold. This threshold amount which accounts for interception, depression storage, and the infiltration quantity is termed the initial abstraction, I_a.

After runoff begins, additional loss mainly in the form of infiltration still occurs. Let F be the total actual retention for the event after start of runoff. Both F and Q increase with increasing of rainfall. F will increase up to some maximum retention S. In the limit, both $Q/(P - I_a)$ and F/S approach 1,

$$\frac{Q}{(P - I_a)} = \frac{F}{S} \qquad 2.1$$

After runoff begins, all rainfall, P-I_a becomes runoff, Q and actual retention, F. This relationship is given in equation below,

$$P - I_a = F + Q \qquad 2.2$$

Solving equations 2.1 and 2.2 to find the cumulative runoff, Q,

$$Q = \frac{(P - \mathrm{I_a})^2}{(P - \mathrm{I_a} + S)} \qquad \text{for } P > I_a \qquad 2.3$$

$Q = 0$ when $P \leq I_a$

The retention parameter, S (in mm) is the amount of water storage available in the soil profile, which depends on rate of infiltration at the soil surface. S is related to runoff curve number (CN_2) by the relationship,

$$CN_2 = \frac{25400}{(S + 254)} \qquad 2.4$$

CN_2 value is given in the NRCS document which varies with land cover, soil type, soil moisture contents and rainfall (USDA Natural Resources Conservation Service, 1986). Based on the relationships between cumulative rainfall and runoff in rainfall events, the average value of *CN* (CN_2) can be found. CN_2 value is given in the NRCS document are assumed to be appropriate for 5% slope (Sharpley and Williams, 1990). Therefore in case the area slope differs from 5%, CN_2 needs to be adjusted as follows (Sharpley and Williams, 1990),

$$CN_{2s} = \frac{(CN_3 - CN_2)}{3} * [1 - 2 * \exp(-13.86 * slp] + CN_2 \tag{2.5}$$

$$CN_1 = CN_2 - \frac{20 * (100 - CN_2)}{(100 - CN_2 + exp[2.533 - 0.0636 * (100 - CN_2)])} \tag{2.6}$$

$$CN_3 = CN_2 * exp[0.00673 * (100 - CN_2)] \tag{2.7}$$

where CN_1, CN_2, CN_3 are curve numbers (unitless) in three conditions 1 (dry), 2 (average) and 3 (wet) water contents, respectively; CN_{2s} is the adjusted CN_2 for slope different from 5%; and *slp* is the area slope (in m/m),

Another method which is also used to simulate surface runoff is Green-Ampt Infiltration method. The Green-Amp infiltration is an indirect method to calculate the runoff in every time step or runoff rate based on the actual infiltration rate and rainfall intensity in every time step. The actual infiltration rate is determined by the relationship between rainfall intensity and potential infiltration rate. When rainfall intensity is smaller than potential infiltration rate, all rainfall becomes infiltration and no runoff occurs. When rainfall intensity is greater than potential infiltration rate, the actual infiltration rate is equal to potential infiltration rate. In this case, the runoff rate is determined by the subtraction between rainfall intensity and actual infiltration rate (or potential infiltration rate for this case). The Green-Amp infiltration method was developed by Green and Ampt (cited by Chow et al., 1988), to calculate the maximum or potential cumulative infiltration and potential infiltration rate under the assumed a small ponding depth on the soil surface. This method was originally developed to simulate runoff under uniform rainfall intensity. To accurately simulate surface runoff based on Green-Ampt infiltration method, the related parameters used in this method need to be determined carefully.

The following terms which were used in the SPEC model are explained as below,

Infiltration is the process of water penetrating from the ground surface into the soil (Chow et al., 1988). The infiltration is the input for the change of water in soil.

Percolation can be considered as the flow of soil water through a porous media of soil (Parvizi et al., 2018). Percolation water is the vertical transport of water from the upper to the lower soil layers. The vertical transport of pesticides in the soil layers thanks to the percolation of water.

Residual water content is the soil water content at which no more soil water removed by the evaporation in soil, thus it is the lowest water content in soil. This value is the lower bound of water content in the SPEC model. This parameter is quite difficult to obtain in practice because it relates to very high suction pressure. This value is normally obtained by extrapolation of observed pairs of water content and suction head. In the regions where rainfall occurs almost all seasons like Japan, the lowest water content in the soil could be greater than residual water content. Therefore, the applied residual water content in the SPEC model can be used a higher value than its actual value.

Wilting point is the soil water content that is held so tightly by the soil matrix that roots cannot absorb this water and a plant will wilt. This parameter is lower than field capacity. It is usually referred at the matric potential of -1.5 MPa or -1500 kPa (Kirkham, 2014). It is considered as a lower limit of water content in soil in SWAT model. In Japan, without dry season, the Wilting point can be taken at the matric potential of -1 bar or -100 MPa (Maeda et al., 1983).

Field capacity is the water content in soil at which the equilibrium between suction force of soil and the gravity is obtained. However, the static equilibrium is never reach because soil water is dynamic and affected by many factors such as drainage to lower soil, evaporation, rainfall, irrigation, dewdrops and thus there is no single value for field capacity (Kirkham, 2014). The field capacity varies with the soil types and can be measured directly or indirectly referred at the matric potential of -0.033 MPa or -33 kPa (Kirkham, 2014). The field capacity in most of soils can be refereed at matric potential of -1/3 bar or -33.3 kPa; however, in Japan soils, the field capacity should be referred at the matric potential of -1/20 bar or -5kPa for soils with large amount of precipitation (Maeda et al., 1983).

Porosity is the ratio between the void and the total soil volumes. It is often expressed in percentage or m^3/m^3 or m/m in the SI (International System) unit.

Saturated water content is the water content in soil at which the whole void in soil occupied by the water. In theory, the saturated water content can be equal to porosity; however in the soil often exists air trapped, thus the saturated water content is smaller than porosity. It can be approximately equal to 90-95% of porosity (Van Genuchten et al., 1991). When the soil water content at saturation (equal to the saturated water content), the part of water that higher than field capacity is drained to below layer. The time for saturated water content to drain downward and is reduced to field capacity is from 1 to 3 days. Therefore, the transport of water from above soil layer to below soil layers occurs only when the water content in above soil layer is higher than its field capacity and the water content in right below layer is less than saturated water content. In numerical models, the saturated water content is used as the upper limit for simulating soil water content.

2.1.2 Sediment model

The Modified Universal Soil Loss Equation (MULSE) was developed by Williams (Williams, 1975) from the Universal Soil Loss Equation (USLE), in which the runoff replaced the rainfall factor. The USLE in US (The United States) unit is shown as below (Wischmeier and Smith, 1965),

$$SED = R * K * L * S * C * P \qquad 2.8$$

where *SED* is the computed soil loss per unit area; *R* is the rainfall factor which is the number of erosion-index units in a normal year's rain. The erosion index is a measure of the erosive force of specific rainfall; *K* is the soil-erodibility factor which is the erosion rate per unit of erosion index for a specific soil in cultivated continuous fallow, on a 9-percent slope 72.6 feet long; L is the slope-length factor which is the ratio of soil loss from the field slope length to that from a 72.6-foot length on the same soil type and gradient; *S* is the slope-gradient factor which is the ratio of soil loss from the field gradient to that from a 9-percent slope; *C* is the cropping-management factor which is the ratio of soil loss from a field with specified cropping and management to that from the fallow condition on which the factor *K* is evaluated; *P* is the erosion-control practice factor which is the ratio of soil loss with contouring, strip-cropping, or terracing to that with straight-row farming, up-and-down slope. Later, in the study of Wischmeier (Wischmeier and Smith, 1978) the conversion factors between US and SI units for all terms in the USLE were given to calculate soil loss in SI unit.

To improve the sediment prediction, MUSLE (in US unit) was developed by Williams based on the USLE, which is shown as below (Williams, 1975),

$$SED1 = 95 * \left(Q_j * A * q_p\right)^{0.56} * K * LS * C * P \qquad 2.9$$

where $SED1$ is the cumulative sediment yield (in US ton), Q_j is the runoff volume (in acre-feet), q_p is the peak flow rate (in cubic feet per second), *LS* is the topographic factor and other terms were similar to those in ULSE. The SI unit of MUSLE was then given in the study of Williams (1995);

however, the unit of K was not reported. Fortunately, in another study the MUSLE in the SI unit was given (Smith et al., 1984),

$$SED1 = 11.8 * (Q_j * A * q_p)^{0.56} * K * LS * C * P \tag{2.10}$$

where $SED1$ is the cumulative sediment yield (in metric ton), Q_j is the runoff volume (in m^3), q_p is the peak flow rate (in m^3/s). In this study (Smith et al., 1984), the authors reported that *K* was obtained from Agricultural Handbook 537 (Wischmeier and Smith, 1978). In this Handbook, K was given in US unit. In addition, K can be computed directly based on sand, clay and organic carbon percentages (Sharpley and Williams, 1990; Williams, 1995). This equation will be presented in next chapter.

2.1.3 Pesticide model

Pesticide models have been used to forecast the pesticide concentration in water and soils. In the theoretical documentation of a popular model, SWAT (Soil and Water Assessment Tool), a series of equations were given to simulate pesticide fate and transport (Neitsch et al., 2011). Most of equations from SWAT model were selected for the pesticide simulation in the SPEC model.

Photodegradation is one of the degradation of pesticides after their release into the environment. It becomes important when a pesticide is directly applied to soil or not significantly intercepted by plants (Katagi, 2004). The half-life for a pesticide defines the number of days required for a given pesticide concentration to be reduced by one-half (Neitsch et al., 2011). Therefore, the photodegradation half-life for a pesticide is the required days for that pesticide to be reduced by one-half by photodegradation process. This pesticide parameter is used to calculate the fate and transport of pesticide.

Biodegradation is the process by which organic substances are broken down into smaller compounds by living microbial organisms (Joutey et al., 2013). Similar to photodegradation half-life, the biodegradation half-life for a pesticide is the required days for that pesticide to be reduced by one-half by biodegradation process. This pesticide parameter is used to calculate the fate and transport of pesticide.

The *Q10* is a measure of the degree to which a biological process depends on temperature. It is defined as the ratio between the rate of a biological process at two temperatures separated by 10 degrees Celsius (Sterratt, 2013).

The distribution coefficient, *Kd*, is the soil-water partitioning coefficient. *Kd* (L/kg) is the ratio of the sorbed concentration (mg/kg) to the dissolved concentration (mg/L) at equilibrium of a chemical (Neitsch et al., 2011; U.S. EPA, 1996).

The soil organic carbon-water partitioning coefficient, *Koc*, is the ratio of the mass of a chemical that is adsorbed in the soil per unit mass of organic carbon in the soil per the equilibrium chemical concentration in solution. It is the "distribution coefficient" (*Kd*) normalized to total organic carbon content. *Koc* (L/kg) values are used to calculate the mobility of organic soil contaminants (U.S. EPA, 1996).

In the application of the SPEC model, four types of pesticides (including herbicides and insecticides) were used, which were Atrazine, Metolachlor, Clothianidin, and Imidacloprid. Some important factors that affect the fate and transport of pesticides are discussed as below,

Atrazine is a herbicide (Hayes et al., 2010). Atrazine is thought to maintain high to medium mobility in soil, and should not adsorb readily to sediment. Atrazine is is very stable in soil and dissipate slowly through degradation by soil microorganisms. Although the half-life of 50 days was reported for laboratory conditions, in practice atrazine persisted in soil for more than four months. Atrazine is thought not to volatilize (FAO, 2000). The photodegradation half-life of 45 days was reported in laboratory conditions for Atrazine applied in California loam soil (CDPR, 2001).

Metolachlor is a herbicide (Heydens et al., 2010). Metolachlor was registered with the EPA in 1976. It is a selective herbicide for the control of annual grass weeds, yellow nutsedge, and some broadleaf species (Heydens et al., 2010). Metolachlor is expected to be moderately to highly mobile in soil due to the relatively low soil/water partitioning (U.S. EPA, 2008). Substantial leaching of metolachlor from soil by run-off is expected to occur (U.S. EPA, 1995). The mobility of metolachlor in soil varies depending on the characteristics of the soil where it is applied: high organic content may increase sorption (U.S. EPA, 1995). The soil photolysis half-life of metolachlor when exposed to natural sunlight was reported to be 8 days (U.S. EPA, 1995).

Clothianidin is an insecticide (Vernon and van Herk, 2013). Clothianidin appears to be a persistent compound under most field conditions (U.S. EPA, 2010). Biodegradation half-life of clothianidin was reported to be 148 - 365 days, and *Koc* of 84 - 129 L/kg in laboratory conditions (U.S. EPA, 2010). The very slow rate of dissipation that was observed in field studies suggests that photolysis probably is not significant under most actual-use conditions (U.S. EPA, 2010).

Imidacloprid is an insecticide (Vernon and van Herk, 2013). Biodegradation half-life in field condition was reported to be 26.5 - 229 days, soil photolysis half-life was reported to be 38.9 days, *Koc* range was 132 - 310 L/kg (CDPR, 2016).

2.2 Field scale experiment

In calibration and validation of the model, the observed data are required to check the match between the simulated results of the model with the observed data. In pollutant runoff model, the observed data of runoff water, sediment and studied pesticides are required. These kinds of data require rainfall and other related weather data as their inputs. However, it is difficult to conduct pollutant runoff if using natural rainfalls because we don't know exact the time for occurring of rainfall. To overcome this difficulty, the using of rainfall simulator could be effective way. Rainfall simulators are widely used for numerous soil, agricultural and environmental studies (Abudi et al., 2012). The main advantages of rainfall simulators are the ability to take many measurements quickly without having to wait for natural rain; to work with constant controlled rain; it is usually quicker and simpler to set up a simulator over existing cropping treatments than to establish the treatments on runoff plots (Hudson, 1993). However, there are some disadvantages of rainfall simulators, such as measurements of runoff and erosion from simulator tests on small plots cannot be extrapolated to field conditions; simulators are likely to be affected by wind, but having to erect windshields undermines the advantage of simplicity (Hudson, 1993).

Chapter 3. Materials and Methods

3.1 Model development

3.1.1 SPEC model description

SPEC is a one directional physical based mathematic model developed (Boulange et al., 2016) to access Soil-PEC (Predicted Environmental Concentrations in agricultural Soils) for pesticide residues in upland field environments. It was coded in Excel Visual Basic Application thus it is very easy to use as well as to perform post processing of the simulation results. In addition, it requires relatively less input data. It was successfully calibrated and validated for predicting the water content and concentrations of atrazine and metolachlor in 5 cm deep soil (Boulange et al., 2016). However, there are some limitations in the SPEC model. The code for Curve Number (CN) method applied to simulate runoff water was not accurate. The simulations of runoff sediment and pesticide concentrations in runoff water and in sediment were not available. The sediment simulation is need for simulating the sediment yield and sediment concentration in runoff water as well as the pesticide concentration in runoff sediment. Another limitation in the SPEC model is that it simulates the pesticide concentration in two layers of soil only. In this study, the development will focus on writing codes for pollutant runoff module as well as improving simulation of pesticide in soil by increasing numbers of soil layers. The model was developed with the assumptions (1) two vertical boundary conditions which are the flux from rainfall or irrigation at the top and the free discharge at the bottom of the system; and (2) lateral flow in subsoil layer was assumed to be zero.

The improvements were made for simulating the pollutant runoff in small time steps. The pollutant runoff includes the time to first runoff, runoff rate, cumulative runoff, sediment yield, and sediment concentration, pesticide concentrations in runoff water and in sediment. The improvement of this study allows the users to calculate pesticide concentration in every soil layer with unlimited numbers of soil layers.

The order of simulations in improved SPEC model is presented in Figure 3.1. The first simulation should be conducted for the runoff, next simulation for sediment and finally for the simulation of pesticide concentration in soil layers. There kinds of observed data are required for calibration and validation. The first observed data are used for runoff simulation including runoff rate, cumulative runoff, and the time to first runoff. The second observed data are used for sediment simulation including sediment yield and sediment concentration. The third observed data are used for simulating pesticide including the pesticide concentration in runoff water and in sediment as well as the pesticide concentrations in soil layers.

The additional codes were also integrated in the SPEC model for simulating the statistical indexes and Monte Carlo simulations. The statistical indexes allow the users to quick evaluate the model performance. The Monte Carlo simulations (MCS) in combination with a regression analysis in Microsoft Excel support the users in sensitivity analysis. MCS also supports the users in calibration/validation and uncertainty analysis.

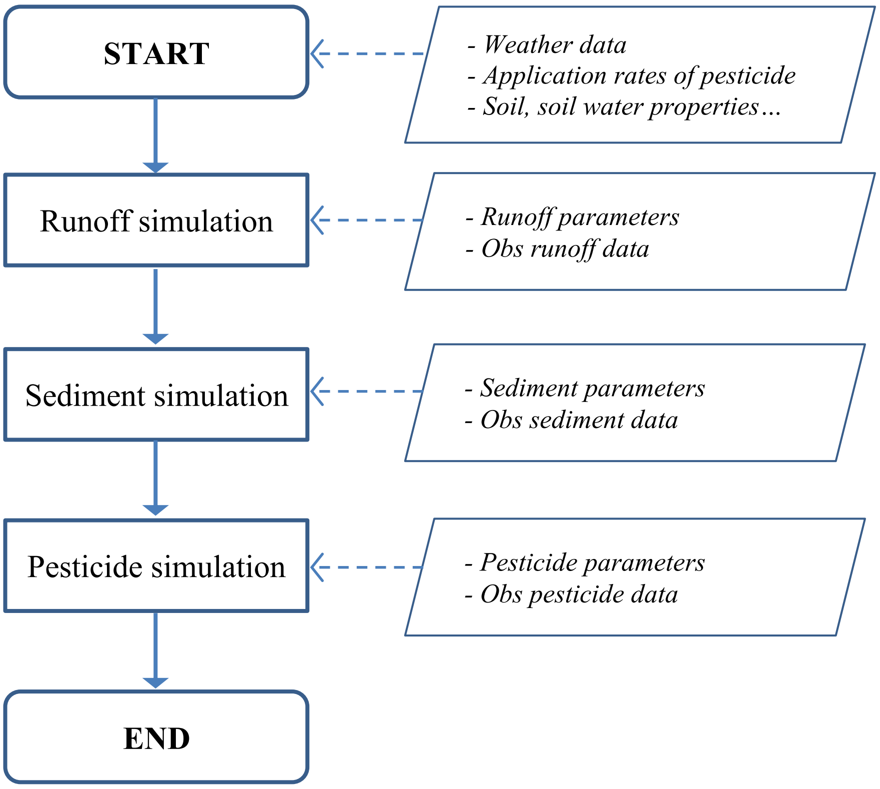


Figure 3.1. Flowchart for pesticide simulation in SPEC model

3.1.2 Simulation of surface runoff water

The code was built to calculate surface runoff using two methods, which were NRCS (National Resources Conservation Service) Curve number (CN) method and Green-Ampt method. The CN method is a direct method to calculate the cumulative runoff while the Green-Ampt method is an indirect method to calculate the runoff rate.

3.1.2.1 The Curve number method

In CN method, the runoff, Q, occurs only when the rainfall, P, exceeds a threshold, I_a. The general form of cumulative surface runoff in time step j is determined in equation below,

$$Q_{j,1} = \frac{\left(RF_{j,1} - Ia_{j,1}\right)^2}{\left[RF_{j,1} + (1 - Ia_{j,1}) * S_{j,1}\right]} \qquad \text{for } RF_{j,1} > Ia_{j,1} \qquad 3.1$$

$$Q_{j,1} = 0 \qquad \text{for } RF_{j,1} \leq Ia_{j,1} \qquad 3.2$$

$Ia_{j,1}$ is the initial abstraction in time step *j*, $S_{j,1}$ is the retention parameters at time step *j*. The relationship between $Ia_{j,1}$ and $S_{j,1}$ ($Ia_{j,1}$ = 0.2*$S_{j,1}$) is used by NRCS (USDA Natural Resources Conservation Service, 1999). Let $\lambda = Ia_{j,1}/S_{j,1}$ be the initial abstraction ratio which is required to be entered in SPEC model by the users. The λ value will be found in calibration/validation procedure of cumulative runoff and runoff rate.

The runoff amount in every time step (or the runoff rate) is calculated by subtracting two values of cumulative runoffs at two consecutive time steps,

$$dQ_{j,1} = Q_{j,1} - Q_{j-1,1} \qquad 3.3$$

where $dQ_{j,1}$ is the runoff rate in time step j (in mm), $Q_{j,1}$, $Q_{j-1,1}$ are the cumulative runoff at time step *j* and *j-1* (in mm), respectively.

The retention parameter, $S_{j,1}$ (in mm) is the amount of water storage available in the soil profile, which depends on rate of infiltration at the soil surface. *S* is related to runoff curve number (CN_2) by the relationship,

$$CN_2 = \frac{25400}{(S + 254)} \qquad 2.4$$

CN_2 value is given in the NRCS document which varies with land cover, soil type, soil moisture contents and rainfall (USDA Natural Resources Conservation Service, 1986). Based on the relationships between cumulative rainfall and cumulative runoff in several rainfall events, the average value of *CN* ($CN2_{j,1}$) can be found. In case the area slope differs from 5%, CN_2 needs to be adjusted as follows,

$$CN_{2s} = \frac{(CN_3 - CN_2)}{3} * [1 - 2 * \exp(-13.86 * slp] + CN_2 \qquad 2.5$$

$$CN_1 = CN_2 - \frac{20 * (100 - CN_2)}{(100 - CN_2 + exp[2.533 - 0.0636 * (100 - CN_2)])} \qquad 2.6$$

$$CN_3 = CN_2 * exp[0.00673 * (100 - CN_2)] \tag{2.7}$$

where CN_1, CN_2, CN_3 are curve numbers (unitless) in three conditions 1 (dry), 2 (average) and 3 (wet) water contents, respectively; CN_{2s} is the adjusted CN_2 for slope different from 5%; and *slp* is the area slope (in m/m). In case *CN* varies with water content is selected in SPEC option, the *S* will be updated with the change of soil water content (Neitsch et al., 2011).

$$S_{j,1} = S_{max} * \left[1 - \frac{WC_j - WCr}{\left[(WC_j - WCr) + exp\left(w_1 - w_2 * \left(WC_j - WCr\right)\right)\right]}\right] \tag{3.4}$$

$$S_{max} = 25.4\left(\frac{1000}{CN1} - 10\right) \tag{3.5}$$

$$S_3 = 25.4\left(\frac{1000}{CN3} - 10\right) \tag{3.6}$$

$$w_2 = \frac{\left(ln\left[\frac{WCf}{1 - S_3 * S_{max}{}^{-1}} - WCf\right] - ln\left[\frac{WCs}{1 - 2.54 * S_{max}{}^{-1}} - WCs\right]\right)}{WCs - WCf} \tag{3.7}$$

$$w_1 = ln\left[\frac{WCf}{1 - S_3 * S_{max}{}^{-1}} - WCf\right] - w_2 * WCf \tag{3.8}$$

where S_{max}, S_j, S_3 are the retention parameters (in mm) for three water content conditions, 1 (for dry water content), 2 (for average water content) and 3 (for wet water content), respectively; WC_j, is the water content in the soil profile (in mm^3/mm^3) at time step j, *WCs*, *WCs*, *WCr* are the saturated water content, the field capacity and the residual water content (in mm^3/mm^3), respectively; *w1* and *w2* are the first and the second shape coefficients (unitless), respectively. Equations 3.4, 3.7, and 3.8 use average values from all soil layers. In the new time step, water contents will be updated, and thus $S_{j,1}$ will be updated.

3.1.2.2 The Green & Ampt method

The Green-Ampt method (Green and Ampt, 1911) determines the potential cumulative infiltration and thus the potential infiltration rate is found. The potential infiltration rate is determined by the subtraction of the potential cumulative infiltration values in 2 time steps. Comparing the potential infiltration rate to the rainfall intensity, the actual infiltration rate in every time step is determined. The actual infiltration rate is the smaller value between the potential infiltration rate and the rainfall intensity. The potential cumulative infiltration is given as below (Green and Ampt, 1911),

$$F_{C,t} = K_e * t + MP * d\theta * ln\left[1 + \frac{F_{C,j}}{MP * d\theta}\right] \qquad 3.9$$

where $F_{C,t}$ is the potential cumulative infiltration at time t (in mm), K_e is the effective hydraulic conductivity (in mm/min), t is the time after rainfall starts (in min), MP is the matric potential at wetting front (in mm), $d\theta$ is the effective water content (in mm³/mm³). However, it is difficult to solve Eq. 3.9 when simulation for a long term. Another equation to solve potential cumulative infiltration is more convenient which is given as below (Neitsch et al., 2011),

$$F_{C,j} = F_{C,j-1} + K_e * ts + MP * d\theta * ln\left[\frac{F_{C,j} + MP * d\theta}{F_{C,j-1} + MP * d\theta}\right] \qquad 3.10$$

where $F_{C,j}$, $F_{C,j-1}$ are the potential cumulative infiltration at time j and j-1, (in mm), respectively, ts is the time interval (in min), other terms were defined above. The Eq. 3.10 is solved to find $F_{C,j}$ by trial-and-error method. K_e is approximately equivalent to one-half the saturated hydraulic conductivity of the soil, K_s (Bouwer, 1966). K_e range (0.34 to 14.18 mm/h) for a fallow land or bare soil can be found in the study of Nearing (Nearing et al., 1996). The matric potential across the wetting front, MP (in mm) is determined by formula below (Rawls and Brakensiek, 1985),

$$\begin{aligned} MP = 10 * \exp(&6.5309 - 7.32561 * por + 0.001583 * m_c^2 + 3.809479 * por^2 \\ &+ 0.000344 * m_s * m_c - 0.049837 * m_s * por + 0.001608 * m_s^2 * por^2 \\ &+ 0.001602 * m_c^2 * por^2 - 0.0000136 * m_s^2 * m_c - 0.003479 * m_c^2 * por \\ &- 0.000799 * m_s^2 * por) \end{aligned} \qquad 3.11$$

where por is the porosity of the soil (in mm³/mm³), m_c is the clay percent, and m_s is the sand percent. The difference between the final and the initial water contents can be determined by equation below,

$$d\theta = por - \theta_0 \qquad 3.12$$

where $d\theta$ is the difference between the final and the initial water contents (in mm³/mm³) and θ_0 is the initial water content (in mm³/mm³).

In Green-Ampt method, the potential infiltration rate is determined based on the effective hydraulic conductivity, the potential cumulative infiltration, the matric potential at wetting front and the difference between the final and the initial water contents which is given in the equation below

(Green and Ampt, 1911),

$$dF_{C,j} = K_e * \left[1 + \frac{MP * d\theta}{F_{C,j}}\right] \qquad 3.13$$

where $dF_{C,j}$ is the potential infiltration rate at time step j (in mm/min), other terms were defined above.

The actual infiltration rate is determined by comparing the potential infiltration rate with rainfall intensity. When the potential infiltration rate is greater than the rainfall intensity, the actual infiltration rate equals to the rainfall intensity, otherwise, the actual infiltration rate equals to the potential infiltration rate.

$$dF_j = I_j \qquad \text{when } dF_{C,j} > I_j \qquad 3.14$$

$$dF_j = dF_{C,j} \qquad \text{when } dF_{C,j} \le I_j \qquad 3.15$$

where dF_j is the actual infiltration rate at time step j (in mm/min), I_j is the rainfall intensity at time step j (in mm/min), other terms were defined above.

The surface runoff occurs only when the rainfall intensity is greater than the potential infiltration rate. The surface runoff rate calculated by the subtraction between the rainfall intensity and the actual infiltration rate as below,

$$dQ_j = I_j - dF_{C,j} \qquad \text{when } I_j > dF_{C,j} \qquad 3.16$$

The cumulative runoff is determined based on the cumulative runoff in the previous time step and the runoff rate in current time step which is given in the equation below,

$$Q_j = Q_{j-1} + dQ_j \qquad 3.17$$

3.1.3 Simulation of soil water content

3.1.3.1 Soil evaporation

The soil evaporation in each soil layer is the water loss from that layer. The soil evaporation in each soil layer is needed for calculating water content in each soil layer. The procedure to calculate the soil evaporation is as follows (Neitsch et al., 2011),

Firstly, the evaporative demand is determined by,

$$Ez_i = \frac{ET * z_i}{[z_i + exp(2.374 - 0.00713 * z_i)]} \qquad 3.18$$

where Ez_i is the evaporative demand (in mm), ET is the potential evaporation (in mm), z_i is the bottom depth of soil layer i (in mm).

Secondly, the evaporation for soil layer is determined by,

$$Es_i = Ez_{i,zl} - Ez_{i,zu} * esco \qquad 3.19$$

where Es_i is the evaporation for the soil layer i (in mm), z_l is the bottom depth of the layer (in mm), z_u is the top depth of the layer (in mm), *esco* is the evapotranspiration coefficient (unitless). As the value for esco is reduced, the model is able to extract more of the evaporative demand from lower levels. The default value of *esco* is 1.0.

Thirdly, the evaporative demand adjusted for water content below field capacity is determined by,

$$Es1_i = Es_i * exp\left[\frac{2.5(WC_i - WCf_i)}{WCf_i - WCr_i}\right] \qquad \text{when } WC_i < WCf_i \qquad 3.20$$

$$Es1_i = Es_i \qquad \text{when } WC_i \geq WCf_i \qquad 3.21$$

where $Es1_i$ is the evaporative demand adjusted for water content below field capacity for soil layer i (in mm), other terms were defined above.

3.1.3.2 Water content simulation

In improved SPEC model, the water contents are calculated for all soil layers for every time step. The input and output of water for soil layers are described in Figure 3.2. In every time step, the water content in each soil layer is calculated based on its current water content, supplied water (percolation) received from above layer or infiltration (for the first layer), and water loss through soil water evaporation. The input water for the first layer and for layer i ($i > 1$) are the infiltration and percolation water from right above its layer. The water outputs for each soil layer are percolation water to the layer right below its layer and evaporation from its layer. The procedure for calculating water content in every soil layer is described as below,

First, the water capacity defined as a water content in the soil layer after considering the infiltration and evaporation and the water capacity in each layer is calculated by equation below,

$$WCc_{j,1} = WC_{j,1} + \frac{dF_j - Es1_{j,1}}{L_1} \qquad \text{for layer 1} \qquad 3.22$$

$$WCc_{j,i} = WC_{\mathrm{j,i}} + \frac{Per_{j,i-1} - Es1_{j,i}}{L_i} \qquad \text{for layer } i > 1 \qquad 3.23$$

where $WCc_{j,1}$, $WCc_{j,i}$ are the water capacities for soil layer 1 and $i > 1$ in time step j (in mm^3/mm^3 or unitless), respectively, $WC_{j,1}$, $WC_{j,i}$ are the volumetric water contents for soil layer 1 and $i > 1$ in time step j (in mm^3/mm^3), dF_j is the actual infiltration rate in time step j (mm), $Per_{j,i-1}$ is the percolation water from right above layer i-1 in time step j (in mm), L_i is the depth for soil layer i (in mm), and other terms were defined as above.

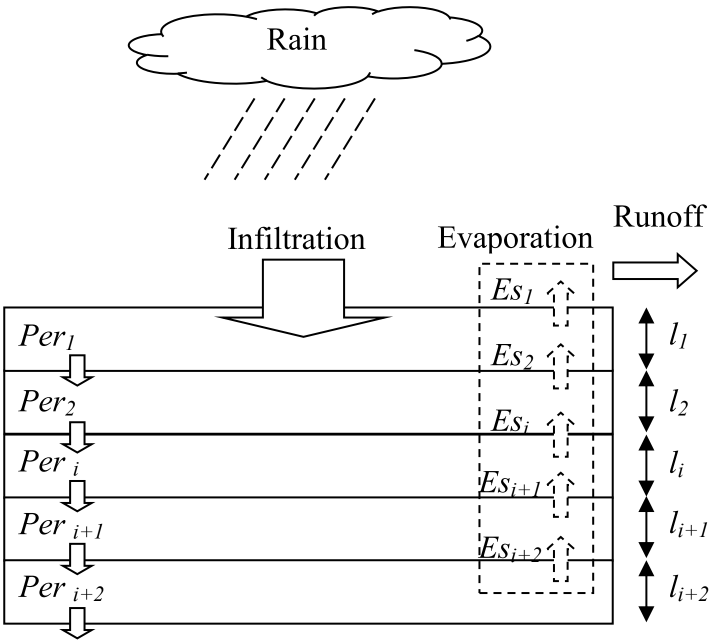


Figure 3.2. Conceptual hydrological processes for multiple soil layers in SPEC model

The minimum value of water content in each soil layer is the residual water content. There is no soil water content removed by the soil evaporation in the case water content in the soil layer equals to the residual water content. In case the water content is higher than field capacity (the water excess) the water content is allowed to discharge into the right below layer. The travel time for the excess of water in the soil layer is assumed to be equal to the time for saturated water content reduced to field capacity which is often occurred in one to two days. Therefore, the portion of the excess of water which is allowed to flow to under layer is proportional to the excess of water, the time step and inversely proportional to the travel time. The updated water content in layer i at time step j is calculated by equation below,

$$WCu_{j,i} = WCc_{j,i} - \frac{ts}{T\_travel * 60} * \left(WCc_{j,i} - WCf_i\right) \qquad 3.24$$

where $WCc_{j,1}$, $WCc_{j,i}$ are the water capacities for soil layer 1 and $i > 1$ (in mm³/mm³ or unitless), respectively, $WC_{j,1}$, $WC_{j,i}$ are the volumetric water contents for soil layer 1 and $i > 1$ (in mm³/mm³), $Per_{j,i-1}$ is the percolation water from right above layer i-1 (in mm), L_i is the depth for soil layer *i* (in mm), and other terms were defined as above.

The available water that is ready for percolation (portion of excess of water) (discharging to right below layer) in every time step *j* in the soil layer *i* is determined by equation below,

$$WCX_{j,i} = \left(WCc_{j,i} - WCu_{j,i}\right) * L_i \qquad \text{if } WCc_{j,i} > WCf_i \qquad 3.25$$

where $WCX_{j,i}$ is the available water for soil layer *i* at time step *j* (in mm), other terms were defined as above.

The actual percolation which modified from the SWAT theory is determined by equation below (Neitsch et al., 2011),

$$Per_{j,i} = WCX_{j,i} * \left[1 - Exp\left[\frac{-Ks_i * ts/60}{(WCs_i - WCf_i) * L_{\mathrm{i}}}\right]\right] \qquad 3.26$$

where $Per_{j,i}$ is the actual percolation discharged from soil layer *i* at time step *j* (in mm), Ks_i is the saturated hydraulic conductivity for soil layer *i* (in mm/ time step), other terms were defined as above.

3.1.4 Simulation of water induced erosion

The Modified Universal Soil Loss Equation (MUSLE) in US unit was developed (Williams, 1975) which originated from Universal Soil Loss Equation (USLE) (Wischmeier and Smith, 1978, 1965). This MUSLE estimates sediment more accurate than that in USLE (Williams, 1975), it uses runoff influence instead of rainfall in USLE. Later, the MUSLE was converted to use in SI unit as below (Smith et al., 1984; Williams, 1995),

$$Sed_j = coef * \left(Q_j * 10^{-3} * A * q_p\right)^{exp} * K * C * P1 * LS * 10^6 \qquad 3.27$$

where Sed_j is the cumulative sediment yield at time step *j* (in g), Q_j is the cumulative surface runoff volume at time step *j* (in mm), q_p is the peak runoff rate (in m³/s), A is the plot area (in m²), K is the soil erodibility factor, C is the cover and management factor, $P1$ is the erosion-control practice factor, and LS is the topographic factor. In bare soil upland field condition and if there is no erosion-control practice, C and $P1$ are 1.0 (Wischmeier and Smith, 1978). The default values for $coef$ and exp are 11.8 and 0.56, respectively (Smith et al., 1984). The *coef* and *exp* of the MUSLE can be found by comparing the observed sediment with the simulated sediment. The additional observed data include cumulative runoff and peak discharge as well as soil type. This simulation using the Least squares method (Hodges and Moore, 1972; Watson, 1967). The peak runoff rate in rational method is determined by (Chow et al., 1988),

$$q_p = C_{ro} * I * A * 10^{-5}/36 \tag{3.28}$$

where q_p is the peak runoff rate (in m^3/s), C_{ro} is the runoff coefficient (unitless), I is the 30-minute rainfall intensity (in mm/h); and $10^{-5}/36$ is the unit conversion factor. Both C_{ro} and I must be entered into SPEC model for sediment simulation.

Runoff coefficient is the ratio of the inflow rate to the peak discharge rate in a rainfall event. The coefficient varies from storm to storm which is calculated by equation below (Chow et al., 1988),

$$C_{ro} = \frac{Q}{RF} \tag{3.29}$$

where Q is the cumulative surface runoff (in mm) and RF is the cumulative rainfall (in mm).

The soil erodibility factor, K, is determined by equation below (Sharpley and Williams, 1990; Williams, 1995),

$$K = f_{c-s} * f_{cl-si} * f_{oc} * f_{hi-s} \tag{3.30}$$

where K is the soil erodibility factor, the unit of K is still in US unit and is given in Agricultural Handbook 537 (Wischmeier and Smith, 1978) which is 0.01 ton.acre.h/(acre.ft-ton.in); f_{c-s} is a factor that gives low soil erodibility factors for soils with high coarse-sand contents and high values for soils with little sand, f_{cl-si} is a factor that gives low soil erodibility factors for soils with high clay to silt ratios, f_{oc} is a factor that reduces soil erodibility for soils with high organic carbon content, and f_{hi-s} is a factor that reduces soil erodibility for soils with extremely high sand contents. The factors are calculated as below,

$$f_{c-s} = \left(0.2 + 0.3 * exp\left(-0.256 * m_s * (1 - m_{si}/100)\right)\right) \tag{3.31}$$

$$f_{cl-si} = \left(\frac{m_{si}}{m_c + m_{si}}\right)^{0.3} \tag{3.32}$$

$$f_{oc} = \left(1 - \frac{0.25 * OC}{OC + exp(3.72 - 2.95 * OC)}\right) \tag{3.33}$$

$$f_{hi-s} = \left(1 - \frac{0.7 * (1 - m_s/100)}{(1 - m_s/100) + exp\left(-5.51 + 22.9 * (1 - m_s/100)\right)}\right) \tag{3.34}$$

where m_s is the percent sand content (0.05-2.00 mm diameter particles), m_{si} is the percent silt content (0.002-0.05 mm diameter particles), m_c is the percent clay content (< 0.002 mm diameter particles), and OC is the percent organic carbon content of the layer (%).

The topographic factor, LS, is the expected ratio of soil loss per unit area from a field slope to that from a 22.1-m length of uniform 9 percent slope under otherwise identical conditions. The topographic factor is calculated by (Wischmeier and Smith, 1978),

$$LS\_USLE = \left(\frac{L_{slp}}{22.1}\right)^m * (65.41 * sin^2\theta + 4.56 * sin\theta + 0.065) \tag{3.35}$$

where LS_USLE is the topographic factor (unitless), L_{slp} is the slope length (in m), m is the exponential term (unitless), and θ is the angle of the slope.

The exponential term, m, is calculated by (Neitsch et al., 2011),

$$m\_USLE = 0.6 * \left(1 - exp(-35.835 * slp)\right) \tag{3.36}$$

where m_USLE is the exponential term (unitless), slp is the slope of the plot expressed as rise over run (in m/m). The relationship between θ angle (between slope and horizontal line) and slp is determined as below (Wischmeier and Smith, 1978),

$$slp = \tan(\theta) \tag{3.37}$$

The concentration of sediment in surface runoff is calculated as below (Neitsch et al., 2011),

$$Csed_j = \frac{dSed_j}{A * dQ_j} \tag{3.38}$$

where $Csed_j$ is the concentration of runoff sediment at time step j (in g/L), $dSed_j$ is the sediment yield increment at time step j (in g), other terms were defined as above.

3.1.5 Simulation of pesticide

3.1.5.1 Pesticide parameter

The reference first-order rate constant of biodegradation is determined by equation below (Boesten et al., 1997),

$$K_{bio\_ref} = \frac{\ln 2}{HL_{bio} * 24 * 60} \qquad 3.39$$

where K_{bio_ref} is the reference first-order rate constant of biodegradation at 25°C (in $1/ts$), HL_{bio} is the biodegradation half-life of the pesticide (in d).

The first-order rate constant of biodegradation adjusted for the change of temperature is determined by equation below (Boesten et al., 1997),

$$K_{bioj} = K_{bio\_ref} * Q_{10}^{(T-25)/10} \qquad 3.40$$

where K_{bioj} is the first-order rate constant of biodegradation adjusted for the change of temperature (in $1/ts$), Q_{10} is the change of half-life given a 10°C change in temperature (unitless), and T is the temperature at which the half-life of the pesticide must be calculated (in °C).

The first-order rate coefficient of photodegradation is determined by equation below (Boulange et al., 2016),

$$K_{pho} = \frac{\ln 2}{HL_{pho} * f_{\mathrm{US}} * Energ * 1000} \qquad 3.41$$

where K_{pho} is the first-order rate coefficient of photodegradation (in m^2/kJ), HL_{pho} is the photochemical degradation half-life of the pesticide (in d), *Energ* is the average solar radiation measured during the experiment duration (in $\mathrm{MJ/m^2/d}$), f_{US} is the fraction of the UV-B radiation over the solar radiation (unitless), $f_{\mathrm{US}} = 0.001232$ (Watanabe et al., 2006).

The coefficient of photodegradation in every time step is determined by equation below,

$$K_{phoj} = K_{pho} * f_{US} * SR_j \qquad 3.42$$

where K_{phoj} is the coefficient of photodegradation (in $1/ts$), SR_j is the solar radiation in time step j (in $\mathrm{kJ/m^2}/ts$), other terms were defined as above.

The soil adsorption coefficient is determined by equation below,

$$K_d = \frac{C_{ds}}{C_w} \qquad 3.43$$

where K_d is the soil adsorption coefficient (in L/kg), C_{ds} is the pesticide concentration in dry soil compartment (in mg/kg), C_w is the pesticide concentration in solution (in mg/L).

The relationship between the soil adsorption coefficient and the soil adsorption coefficient normalized for soil organic carbon content is determined as below,

$$K_d = K_{oc} * OC/100 \qquad 3.44$$

where K_d is the soil adsorption coefficient (in L/kg), K_{oc} is the soil adsorption coefficient normalized for soil organic carbon content (in L/kg), OC is the percent mass of soil organic carbon (in %).

3.1.5.2 Pesticide mass

The mass of pesticides in soil layer i at time step j is determined by the mass balance of pesticides in that layer. Total pesticide masses in dry soil and soil water for soil layer are the subtraction between the input and output of cumulative pesticide masses for that soil layer which are determined as below,

$$Mpst_{j,1} = M0_{j,1} - \begin{pmatrix} Mbio_{j,1} + Mper_{j,1} + Mvol_{j,1} + Mpho_{j,1} \\ +Mrw\_pst_{j,1} + Msed\_pst_{j,1} \end{pmatrix} \qquad \text{for layer 1} \qquad 3.45$$

$$Mpst_{j,i} = Mper\_f_{j,i-1} - \left(Mbio_{j,i} + Mper_{j,i}\right) \qquad \text{for layer } i > 1 \qquad 3.46$$

where $Mpst_{j,1}$ and $Mpst_{j,i}$ are the total pesticide masses in dry soil and soil water for layer 1 (the first layer) and layer $i > 1$ at time step j, respectively (in mg); $M0_{j,1}$ is the input mass of pesticide in layer 1 at time step j, which depends on application time k (in mg); $Mper_{0,i-1}$ is the cumulative pesticide mass loss in percolation received from layer i-1 at time step $j = 0$ (in mg); $Mbio_{j,i}$ and $Mbio_{j,1}$ are the cumulative pesticide mass losses due to biodegradation for layer i and layer 1 at time steps j, respectively (in mg); $Mper_{j,i}$ and $Mper_{j,1}$ are the cumulative pesticide mass losses in percolation water for layer i and layer 1 at time steps j, respectively (in mg); $Mvol_{j,1}$ is the cumulative pesticide mass loss due to volatilization for layer *1* at time steps j (in mg); $Mrw\_pst_{j,1}$ is the cumulative pesticide mass loss in runoff water at time steps j (in mg); and $Msed\_pst_{j,1}$ is the cumulative pesticide mass loss in runoff sediment at time steps j (in mg).

The error in simulation of pesticide masses in soil layer 1 at time step j is determined by equation below,

$$MEr_{j,1} = \frac{100}{M0_{j,1}} * \begin{bmatrix} M0_{j,1} - Mds_{j,1} - Msw_{j,1} - Mbio_{j,1} - Mper_{j,1} - Mvol_{j,1} - Mpho_{j,1} \\ -Mrw_{pst_{j,1}} - Msed\_pst_{j,1} \end{bmatrix} \qquad 3.47$$

where $MEr_{j,1}$ is the pesticide mass error in soil layer 1 at time step j; $Mds_{j,1}$ and $Msw_{j,1}$ are the pesticide masses in dry soil and soil water compartments of soil layer 1 at time step j, respectively (in mg); other terms were defined as above.

The error in simulation of pesticide masses in soil layer i > 1 at time step j is determined by equation below,

$$MEr_{j,i} = \frac{100}{M0_{j,i}} * \left[M0_{j,i} - Mds_{j,i} - Msw_{j,i} - Mbio_{j,i} - Mper_{j,i}\right] \qquad 3.48$$

where $MEr_{j,i}$ is the pesticide mass error in soil layer i at time step j; $Mds_{j,i}$ and $Msw_{j,i}$ are the pesticide masses in dry soil and soil water compartments of soil layer i at time step j, respectively (in mg); other terms were defined as above.

The SPEC model allows the application of pesticides at three different times. The mass of pesticide at any application time is calculated as below,

$$PM_k = 0.1 * PR_k * A \qquad 3.49$$

where PM_k is the pesticide mass at application time k (in mg), PR_j is the application pesticide mass (as active ingredient) at application time k (in g/ha) (k = 1, 2, 3) , other terms were defined as above.

The input of pesticide in layer 1 at every application time, k, is calculated for 3 different application times as below,

Pesticide mass at the first application time is determined by,

$$M0_{j,1} = Mds0_1 + Msw0_1 + PM_1 \qquad 3.50$$

where $M0_{j,1}$ is the input of pesticide in layer 1 at the application time (in mg), $Mds0_1$ and $Msw0_1$ are the residual pesticide masses in dry soil and soil water in the first layer at the first application time (in mg), other terms were defined as above.

Pesticide mass at the second application time is determined by,

$$M0_{j,1} = Mds0_1 + Msw0_1 + PM_1 + PM_2 \tag{3.51}$$

Pesticide mass at the third application time is determined by,

$$M0_{j,1} = Mds0_1 + Msw0_1 + PM_1 + PM_2 + PM_3 \tag{3.52}$$

The input of pesticide mass for layer $i > 1$ at time step $j = 0$ is determined by,

$$Mper\_f_{0,i-1} = Mper_{0,i-1} + Mds0_i + Msw0_i \tag{3.53}$$

where $Mper_{0,i-1}$ is the cumulative pesticide mass loss in percolation received from layer i-1 at time step $j = 0$ (in mg), $Mper\_f_{0,i-1}$ is the input of pesticide mass for layer i at time step $j = 0$ (in mg), $Mds0_i$ and $Msw0_i$ are the residual pesticide masses in dry soil and soil water for layer i at time step $j = 0$ (in mg).

The input of pesticide mass for layer $i > 1$ at time step $j > 0$ is determined by,

$$Mper\_f_{j,i-1} = Mper\_f_{j-1,i-1} + dMper_{j,i-1} \tag{3.54}$$

where $Mper\_f_{j,i-1}$, $Mper\_f_{j-1,i-1}$ are the inputs of pesticide masses for layer i at time step j and j-1 (in mg), $dMper_{j,i-1}$ is the pesticide mass increment in percolation from right above layer i-1 transported to layer i at time step j (in mg).

The total mass of pesticide in dry soil and soil water compartment is determined by,

$$Mpst_{j,i} = Mds_{j,i} + Msw_{j,i} \tag{3.55}$$

The pesticide mass in dry soil compartment of layer i at time step j is determined by equation below,

$$Mds_{j,i} = Cds_{j,i} * A * L_i * Rb_i * ts \tag{3.56}$$

where $Cds_{j,i}$ is the pesticide concentration in dry soil compartment of layer i at time step j (in mg/kg); other terms were defined as above.

The pesticide mass in soil water compartment of layer i at time step j is determined by equation below,

$$Msw_{j,i} = Csw_{j,i} * A * WCu_{j,i} * L_i \tag{3.57}$$

where $Csw_{j,i}$ is the pesticide concentration in soil water of layer i at time step j (in mg/L); other terms were defined as above.

The output of cumulative pesticide masses in every layer including percolation, biodegradation, photodegradation, volatilization, runoff water and sediment are determined in the following equations.

The increment of pesticide mass loss in percolation water for layer i at time step j is determined as below,

$$dMper_{j,i} = Cper_{j-1,i} * A * Per_{j,i} * ts \tag{3.58}$$

where $dMper_{j,i}$ is the increment of pesticide mass loss in percolation water for layer *i* at time step *j* (in mg), $Cper_{j-1,i}$ is the pesticide concentration in percolation water (in mg/L), $Per_{j,i}$ is the percolation water (in mm/*ts*), other terms were defined as above.

The cumulative pesticide mass loss in percolation water for layer *i* at time step *j* is determined as below,

$$Mper_{j,i} = Mper_{j-1,i} + dMper_{j,i} \tag{3.59}$$

where $Mper_{j,i}$, $Mper_{j-1,i}$ are the cumulative pesticide mass losses in percolation water for layer *i* at time steps *j* and *j* - 1, respectively (in mg), other terms were defined as above.

The increment of pesticide mass loss due to biodegradation for layer i at time step j is determined as below,

$$dMbio_{j,i} = k_{bioj,i} * Cs_{j-1,i} * A * L_i * Rb_i * ts \tag{3.60}$$

where $dMbio_{j,i}$ is the increment of pesticide mass loss due to biodegradation for layer *i* at time step *j* (in mg), $k_{bioj,i}$ is the biodegradation coefficient adjusted for the change of temperature for layer *i* at time step j (in 1/*ts*), $Cs_{j-1,1}$ is the pesticide concentration in soil layer *1* at time step *j*-1 (in mg/kg), Rb_1 is the dry soil bulk density for layer *1* (in g/cm^3), other terms were defined as above.

The cumulative pesticide mass loss due to biodegradation for layer i at time step j is determined as below,

$$Mbio_{j,i} = Mbio_{j-1,i} + dMbio_{j,i} \tag{3.61}$$

where $Mbio_{j,i}$, $Mbio_{j-1,i}$ are the cumulative pesticide mass losses due to biodegradation for layer *i* at time steps j and j - 1, respectively (in mg), other terms were defined as above.

Similarly, the increment of pesticide mass loss due to photodegradation for layer *1* (the first layer) at time step j is determined as below,

$$dMpho_j = k_{phoj} * Cs_{j-1,1} * A * L_1 * Rb_1 * ts \tag{3.62}$$

where $dMpho_j$ is the pesticide mass increment due to photodegradation for layer *1* at time step j (in mg), k_{phoj} is the coefficient of photodegradation at time step *j* (1/*ts*), other terms were defined as above.

The cumulative pesticide mass loss due to photodegradation for layer *1* at time step *j* is determined as below,

$$Mpho_{j,1} = Mpho_{j-1,1} + dMpho_{j,1} \tag{3.63}$$

where $Mpho_{j,1}$, $Mpho_{j-1,1}$ are the cumulative pesticide mass losses due to photodegradation for layer *1* at time steps j and j - 1, respectively (in mg), other terms were defined as above.

The increment of pesticide mass loss due to volatilization for layer *1* at time step *j* is determined as below,

$$dMvol_{j,1} = k_{vj} * Cs_{j-1,1} * A * L_1 * Rb_1 * ts \tag{3.64}$$

where $dMvol_{j,1}$ is the increment of pesticide mass loss due to volatilization for layer *1* (the first layer) at time step *j* (in mg), k_{vj} is the volatilization coefficient at time step *j* (1/*ts*), other terms were defined as above.

The cumulative pesticide mass loss due to volatilization for layer *1* (the first layer) at time step j is determined as below,

$$Mvol_{j,1} = Mvol_{j-1,1} + dMvol_{j,1} \tag{3.65}$$

where $Mvol_{j,1}$, $Mvol_{j-1,1}$ are the cumulative pesticide mass losses due to volatilization for layer *1* at time steps j and j - 1, respectively (in mg), other terms were defined as above.

Two additional parameters accounted for the differences of pesticide concentrations in three solution components, which are runoff water, percolation water and soil water, were added in this SPEC model version. The first parameter, *alpha*, accounts for the difference of pesticide concentrations in mobile water (runoff water and percolation water) and in static water (soil water), and the second parameter, *beta*, accounts for the difference of pesticide concentrations in runoff water and in percolation water. In the SPEC model, it is assumed that ratios of pesticide concentrations are maintained throughout the model.

The pesticides in solution include pesticide in mobile water (percolation water and runoff water for soil layer 1) and pesticide in static water (or soil water). The relationship between the pesticide concentrations in solution and in its components (in mobile water and static water) for soil layer 1 is determined by equation below,

$$Cw_{j,1} * Vw_{j,1} = Cmw_{j,1} * Vmw_{j,1} + Csw_{j,1} * Vsw_{j,1} \qquad 3.66$$

where $Cw_{j,1}$, $Cmw_{j,1}$, $Csw_{j,1}$ are pesticide concentrations in solution, mobile water and static water, respectively (in mg/L); $Vw_{j,1}$, $Vmw_{j,1}$, $Vsw_{j,1}$ are volumes of solution, mobile water and static water, respectively (in L).

The relationship between pesticide concentrations in mobile water and in its components (runoff water and percolation water) is determined by,

$$Cmw_{j,1} * Vmw_{j,1} = Cper_{j,1} * Vper_{j,1} + Crw_{j,1} * Vrw_{j,1} \qquad 3.67$$

The ratio of pesticide concentrations in mobile water and in static water, *alpha*, is determined by,

$$alpha = \frac{Cmw_{j,1}}{Csw_{j,1}} \qquad 3.68$$

where $alpha$ is the ratio of pesticide concentrations in mobile water and in static water (unitless), $Cmw_{j,1}$ and $Csw_{j,1}$ are the pesticide concentrations in mobile water (runoff water and percolation water) and in static water (soil water) for soil layer 1, respectively.

$$Cw * Vw = Cmw * Vmw + Csw * Vsw \qquad 3.69$$

The ratio of pesticide concentrations in runoff water and in percolation water, *beta*, is determined by,

$$beta = \frac{Crw\_pst_{j,1}}{Cper\_pst_{j,1}} \tag{3.70}$$

where $beta$ is the ratio of pesticide concentrations in runoff water and in percolation water (unitless), $Crw\_pst_{j,1}$ and $Cper\_pst_{j,1}$ are the pesticide concentrations in runoff water and in percolation water (in mg/L) in soil layer 1, respectively.

The increment of pesticide mass loss in runoff water at time step j is determined as below,

$$dMrw\_pst_{j,1} = beta * Cper\_pst_{j-1,1} * A * dQ_j * ts \tag{3.71}$$

where $dMrw\_pst_{j,1}$ is the increment of pesticide mass loss in runoff water at time step j (in mg), other terms were defined as above.

The cumulative pesticide mass loss in runoff water at time step j is determined as below,

$$Mrw\_pst_{j,1} = Mrw\_pst_{j-1,1} + dMrw\_pst_{j,1} \tag{3.72}$$

where $Mrw\_pst_{j,1}$, $Mrw\_pst_{j-1,1}$ are the cumulative pesticide mass losses in runoff water at time steps j and j - 1, respectively (in mg), other terms were defined as above.

The increment of pesticide mass loss in runoff sediment at time step j is determined as below,

$$dMsed\_pst_{j,1} = epsilon_j * Cs_{j-1,1} * \left(dSed_j/1000\right) * ts \tag{3.73}$$

where $dMsed\_pst_{j,1}$ is the increment of pesticide mass loss in runoff sediment at time step j (in mg), $epsilon_j$ is, the pesticide enrichment ratio at time step j (unitless), 1000 is unit conversion, other terms were defined as above.

The pesticide enrichment ratio is determined by (Menzel, 1980),

$$epsilon_j = e\_coef * \left(C\_sed_j/1000\right)^{-0.2468} \tag{3.74}$$

where *e_coef* is the pesticide enrichment coefficient, the default value equals to 0.78 (Menzel, 1980). However, this parameter value can be calibrated in the SPEC model by the user.

The cumulative pesticide mass loss in runoff sediment at time step j is determined as below,

$$Msed\_pst_{j,1} = Msed\_pst_{j-1,1} + dMsed\_pst_{j,1} \qquad 3.75$$

where $Msed\_pst_{j,1}$, $Msed\_pst_{j-1,1}$ are the cumulative pesticide mass losses in runoff sediment at time steps j and j - 1, respectively (in mg), other terms were defined as above.

3.1.5.3 Pesticide concentration

There are two options to calculate pesticide concentration in every soil layer; these are pesticide concentration in soil with soil water content and that without soil water content.

The pesticide concentration in soil layer i at time step j (wet soil condition) is determined by the ratio between the pesticide mass (in dry soil and soil water) and the wet soil mass as below,

$$Cs_{j,i} = \frac{Mpst_{j,i}}{A * L_i * \ (Rb_i + \ WCu_{j,i})} \qquad 3.76$$

where $Cs_{j,i}$ is the pesticide concentration in soil layer i at time step j (wet soil condition) (in mg pesticides in dry soil and in soil water /kg wet soil), other terms were defined as above.

The pesticide concentration in soil layer i at time step j (dry soil condition) is determined by the ratio between the pesticide mass (in dry soil and soil water) and the dry soil mass as below,

$$Cs\_0W_{j,i} = \frac{Mpst_{j,i}}{A * L_i * \ Rb_{\mathrm{i}}} \qquad 3.77$$

where $Cs\_0W_{j,i}$ is the pesticide concentration in soil layer i at time step j (dry soil condition) (in mg pesticides in dry soil and in soil water /kg dry soil), other terms were defined as above.

The pesticide concentration in solid compartment of soil layer *1* is determined by,

$$Cds_{j,1} = \frac{Mpst_{j,1} * Kd_1}{A * L_1 * \left[Rb_1 * Kd_1 + \frac{WCu_{j,1} * (WCu_{j,1} * L_1 + Per_{j,1} + dQ_{j,1})}{WCu_{j,1} * L_1 + alpha * \left(Per_{j,1} + dQ_{j,1}\right)}\right]} \qquad 3.78$$

where $Cds_{j,1}$ is the pesticide concentration in solid compartment of soil layer *1* at time step j (in mg pesticide in dry soil/kg dry soil), Kd_1 is the soil adsorption coefficient in layer *1* (in L/kg), other terms were defined as above.

$$Cds_{j,i} = \frac{Mpst_{j,i} * Kd_{\mathrm{i}}}{A * L_i * \left(Rb_{\mathrm{i}} * Kd_{\mathrm{i}} + WCu_{j,i}\right)}$$

The pesticide concentration in solid compartment of soil layer $i > 1$ is determined by,

$$Cds_{j,i} = \frac{Mpst_{j,i} * Kd_{\mathrm{i}}}{A * L_i * \left[Rb_{\mathrm{i}} * Kd_{\mathrm{i}} + \frac{WCu_{j,i} * (WCu_{j,i} * L_i + Per_{j,i})}{WCu_{j,i} * L_i + alpha * Per_{j,i}}\right]} \qquad 3.79$$

where $Cds_{j,i}$ is the pesticide concentration in solid compartment of soil layer i at time step j (in mg pesticide in dry soil/kg dry soil), Kd_i is the soil adsorption coefficient in layer i (in L/kg), other terms were defined as above.

The pesticide concentration in solution phase in soil layer i at time step j is determined as below,

$$Cw_{j,i} = \frac{Cds_{j,i}}{Kd_{\mathrm{i}}} = \frac{Mpst_{j,i}}{A * L_i * (Rb_{\mathrm{i}} * Kd_{\mathrm{i}} + WCu_{j,i})} \qquad 3.80$$

where $Cw_{j,i}$ is the pesticide concentration in solution phase in layer i at time step j (in mg/L), other terms were defined as above.

The pesticide concentration in soil water is determined by equation below,

$$Csw_{j,i} = \frac{Cw_{j,i} * \left(dQ_j + Per_{j,i} + WCu_{j,i} * L_i\right)}{alpha * \left(dQ_j + Per_{j,i}\right) + WCu_{j,i} * L_i} \qquad 3.81$$

where $Csw_{j,i}$is the pesticide concentration in soil water in layer i at time step j (in mg/kg), other terms were defined as above.

The pesticide concentration in percolation water is determined by the equation below,

$$Cper\_pst_{j,1} = \frac{alpha * Csw_{j,1} * \left(dQ_j + Per_{j,1}\right)}{beta * dQ_j + Per_{j,1}} \qquad \text{for layer 1} \qquad 3.82$$

$$Cper\_pst_{j,i} = alpha * Csw_{j,i} \qquad \text{for layer } i > 1 \qquad 3.83$$

where $Cper\_pst_{j,i}$ is the pesticide concentration in percolation water for layer i at time step j (in mg/L), other terms were defined as above.

The pesticide concentration in runoff water is determined by the equation below,

$$Crw\_pst_j = \frac{dMrw\_pst_j}{A * dQ_j} \qquad 3.84$$

where Crw_pst_j is the pesticide concentration in runoff water at time step j (in mg/L), other terms were defined as above.

The pesticide concentration in runoff sediment is determined by the equation below,

$$C\_sed\_pst_{j,1} = epsilon_j * Cds_{j,1} \tag{3.85}$$

where $C\_sed\_pst_{j,1}$ is the pesticide concentration in runoff sediment at time step j (in mg/kg), other terms were defined as above.

3.2 Sensitivity analysis, calibration and validation

The model can be used for prediction only when it was calibrated and validated to ensure the model can generate the similar results of observed data. Both calibration and validation require observed data. Calibration is a procedure that adjusts the value of parameters to give a best fit of an output with corresponding observed data. The result of calibration is the final values of parameters (Trucano et al., 2006). Validation is a procedure to check the final values of parameters. If the model result fit the observed data then a validation is finished. If the parameters needed to be adjust to fit the output with the observed data then the validation becomes the calibration (Trucano et al., 2006). The difference between calibration and validation is that in the calibration, parameters are adjusted to fit the model output with observed data however in the validation, parameters cannot be adjusted but using the values of parameters obtained from the calibration to generate the output that fits the observed data (Trucano et al., 2006).

Prior to calibrate and validate the parameters for the specific model output, it requires to do sensitivity analysis to find the parameters affected most to the output results (Jacques et al., 2006; Trucano et al., 2006). This procedure is supported by Monte Carlo simulation and Regression analysis in Excel.

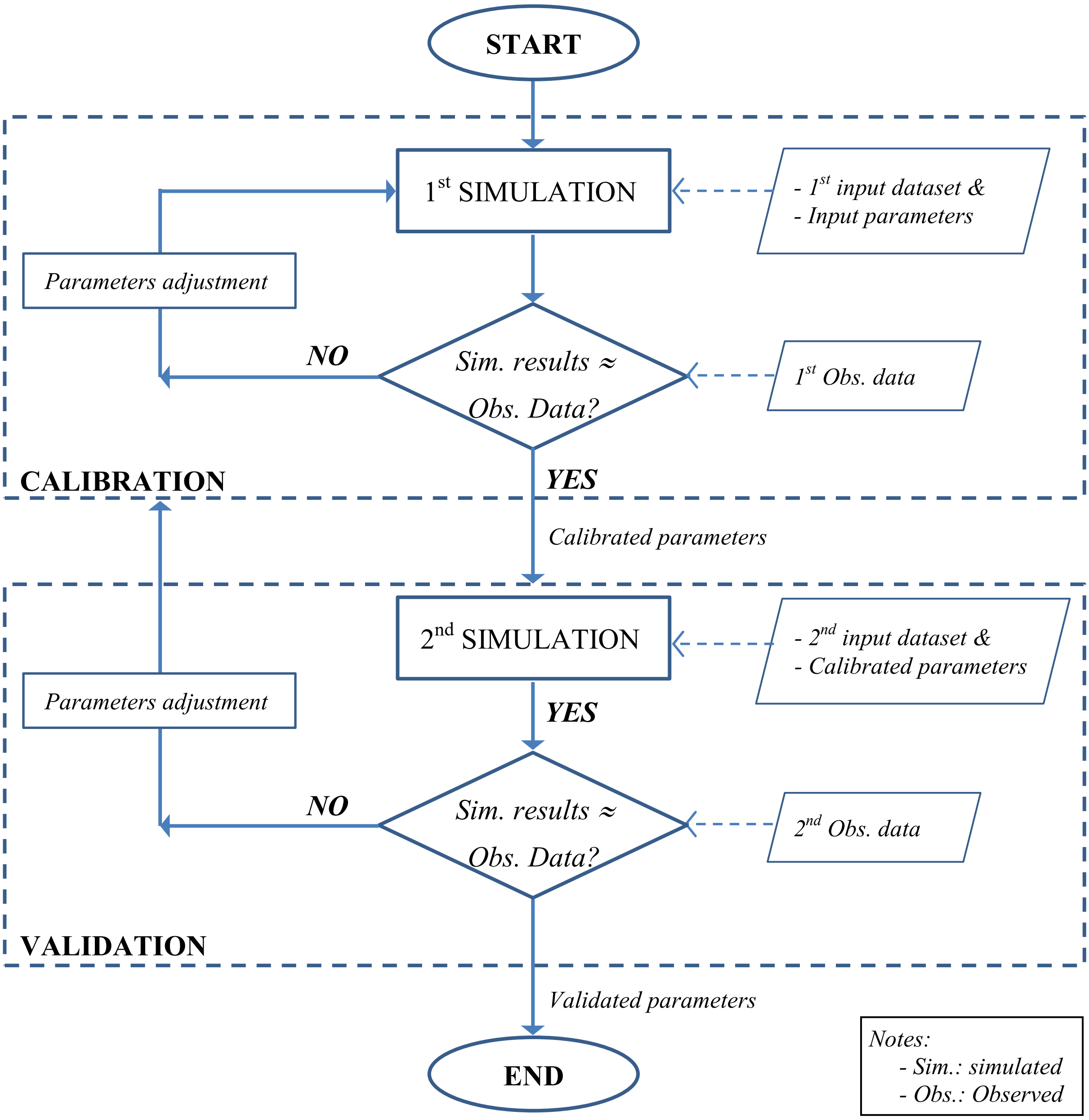


Figure 3.3. Flowchart for calibration and validation in SPEC model

As shown in Figure 3.3 that there are two datasets required for calibration and validation. In calibration procedure, the sensitive parameters are found if the simulated results are approximately equal to the corresponding observed data. The criteria to evaluate the agreement between simulated results and the observed data are based upon the statistical indexes which will be discussed in next section and the graph for simulated results and the observed data. The validation is conducted by using another input dataset and corresponding observed data to check the validity of the sensitive parameters found in calibration. If the agreement between the simulated results and the observed data is not satisfied and it needs some adjustment of parameters to obtain the agreement then the validation becomes calibration. In this case, the additional dataset and the observed data are required to complete the validation.

3.3 Model performance

The model performance can be evaluated in quantitative way through means of statistical indexes. There are four popular statistical indexes often used for evaluating model performance which are Root Mean Squared Error (*RMSE*), Coefficient of determination (R^2), Nash-Sutcliffe Efficiency (*NSE*) and Percent mean error or Percent Bias (*PBIAS*). The VBA code was built for these four indexes which integrated in SPEC model to evaluate the model performance as well as to support Monte Carlo simulation for specific objective output.

3.3.1 Root mean square error (RMSE)

Root mean square error (*RMSE*) is one of the commonly used error indexes. It is commonly accepted that the lower the *RMSE* the better the model performance (Guo et al., 2014; Moriasi et al., 2015, 2007). *RMSE* is determined as below,

$$RSME = \frac{100\%}{\bar{O}} * \sum_{i=1}^{n} \sqrt{\frac{(O_i - P_i)^2}{n}} \qquad 3.86$$

where *RMSE* is the root mean square error (in %), P_i is the predicted value or model outputs, O_i is the observed value, n is numbers of observed samples, and $\bar{O}$ is the observed average value.

3.3.2 Coefficient of determination - R square (R^2)

Coefficient of determination - R square (R^2) describes the degree of collinearity between simulated and observed data which is determined by,

$$R^2 = \left[\frac{n * \sum_{i=1}^{n} O_i * P_i - \sum_{i=1}^{n} O_i * \sum_{i=1}^{n} P_i}{\sqrt{\left[n * \sum_{i=1}^{n} O_i{}^2 - (\sum_{i=1}^{n} O_i)^2\right] * \left[n * \sum_{i=1}^{n} P_i{}^2 - (\sum_{i=1}^{n} P_i)^2\right]}} \right]^2 \qquad 3.87$$

where R^2 is the coefficient of determination (unitless), other terms were defined above.

R^2 ranges from 0.0 to 1.0. Higher values indicate less error and values greater than 0.5 are considered acceptable performance (Santhi et al., 2001).

3.3.3 Nash - Sutcliffe efficiency (NSE)

The efficiency of the model can be evaluated by Nash - Sutcliffe efficiency (*NSE*) which is determined by the equation below (Nash and Sutcliffe, 1970),

$$NSE = 1 - \frac{\sum_i^n (O_i - P_i)^2}{\sum_i^n (O_i - \bar{O})^2} \tag{3.88}$$

where *NSE* is the Nash - Sutcliffe efficiency (unitless), other terms were defined above.

NSE may range from 1 to - ∞. The *NSE* value of 1 indicates the model perfectly predict the measured data. The *NSE* value of 0 indicates the sum of squares of the difference between the measured and the predicted is equal to the sum of squares difference between the observed values and the mean of the observed values. The *NSE* values in range ($0 < NSE < 1$) are considered acceptable model performance. Negative values of *NSE* are considered unacceptable performance (Guo et al., 2014; Gupta et al., 2009; Krause et al., 2005; Moriasi et al., 2015, 2007; Moussa, 2010; Yuan et al., 2012).

3.3.4 Percent bias

Mean absolute error or Bias between observed data and predicted results, is expressed in percentage as below,

$$PBIAS = \frac{100\%}{n * \bar{O}} \sum_{i=1}^{n} (O_i - P_i) \tag{3.89}$$

where *PBIAS* is the mean error (in %), other terms were defined above. The optimal value of *PBIAS* is 0.0. The low values indicate accurate model simulation, positive values indicate model underestimation, and negative values indicate model overestimation (Gupta et al., 2009; Moriasi et al., 2007; Yuan et al., 2012).

The criteria to evaluate model performance are based mainly on *NSE* and *PBIAS*. The evaluation criteria to evaluate results water, sediment and pesticide are same for *NSE* criteria but different for *PBIAS*. The modification of model performance criteria which was made from criteria for evaluating model performance for monthly time step in the previous study is shown in Table 3.1 (Moriasi et al., 2007).

Table 3.1. Evaluation criteria for model performance

Performance Rating	***NSE***	***PBIAS* (%)**		
		Streamflow	Sediment	Pesticide*
1/ Very good	$0.75 < NSE \leq 1.00$	$PBIAS < \pm 10$	$PBIAS < \pm 15$	$PBIAS < \pm 25$
2/ Good	$0.65 < NSE \leq 0.75$	$\pm 10 \leq PBIAS < \pm 15$	$\pm 15 \leq PBIAS < \pm 30$	$\pm 25 \leq PBIAS < \pm 40$
3/ Satisfactory	$0.50 < NSE \leq 0.65$	$\pm 15 \leq PBIAS < \pm 25$	$\pm 30 \leq PBIAS < \pm 55$	$\pm 40 \leq PBIAS < \pm 70$
4/ Acceptable*	$0 < NSE \leq 0.5$			
5/ Unsatisfactory	$NSE < 0$	$PBIAS \geq \pm 25$	$PBIAS \geq \pm 55$	$PBIAS \geq \pm 70$

Notes: *: modified from the study of Moriasi et al., 2007

3.4 Monte Carlo simulation (MCS)

The Monte Carlo algorithm was applied in the SPEC model to (1) support the sensitivity analysis; (2) in combined with statistical code to support the calibration/validation procedure; and (3) generate output range with 95% confidence level. To run the MCS, the user need to enter numbers of iterations or loops (sample size), the ranges or percent changes of given parameters associated with specific output and click the MCS for that output. The sample size should be 250 (Boulange et al., 2016) to meet the normal distribution assumption.

3.4.1 MCS for sensitivity analysis

For specific output, assign possible ranges or percent changes of possible parameters to generate numbers of input parameters (independent variables) and output variables. Then, analyzed all independent as well as dependent variables using regression analysis in Microsoft Excel® to find the weighted factor of parameters. Parameters with significant level less than 5% and having high factor will be used in calibration/validation procedure.

The sample size of 250 is recommended as the program assumed a normal distribution for input parameter as well as output variables. In every iteration, the MCS assigns random values to individual parameters in their ranges or their percent changes, then this input parameters set are entered in the main SPEC program to generate corresponding output. Next, the statistical code is called to do statistical analysis to generate *RMSE*, R^2, *NSE* and *PBIAS*. Based on numbers of iterations, the MCS will determine if it use the parameters set having average (average option) or highest value of *NSE* (optimal option). In the next iteration, this parameters set is used for input parameters of the SPEC model.

3.4.2 MCS for calibration/validation procedure

By selecting optimal option and assigning ranges or percent changes of sensitive parameters, calibrated/validated parameters for specific output are found. In every loop, the statistical code is called for analysis to find the highest *NSE* for a given output, then it find the input parameters set that generated the highest *NSE* and assigns this parameters set for next simulation of SPEC. The iteration is completed until the last loop of MCS.

3.4.3 MCS for output range with 95% confidence level

The Monte Carlo code combined with statistical code was integrated in SPEC model to generate the 95% interval of output (or output range with confidence level of 95%). This technique is considered an alternative to overcome small sample size of observed data.

3.4.4 Associated parameters for MCS

The simulated outputs include time to occur first runoff from the start of rainfall, runoff rate, cumulative runoff, sediment yield and concentration, pesticide concentrations in sediment and in runoff water, average water content in soil layers, and average pesticide concentration in all soil layers. These MCSs are available only in case the corresponding observed data are available. The first seven MCSs are available only when availability of observed runoff data, runoff option is allowed and event based is selected.

3.4.4.1 MCS for time to first runoff

This simulation is available only when simulation for rainfall event with small output time step. Seven parameters were assigned in MCS of time to first runoff. These parameters are saturated water content, field capacity, residual and initial water contents, saturated hydraulic conductivity, *CN* and the initial abstraction ratio. The optimal option should be selected to find the calibrated/validated parameters. The *CN* and the initial abstraction ratio affected to outputs results only when NRCS runoff method is selected.

3.4.4.2 MCS for runoff rate

This simulation is available only when simulation for rainfall event with small output time step. Seven parameters were assigned in MCS of runoff rate. These parameters are saturated water content, field capacity, residual and initial water contents, saturated hydraulic conductivity, CN and the initial abstraction ratio. The optimal option should be selected to find the calibrated/validated parameters. The *CN* and the initial abstraction ratio affected to outputs results only when CN runoff method is selected.

3.4.4.3 MCS for cumulative runoff

This simulation is available only when simulation for rainfall event with small output time step. Seven parameters were assigned in MCS of cumulative runoff. These parameters are saturated water content, field capacity, residual and initial water contents, saturated hydraulic conductivity, *CN* and the initial abstraction ratio. The optimal option should be selected to find the calibrated/validated parameters. The *CN* and the initial abstraction ratio affected to outputs results only when CN runoff method is selected.

3.4.4.4 MCS for sediment yield

This simulation is available only when simulation for rainfall event with small output time step. The coefficient of the soil erodibility factor K_{coef}, was the only parameter assigned in MCS for the sediment yield.

3.4.4.5 MCS for sediment concentration

As in Monte Carlo simulation for sediment yield, this simulation is available only when simulation for rainfall event with small output time step. The coefficient of the soil erodibility factor K_{coef}, was the only parameter assigned in MCS for the sediment concentration.

3.4.4.6 MCS for pesticide concentration in sediment

This simulation is available only when simulation for rainfall event with small output time step. Three parameters were assigned in MCS of pesticide concentration in sediment. These are the ratio of pesticide concentrations in mobile and static waters, *alpha*; the ratio of pesticide concentrations in runoff water and percolation water, *beta*; and the partitioning water/organic matter coefficient, *Koc*. In MCS for pesticide concentration in sediment, the *alpha* parameter was found to be the most sensitive parameter. Therefore, this MCS is used to find calibrated *alpha* parameter.

3.4.4.7 MCS for pesticide concentration in runoff water

As in MCS for pesticide concentration in sediment, this simulation is available only when simulation for rainfall event with small output time step. Similarly to MCS of pesticide concentration in sediment, three possible parameters were assigned in MCS of pesticide concentration in runoff water. These are *alpha*, *beta* and *Koc*. In MCS for pesticide concentration in runoff water for some case studies, the *beta* parameter water was found to be the most sensitive parameter. Therefore, this MCS is used to find calibrated *beta* parameter.

3.4.4.8 MCS for water content in specific soil layer

The codes enable to simulate the water content in specific soil layer as well as sampling depth value for both daily and small time steps. The users are require to select the water content at which layer and its time step, as well as the sample size and optimal option in MCS (numbers of iterations) . Seven parameters were assigned in this MCS to find optimal values of parameters. These parameters are saturated water content, field capacity, residual and initial water contents, saturated hydraulic conductivity, *CN* and initial abstraction ratio.

3.4.4.9 MCS for pesticide concentration in specific soil layer

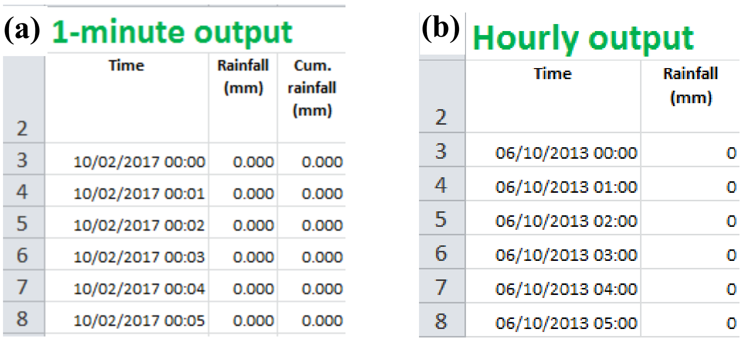
The codes enable to simulate the pesticide concentration in specific soil layer as well as sampling depth value for both daily and small time steps. The users are required to select the pesticide concentration at which layer and its time step, as well as the sample size and optimal option in MCS (numbers of iterations). Ten parameters were assigned in this MCS to find optimal values of parameters. These parameters are saturated water content and field capacity, dry bulk density of soil, half-life photodegradation, half-life biodegradation, the partitioning water/organic matter coefficient, *Q10*, pesticide enrichment ratio, *alpha* and *beta*.

Chapter 4. Results of the pollutant runoff module development

4.1 Results in development of a pollutant runoff module in SPEC model

4.1.1 Results in time step issue

The time step issue is solved by the improved SPEC model in which the smallest time step in improved SPEC model is one minute (Figure 4.1). The output time step is often selected depending on the available time step of rainfall and the time step of observed data. For example, in runoff pollutant observation in artificial rainfall events, the samplings in runoff are often collected in every ten minutes thus the output time step should be ten minutes. For an experiment, the constant intensity of an artificial rainfall allows using the smallest time step of one minute and thus the time to first runoff can be simulated with the precision of a minute. The flexible option of output time steps is shown in Figure 4.1 and Figure 4.2.



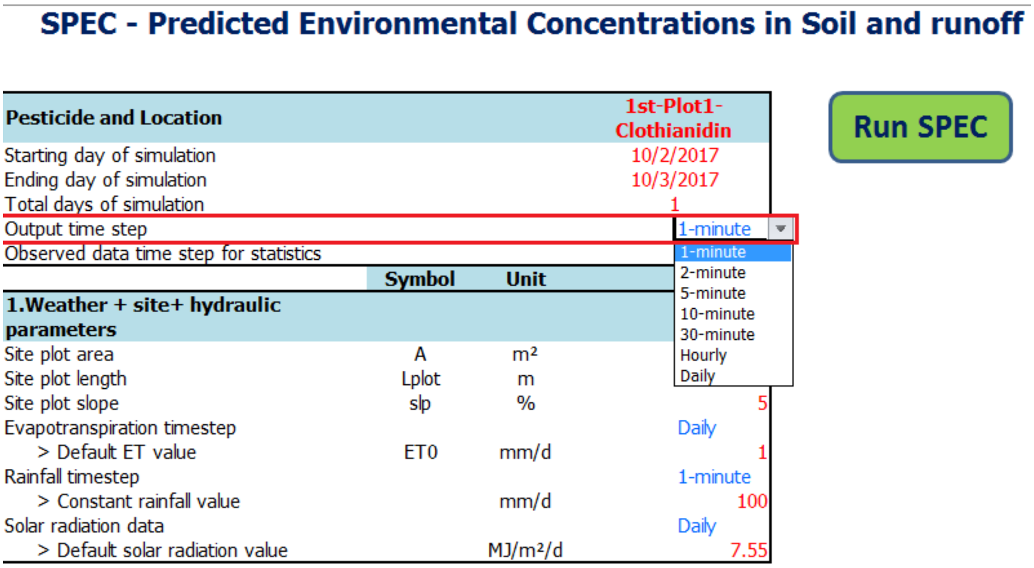
(a) 1-minute output

2	Time	Rainfall (mm)	Cum. rainfall (mm)
3	10/02/2017 00:00	0.000	0.000
4	10/02/2017 00:01	0.000	0.000
5	10/02/2017 00:02	0.000	0.000
6	10/02/2017 00:03	0.000	0.000
7	10/02/2017 00:04	0.000	0.000
8	10/02/2017 00:05	0.000	0.000

(b) Hourly output

2	Time	Rainfall (mm)
3	06/10/2013 00:00	0
4	06/10/2013 01:00	0
5	06/10/2013 02:00	0
6	06/10/2013 03:00	0
7	06/10/2013 04:00	0
8	06/10/2013 05:00	0

Figure 4.1. Example of (a) 1-minute and (b) hourly output time steps in the improved SPEC model



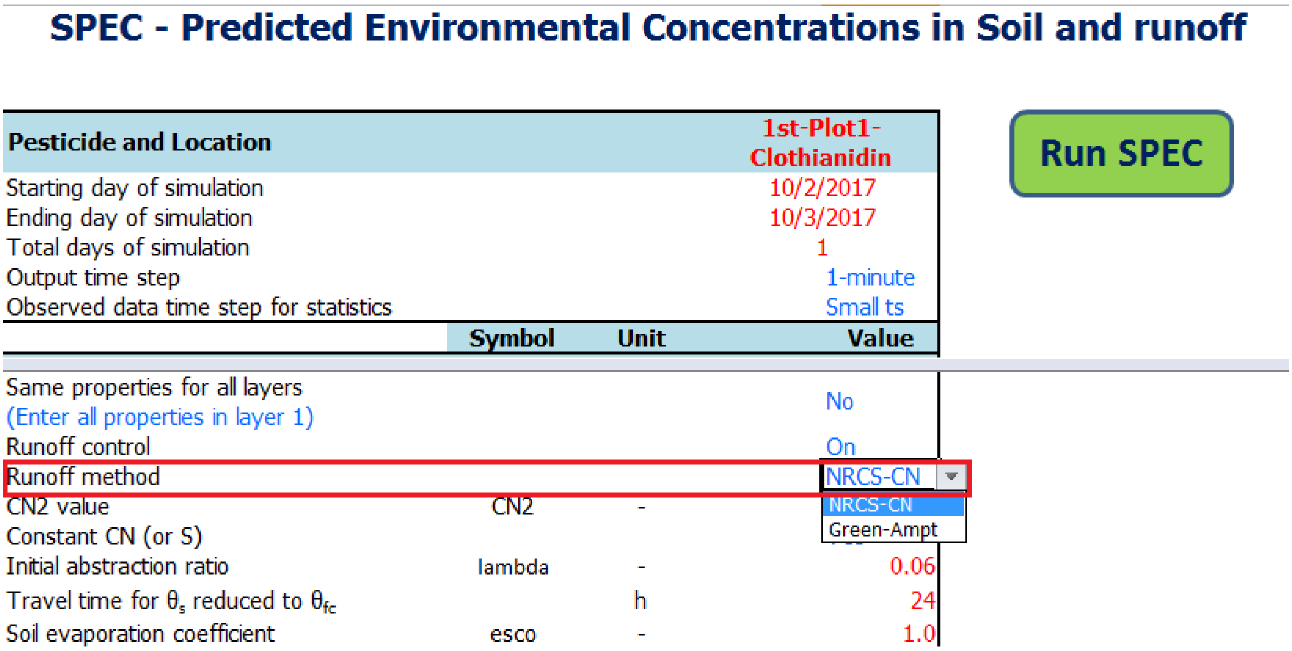
SPEC - Predicted Environmental Concentrations in Soil and runoff

Pesticide and Location			1st-Plot1-Clothianidin
Starting day of simulation			10/2/2017
Ending day of simulation			10/3/2017
Total days of simulation			1
Output time step			1-minute
Observed data time step for statistics			
	Symbol	**Unit**	
1.Weather + site+ hydraulic parameters			
Site plot area	A	m²	
Site plot length	Lplot	m	
Site plot slope	slp	%	5
Evapotranspiration timestep			Daily
> Default ET value	ET0	mm/d	1
Rainfall timestep			1-minute
> Constant rainfall value		mm/d	100
Solar radiation data			Daily
> Default solar radiation value		MJ/m²/d	7.55

Figure 4.2. Flexible output time step in the improved SPEC model

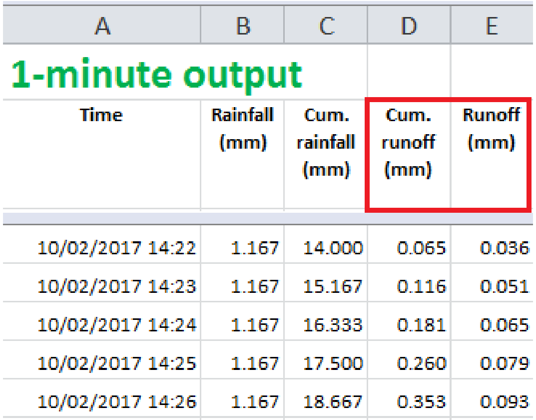
4.1.2 Results in runoff water simulation

The runoff equation in CN method was modified to calculate the cumulative runoff using cumulative rainfall instead of calculating runoff rate using rainfall amount in every time step applied in the previous SPEC model. This improvement enables to accurately simulate the runoff to match with the runoff data. The improved SPEC model not only simulates the cumulative runoff but also simulates runoff rate as well as the time to occur first runoff in single rainfall events. In addition, Green-Ampt method also allows calculating infiltration as well was runoff rate and cumulative runoff in single events as well as continuous simulation.


SPEC - Predicted Environmental Concentrations in Soil and runoff

Pesticide and Location			1st-Plot1-Clothianidin
Starting day of simulation			10/2/2017
Ending day of simulation			10/3/2017
Total days of simulation			1
Output time step			1-minute
Observed data time step for statistics			Small ts
	Symbol	**Unit**	**Value**
Same properties for all layers (Enter all properties in layer 1)			No
Runoff control			On
Runoff method			NRCS-CN
CN2 value	CN2	-	
Constant CN (or S)			
Initial abstraction ratio	lambda	-	0.06
Travel time for θ_s reduced to θ_{fc}		h	24
Soil evaporation coefficient	esco	-	1.0

Figure 4.3. Two methods of runoff simulation in the improved SPEC model

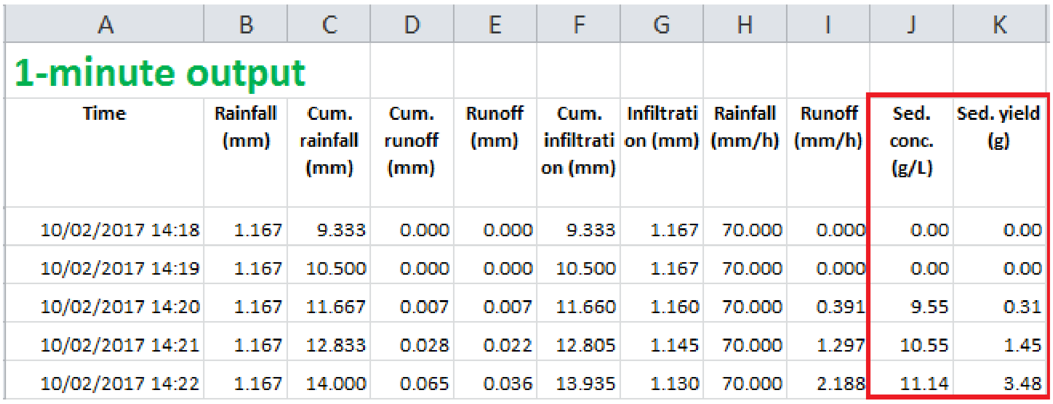

1-minute output

Time	Rainfall (mm)	Cum. rainfall (mm)	Cum. runoff (mm)	Runoff (mm)
10/02/2017 14:22	1.167	14.000	0.065	0.036
10/02/2017 14:23	1.167	15.167	0.116	0.051
10/02/2017 14:24	1.167	16.333	0.181	0.065
10/02/2017 14:25	1.167	17.500	0.260	0.079
10/02/2017 14:26	1.167	18.667	0.353	0.093

Figure 4.4. Results of cumulative runoff and runoff rate in the improved SPEC model

4.1.3 *Results in sediment simulation*

The additional code for sediment simulation allows simulating both sediment yield and sediment concentration with the given data of rainfall intensity, runoff coefficient, the cumulative runoff generated by runoff simulation in the SPEC model. As shown in Figure 4.5, the sediment concentration and the cumulative sediment yield are generated in every one-minute time step.

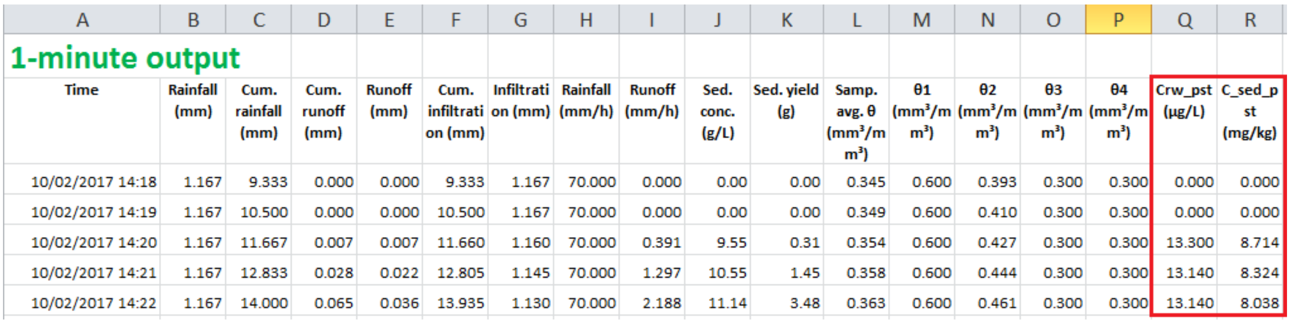


A	B	C	D	E	F	G	H	I	J	K
1-minute output										
Time	Rainfall (mm)	Cum. rainfall (mm)	Cum. runoff (mm)	Runoff (mm)	Cum. infiltration (mm)	Infiltration (mm)	Rainfall (mm/h)	Runoff (mm/h)	Sed. conc. (g/L)	Sed. yield (g)
10/02/2017 14:18	1.167	9.333	0.000	0.000	9.333	1.167	70.000	0.000	0.00	0.00
10/02/2017 14:19	1.167	10.500	0.000	0.000	10.500	1.167	70.000	0.000	0.00	0.00
10/02/2017 14:20	1.167	11.667	0.007	0.007	11.660	1.160	70.000	0.391	9.55	0.31
10/02/2017 14:21	1.167	12.833	0.028	0.022	12.805	1.145	70.000	1.297	10.55	1.45
10/02/2017 14:22	1.167	14.000	0.065	0.036	13.935	1.130	70.000	2.188	11.14	3.48

Figure 4.5. Results of sediment concentration and cumulative sediment yield in the improved SPEC model

4.1.4 *Results in pesticide concentrations in runoff water and in sediment*

The additional code for pollutant runoff allows simulating pesticide concentrations both in runoff water and in sediment. As shown in Figure 4.6, the pesticide concentrations in runoff water and in sediment are generated in every one-minute time step.



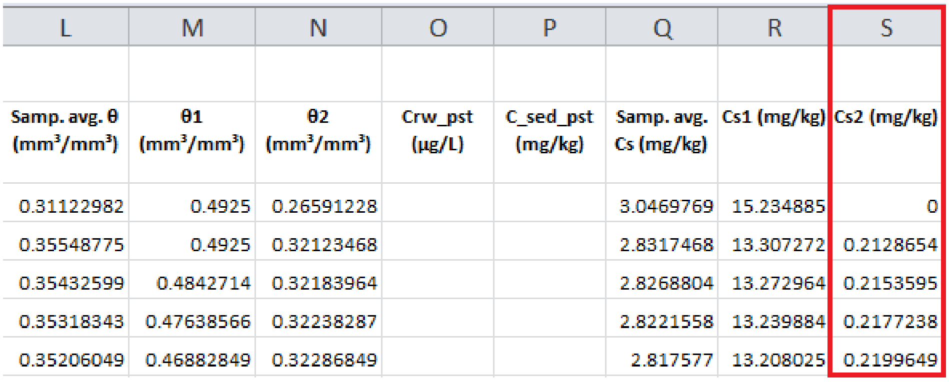
A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
1-minute output																	
Time	Rainfall (mm)	Cum. rainfall (mm)	Cum. runoff (mm)	Runoff (mm)	Cum. infiltration (mm)	Infiltration (mm)	Rainfall (mm/h)	Runoff (mm/h)	Sed. conc. (g/L)	Sed. yield (g)	Samp. avg. θ (mm^3/mm^3)	θ1 (mm^3/mm^3)	θ2 (mm^3/mm^3)	θ3 (mm^3/mm^3)	θ4 (mm^3/mm^3)	Crw_pst (µg/L)	C_sed_pst (mg/kg)
10/02/2017 14:18	1.167	9.333	0.000	0.000	9.333	1.167	70.000	0.000	0.00	0.00	0.345	0.600	0.393	0.300	0.300	0.000	0.000
10/02/2017 14:19	1.167	10.500	0.000	0.000	10.500	1.167	70.000	0.000	0.00	0.00	0.349	0.600	0.410	0.300	0.300	0.000	0.000
10/02/2017 14:20	1.167	11.667	0.007	0.007	11.660	1.160	70.000	0.391	9.55	0.31	0.354	0.600	0.427	0.300	0.300	13.300	8.714
10/02/2017 14:21	1.167	12.833	0.028	0.022	12.805	1.145	70.000	1.297	10.55	1.45	0.358	0.600	0.444	0.300	0.300	13.140	8.324
10/02/2017 14:22	1.167	14.000	0.065	0.036	13.935	1.130	70.000	2.188	11.14	3.48	0.363	0.600	0.461	0.300	0.300	13.140	8.038

Figure 4.6. Results of pesticide concentrations in runoff water and in sediment in the improved SPEC model

4.1.5 *Improvement in output displays*

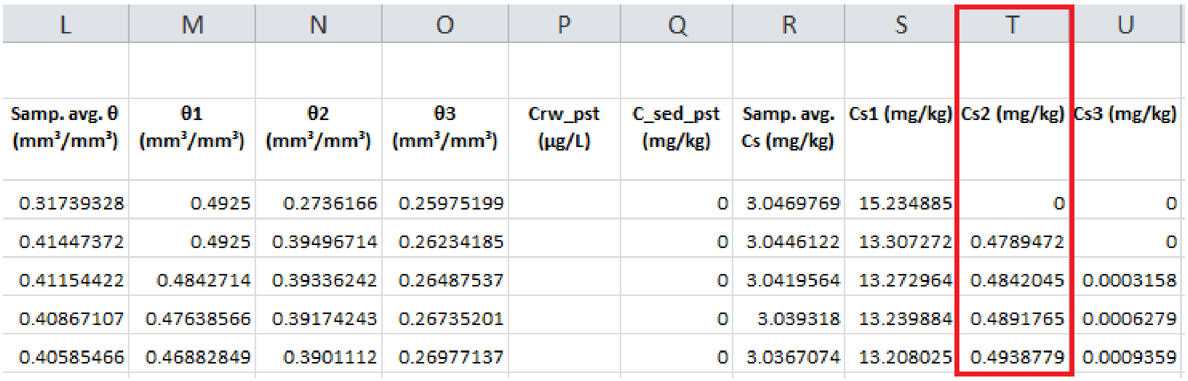
4.1.5.1 *Dynamic tabular display*

The numbers of columns in output sheets will be displayed in response to the numbers of soil layers which are entered into the SPEC model. As can be seen from Figure 4.7, the pesticide concentration in layer 2 (*Cs2*) is displayed in column S if 2 soil layers are entered into the SPEC model (Figure 4.7.a) while that concentration in layer 2 (*Cs2*) is displayed in column T if 3 layers are entered into the SPEC model (Figure 4.7.b).



L	M	N	O	P	Q	R	S
Samp. avg. θ (mm^3/mm^3)	θ1 (mm^3/mm^3)	θ2 (mm^3/mm^3)	Crw_pst (μg/L)	C_sed_pst (mg/kg)	Samp. avg. Cs (mg/kg)	Cs1 (mg/kg)	Cs2 (mg/kg)
0.31122982	0.4925	0.26591228			3.0469769	15.234885	0
0.35548775	0.4925	0.32123468			2.8317468	13.307272	0.2128654
0.35432599	0.4842714	0.32183964			2.8268804	13.272964	0.2153595
0.35318343	0.47638566	0.32238287			2.8221558	13.239884	0.2177238
0.35206049	0.46882849	0.32286849			2.817577	13.208025	0.2199649

a/ Cs2 is displayed in column R in 2-layer simulation



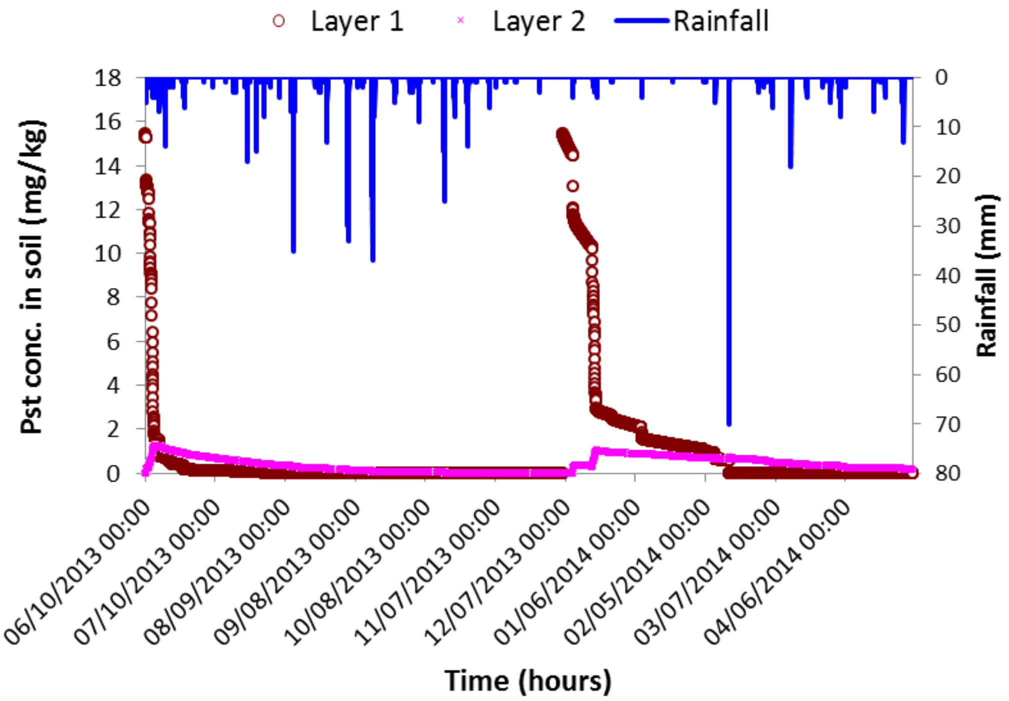
L	M	N	O	P	Q	R	S	T	U
Samp. avg. θ (mm^3/mm^3)	θ1 (mm^3/mm^3)	θ2 (mm^3/mm^3)	θ3 (mm^3/mm^3)	Crw_pst (μg/L)	C_sed_pst (mg/kg)	Samp. avg. Cs (mg/kg)	Cs1 (mg/kg)	Cs2 (mg/kg)	Cs3 (mg/kg)
0.31739328	0.4925	0.2736166	0.25975199		0	3.0469769	15.234885	0	0
0.41447372	0.4925	0.39496714	0.26234185		0	3.0446122	13.307272	0.4789472	0
0.41154422	0.4842714	0.39336242	0.26487537		0	3.0419564	13.272964	0.4842045	0.0003158
0.40867107	0.47638566	0.39174243	0.26735201		0	3.039318	13.239884	0.4891765	0.0006279
0.40585466	0.46882849	0.3901112	0.26977137		0	3.0367074	13.208025	0.4938779	0.0009359

b/ Cs2 is displayed in column T in 3-layer simulation

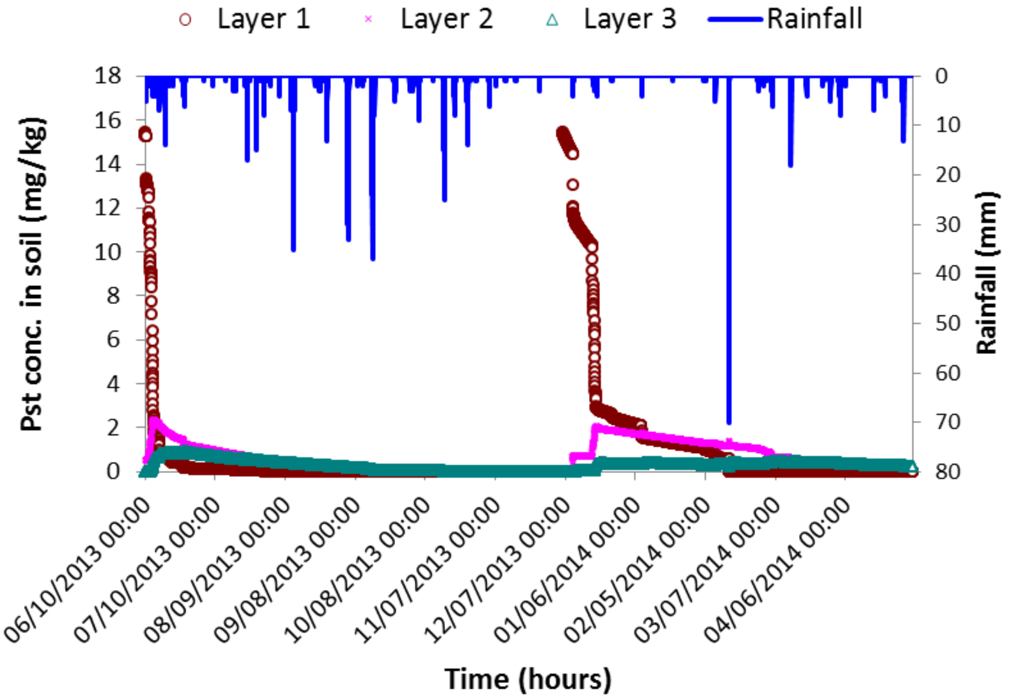
Figure 4.7. Dynamic tabular display in output sheet of the improved SPEC model

4.1.5.2 Dynamic graphic display

The numbers of pesticide concentrations in all soil layers are displayed in the graph depending on the numbers of numbers of soil layers which are entered into the SPEC model input. For example, the pesticide concentrations are displayed in 2 soil layers (Figure 4.8.a/) or 3 soil layers (Figure 4.8.b/) if 2 layers or 3 layers, respectively are entered into the input of SPEC model. In addition, the graph can visualize in respect to the dynamic length of time series. The typical code for (1) calling all charts, (2) deleting all charts and (3) creating chart for daily runoff rate are shown in Appendix 5.



a/ Cs in 2 layers are displayed in the graph in 2-layer simulation

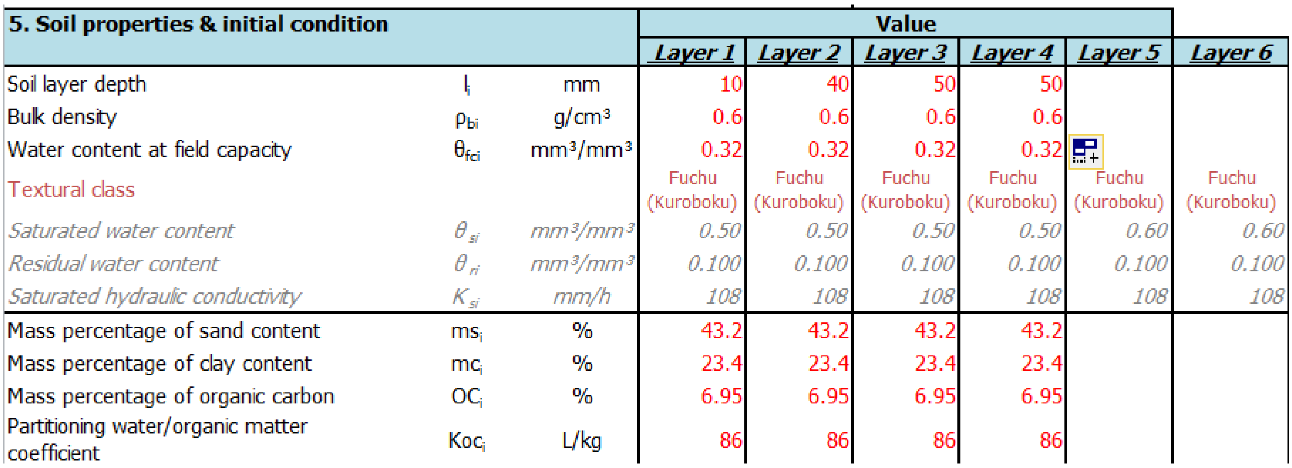


b/ Cs in 3 layers are displayed in the graph in 3-layer simulation

Figure 4.8. Dynamic visual display in the improved SPEC model

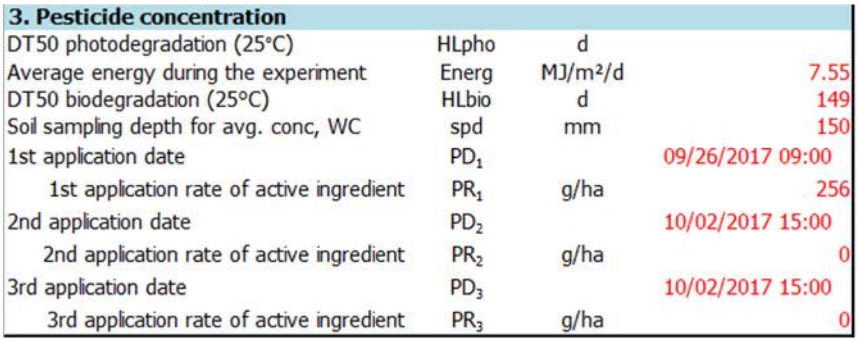
4.2 Results in simulating pesticide concentrations in multiple soil layers

The simulation of pesticides concentration was improved to make the possibility of the simulation of pesticides concentration in multiple soil layers. The code was modified from a single variable into an array form of variable to simulate almost unlimited numbers of soil layers (Figure 4.9). The improvement allows simulating the pesticide concentration at a deeper depth with a higher accurate level. In SPEC model, the pesticide concentration is assumed to be a unique value for the whole layer depth. In the previous SPEC model, the sampling depth is used to simulate the pesticide concentration in the first soil layer. This may not correct because the pesticide layer depth is often assumed to be 1 centimeter (Neitsch et al., 2011). In addition, assigning the large depth for the soil layer with the assumption of the same pesticide concentration seems to be unrealistic. The pesticide concentration is often higher at the soil surface and lower at the deeper depth of soil. Therefore, the adding of multiple soil layers in the improved SPEC model allows the model to approach the real pesticide distribution along the soil depth and thus to have the opportunity to predict more accurate the pesticide concentration in soil layers. In addition, in the improved SPEC model, the pesticide concentration in dry soil and pesticide concentrations in other soil compartments were also improved. The additional option for photodegradation simulation was also added in the improved SPEC model. This kind of data sometimes is not available, with the additional option for photodegradation simulation; the improved SPEC model can simulate the pesticide concentrations in soil layers with or without the given value of photodegradation half-life (Figure 4.10). The code for simulating pollutant runoff as well as pesticide concentrations in multiple soil layers is given in Appendix 4.



5. Soil properties & initial condition			**Value**					
			Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6
Soil layer depth	l_i	mm	10	40	50	50		
Bulk density	ρ_{bi}	g/cm^3	0.6	0.6	0.6	0.6		
Water content at field capacity	θ_{fci}	mm^3/mm^3	0.32	0.32	0.32	0.32		
Textural class			Fuchu (Kuroboku)	Fuchu (Kuroboku)	Fuchu (Kuroboku)	Fuchu (Kuroboku)	Fuchu (Kuroboku)	Fuchu (Kuroboku)
Saturated water content	θ_{si}	mm^3/mm^3	0.50	0.50	0.50	0.50	0.60	0.60
Residual water content	θ_{ri}	mm^3/mm^3	0.100	0.100	0.100	0.100	0.100	0.100
Saturated hydraulic conductivity	K_{si}	mm/h	108	108	108	108	108	108
Mass percentage of sand content	ms_i	%	43.2	43.2	43.2	43.2		
Mass percentage of clay content	mc_i	%	23.4	23.4	23.4	23.4		
Mass percentage of organic carbon	OC_i	%	6.95	6.95	6.95	6.95		
Partitioning water/organic matter coefficient	Koc_i	L/kg	86	86	86	86		

Figure 4.9. Multiple soil layers simulation in the improved SPEC model

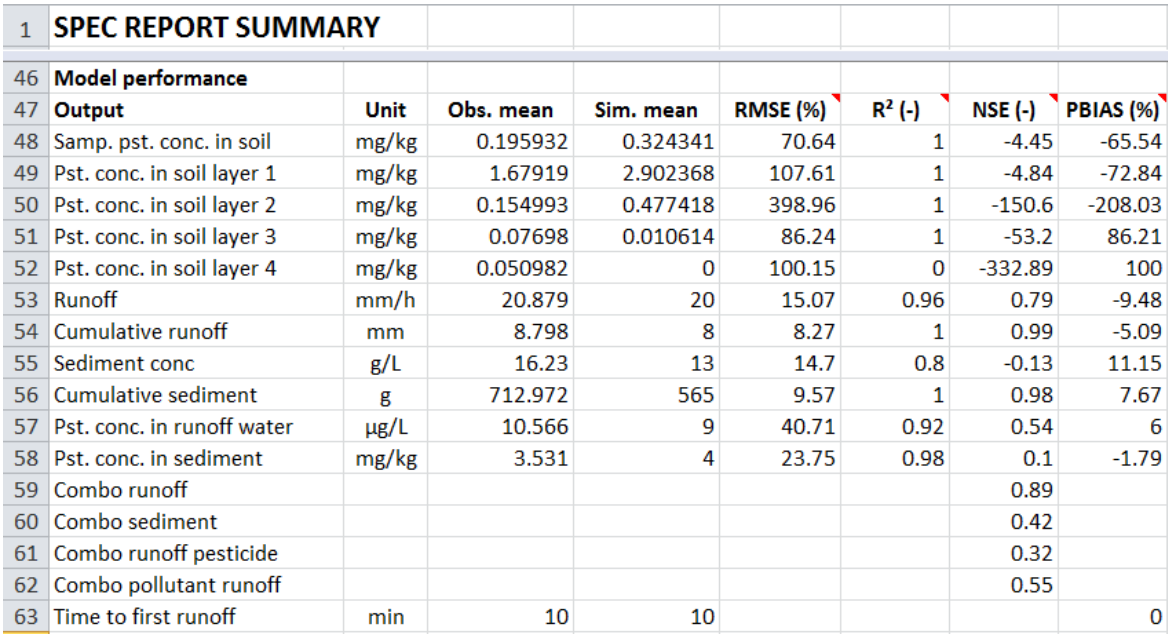


3. Pesticide concentration			
DT50 photodegradation (25°C)	HLpho	d	
Average energy during the experiment	Energ	MJ/m²/d	7.55
DT50 biodegradation (25°C)	HLbio	d	149
Soil sampling depth for avg. conc, WC	spd	mm	150
1st application date	PD_1		09/26/2017 09:00
1st application rate of active ingredient	PR_1	g/ha	256
2nd application date	PD_2		10/02/2017 15:00
2nd application rate of active ingredient	PR_2	g/ha	0
3rd application date	PD_3		10/02/2017 15:00
3rd application rate of active ingredient	PR_3	g/ha	0

Figure 4.10. Pesticide simulation without given photodegradation half-life the improved SPEC model

4.3 Results in statistical indexes

The additional code was developed and integrated in the SPEC model to calculate average values, *RMSE*, *R²*, *NSE* and *PBIAS* for pollutant runoff variables (runoff rate, cumulative runoff, sediment yield and sediment concentration in runoff water, pesticide concentrations in runoff water and in sediment) as well as water contents and pesticide concentrations in all soil layers. As shown in Figure 4.11, with the availability of the observed data, all required statistical indexes are calculated at the same time in the SPEC model. The additional code for statistical indexes simulation supports the users to quick evaluate the performance of the model without the need for using any other software. The typical code for simulating the statistical indexes for all variables (with given observed data in small time steps) is shown in Appendix 6.

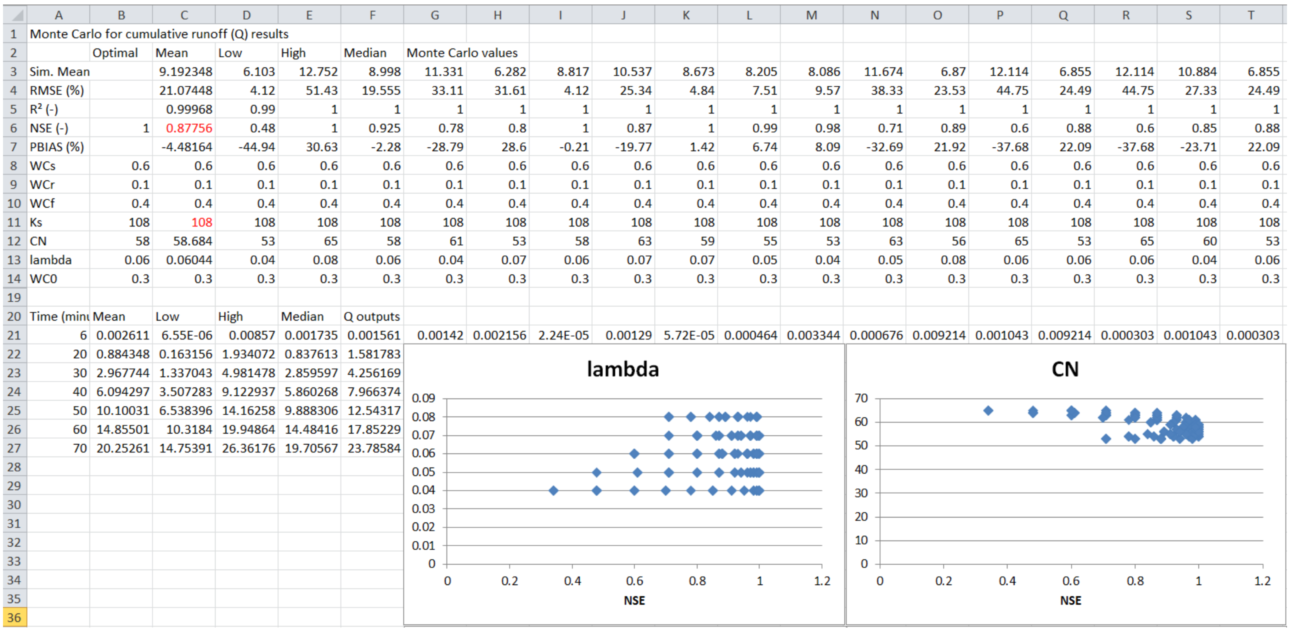


1	SPEC REPORT SUMMARY							
46	Model performance							
47	Output	Unit	Obs. mean	Sim. mean	RMSE (%)	R² (-)	NSE (-)	PBIAS (%)
48	Samp. pst. conc. in soil	mg/kg	0.195932	0.324341	70.64	1	-4.45	-65.54
49	Pst. conc. in soil layer 1	mg/kg	1.67919	2.902368	107.61	1	-4.84	-72.84
50	Pst. conc. in soil layer 2	mg/kg	0.154993	0.477418	398.96	1	-150.6	-208.03
51	Pst. conc. in soil layer 3	mg/kg	0.07698	0.010614	86.24	1	-53.2	86.21
52	Pst. conc. in soil layer 4	mg/kg	0.050982	0	100.15	0	-332.89	100
53	Runoff	mm/h	20.879	20	15.07	0.96	0.79	-9.48
54	Cumulative runoff	mm	8.798	8	8.27	1	0.99	-5.09
55	Sediment conc	g/L	16.23	13	14.7	0.8	-0.13	11.15
56	Cumulative sediment	g	712.972	565	9.57	1	0.98	7.67
57	Pst. conc. in runoff water	µg/L	10.566	9	40.71	0.92	0.54	6
58	Pst. conc. in sediment	mg/kg	3.531	4	23.75	0.98	0.1	-1.79
59	Combo runoff						0.89	
60	Combo sediment						0.42	
61	Combo runoff pesticide						0.32	
62	Combo pollutant runoff						0.55	
63	Time to first runoff	min	10	10				0

Figure 4.11. Statistical indexes are calculated in SPEC model

4.4 Results in Monte Carlo simulations

The additional code for Monte Carlo simulations (MCS) was integrated in the SPEC model to support the sensitivity analysis; in combined with the statistical code to support the calibration/validation procedure; and generate output range with 95% confidence level for uncertainty analysis. The sample size should be 250 (Boulange et al., 2016) which are the numbers of iteration in MCS. For example, the MCS is used to calculate the uncertainty for cumulative runoff in a single rainfall event is shown in Figure 4.12. From the sensitivity analysis result for simulating the cumulative runoff using CN method, the *CN* and *lambda* were found to the most sensitive parameter. In calibration and validation, the values of *CN* and *lambda* are found. By changing ±10% from the validated values of *CN* and *lambda*, the possible range of cumulative runoff with the confident level of 95% can be found for the whole time series. The mean (B21:B27), low (C21:C27), high (D21:D27) of the cumulative runoff are shown in Figure 4.12. The typical code for Monte Carlo simulation of Water content is shown in Appendix 7.



	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
1	Monte Carlo for cumulative runoff (Q) results																			
2		Optimal	Mean	Low	High	Median	Monte Carlo values													
3	Sim. Mean		9.192348	6.103	12.752	8.998	11.331	6.282	8.817	10.537	8.673	8.205	8.086	11.674	6.87	12.114	6.855	12.114	10.884	6.855
4	RMSE (%)		21.07448	4.12	51.43	19.555	33.11	31.61	4.12	25.34	4.84	7.51	9.57	38.33	23.53	44.75	24.49	44.75	27.33	24.49
5	R^2 (-)		0.99968	0.99	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
6	NSE (-)	1	0.87756	0.48	1	0.925	0.78	0.8	1	0.87	1	0.99	0.98	0.71	0.89	0.6	0.88	0.6	0.85	0.88
7	PBIAS (%)		-4.48164	-44.94	30.63	-2.28	-28.79	28.6	-0.21	-19.77	1.42	6.74	8.09	-32.69	21.92	-37.68	22.09	-37.68	-23.71	22.09
8	WCs	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
9	WCr	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
10	WCf	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
11	Ks	108	108	108	108	108	108	108	108	108	108	108	108	108	108	108	108	108	108	108
12	CN	58	58.684	53	65	58	61	53	58	63	59	55	53	63	56	65	53	65	60	53
13	lambda	0.06	0.06044	0.04	0.08	0.06	0.04	0.07	0.06	0.07	0.07	0.05	0.04	0.05	0.08	0.06	0.06	0.06	0.04	0.06
14	WC0	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
19																				
20	Time (minu	Mean	Low	High	Median	Q outputs														
21	6	0.002611	6.55E-06	0.00857	0.001735	0.001561	0.00142	0.002156	2.24E-05	0.00129	5.72E-05	0.000464	0.003344	0.000676	0.009214	0.001043	0.009214	0.000303	0.001043	0.000303
22	20	0.884348	0.163156	1.934072	0.837613	1.581783														
23	30	2.967744	1.337043	4.981478	2.859597	4.256169														
24	40	6.094297	3.507283	9.122937	5.860268	7.966374														
25	50	10.10031	6.538396	14.16258	9.888306	12.54317														
26	60	14.85501	10.3184	19.94864	14.48416	17.85229														
27	70	20.25261	14.75391	26.36176	19.70567	23.78584														
28																				
29																				
30																				
31																				
32																				
33																				
34																				
35																				
36																				

Figure 4.12. Monte Carlo simulations for cumulative runoff

Chapter 5. Model applications

5.1 Case study in Sakaecho in 2017 - a single event simulation

5.1.1 Study area and data input

The details of the SPEC model application in this case study was reported in the previous study (Thinh et al., 2019). The model was applied for the Sakaecho field case study, located in Fuchu, Tokyo, Japan to validate the pollutant runoff module. Three replicates of bare soil field plots under two artificial rainfall events were conducted on October 2nd and 10th, 2017. The plot has one meter in width, five meters in length and five percent in slope. Two types of pesticides, Dantotsu® (16% clothianidin as an active ingredient), and Admiyer® Flowable (20% imidacloprid as an active ingredient), were applied to the plot using a hand sprayer. The data in details were reported in the previous study (Yadav and Watanabe, 2018).

Figure 5.1. The upland bare soil pollutant runoff experiment in Sakaecho, Tokyo (2017) (Yadav and Watanabe, 2018)

The observed data obtained from the study of Yadav and Watanabe (2018) were used to find the pesticide residues on the day of simulation. On the first rainfall event (October 2nd, 2017), the pesticide residues (clothianidin and imidacloprid) were 249.0 g/ha and 294.9 g/ha, respectively. There were 6 datasets of runoff, sediment and pesticides, in which 2 out of 6 datasets were satisfied for calibration (1 dataset in plot 1 on the first rainfall event) and validation (1 dataset in plot 2 on the first rainfall event). The times to first runoff for both plot 1 and plot 2 on the first rainfall event were 10 minutes. For every runoff pollutant dataset, there were 6 data values which were processed from 7 samples collected at 7 time points (at 0, 10, 20, 30, 40, 50, 60 minutes after rainfall starts). The observed data in runoff for plot 1 and plot 2 were used to compare with simulated results in calibration and validation procedures, respectively. The observed runoff coefficients which were 0.23 and 0.28 for plot 1 and plot 2 respectively were used for sediment simulation. In bare soil upland field condition of this study area in which there was no erosion-control practice, C and $P1$ are 1.0 (Wischmeier and Smith, 1978).

Table 5.1. Physical properties of soil

Soil properties	**Symbol**	**Unit**	**Value**	**Reference**
Bulk density	R_b	g/cm³	0.5	Boulange et al., 2016
Hydraulic conductivity	K_s	mm/h	108	Boulange et al., 2016
Field capacity	WCf	mm³/mm³	0.4	Boulange et al., 2016
Saturated water content	WCs	mm³/mm³	0.6	Jaikaew et al., 2015
Residual water content	WCr	mm³/mm³	0.1	Boulange et al., 2016
Sand percent	m_s	%	43.2	Boulange et al., 2016
Clay percent	m_c	%	23.4	Boulange et al., 2016
Organic carbon percent	OC	%	6.95	Boulange et al., 2016

Input data included weather data (rainfall, evaporation, temperature, and solar radiation), soil properties, the *coef* and *exp* of MUSLE. The rainfall data obtained from rainfall simulation on October 2nd, 2017, with the intensity of 70 mm/h, and the duration of 70 minutes (60 mintues plus the time from rainfall starts to the start of the first runoff, both of the observed times to the first runoff were ten minutes for plot 1 and 2) for both plots 1 and 2 (Yadav and Watanabe, 2018). The daily temperature and related data to calculate evaporation and solar radiation as well as hourly temperature were downloaded from the weather station near the study area (Japan Meteorological Agency, 2017). The Excel file using the Food and Agriculture Organization (FAO) Penman-Monteith equation (Allen et al., 1998) to calculate daily evaporation and solar radiation. The soil data which were obtained from previous studies (Boulange et al., 2016; Jaikaew et al., 2015) are shown in Table 5.1.

In this application, four soil layers (0-1 cm, 1-5 cm, 5-10 cm, and 10-15 cm in the study area) were entered into the SPEC model to test the model capability for multiple-layer simulation. The CN method was used to calculate runoff. The simulation period was one day. The input time step for rainfall was 1 minute, that for temperature was hourly, and those for evaporation, solar radiation were daily. The output time step of 1 minute was selected for this simulation.

5.1.2 Results and discussion

5.1.2.1 Results for MUSLE coef and exp

The *coef* and *exp* of MUSLE for calculating cumulative sediment yield in Eq. 3.27 were found by using the least squares error method (Hodges and Moore, 1972; Watson, 1967). Based on the average peak discharge and 36 values of cumulative runoff, sediment (Yadav and Watanabe, 2018), the *coef* and *exp* were found to be 20924.9 and 1.053, respectively. The statistical results for this simulation indicated a very good agreement between simulated and observed sediment yield (R^2 of 0.97, *NSE* of 0.97, *PBIAS* of -0.04%, and *RMSE* of 12.7%). The values of *coef* and *exp* were entered into the SPEC model for simulating sediment yield and sediment concentration.

5.1.2.2 Results for CN runoff

Sensitivity analysis for runoff simulation using CN method was supported by Monte Carlo simulation to identify which parameters affected most to runoff rate and cumulative runoff results. The sample size of 250 in MCS was used which were 250 combinations of all input parameters for runoff randomly generated with their initial values and percent changes to find the corresponding output values. Next all output results were analyzed by regression analysis in Excel to find out the standardized rank regression coefficients (SRRCs). SRRC values can vary from −1 to 1, and high absolute values of SRRCs indicate for sensitive parameters (Boulange et al., 2016). A positive SRRC indicates that increasing the parameter value will increase the output considered, and vice versa (Boulange et al., 2016). For runoff simulation results, the initial abstraction ratio, λ and the curve number *CN* were found to be sensitive parameters. For simulation of runoff rate, the standardized rank regression coefficients for λ and *CN* were -0.39 and 0.93, respectively. The results of λ and *CN* are shown in Table 5.2. The calibrated λ was lower than the original value of 0.2; however it was similar to those (which were 0.05) in the previous studies (Lim et al., 2006; Shi et al., 2009; Woodward et al., 2003) and within the range (0 ÷ 0.142) in the previous study

(Hawkins et al., 2010).

Table 5.2. Calibrated parameters for runoff and sediment transport

Parameter	**Symbol**	**Unit**	**Initial value**	**Final value**
Initial abstraction ratio	λ	none	0.01 ÷ 0.2	0.06
Curve Number	*CN*	none	44 ÷ 66	59

The simulated results of hydrological output including the time to first runoff, runoff rate and cumulative runoff were shown in Table 5.3, Figure 5.2 and Figure 5.3. The times to first runoff in both calibration and validation completely matched the observed data (*PBIAS* = 0 in both calibration and validation (Table 5.3). The simulated runoff rate and cumulative runoff were overestimated for calibration and underestimated for validation (Table 5.3). The difference could be due to the difference in water content and evaporation in two plots. However, the graphs of simulated runoff rates in calibration and validation (Figure 5.2) confirmed a good agreement with the observed runoff rate data and those for cumulative runoffs (Figure 5.3) confirmed a very good agreement with the observed cumulative runoff data. The statistical indexes of runoff rates indicated a good model performance in calibration (R^2 = 0.96, *NSE* = 0.79, *PBIAS* = -9.50%) and a resonable model performance in validation (R^2 = 0.94, *NSE* = 0.56, *PBIAS* = 9.00%) (Table 5.4). The statistical indexes of cumulative runoffs in calibration (R^2 = 1.00, *NSE* = 0.99, *PBIAS* = -5.10%) and validation (R^2 = 1.00, *NSE* = 0.92, *PBIAS* = 17.50%) indicated a very good model performance (Table 5.4).

Table 5.3. Average values for pollutant runoff outputs in calibration and validation

Average values	**Unit**	**Calibration**		**Validation**	
		Obs.	Sim.	Obs.	Sim.
Time to first runoff	min	10	10	10	10
Runoff rate	mm/h	20.9	22.9	25.1	22.9
Cumulative runoff	mm	8.8	9.3	11.2	9.3

Notes: Obs.: observed; Sim.: simulated

Table 5.4. Model performance for pollutant runoff outputs

Statistical results	**Calibration**				**Validation**			
	RMSE (%)	R^2 (-)	*NSE* (-)	*PBIAS* (%)	*RMSE* (%)	R^2 (-)	*NSE* (-)	*PBIAS* (%)
Time to first runoff	-	-	-	0	-	-	-	0
Runoff rate	15.1	0.96	0.79$^{1)}$	-9.5$^{1)}$	15.8	0.94	0.56$^{3)}$	9.0$^{1)}$
Cumulative runoff	8.3	1	0.99$^{1)}$	-5.1$^{1)}$	18.9	1	0.92$^{1)}$	17.5$^{2)}$

Notes: *1)* very good, *2)* good, *3)* satisfactory, *4)* acceptable, *5)* unsatisfactory

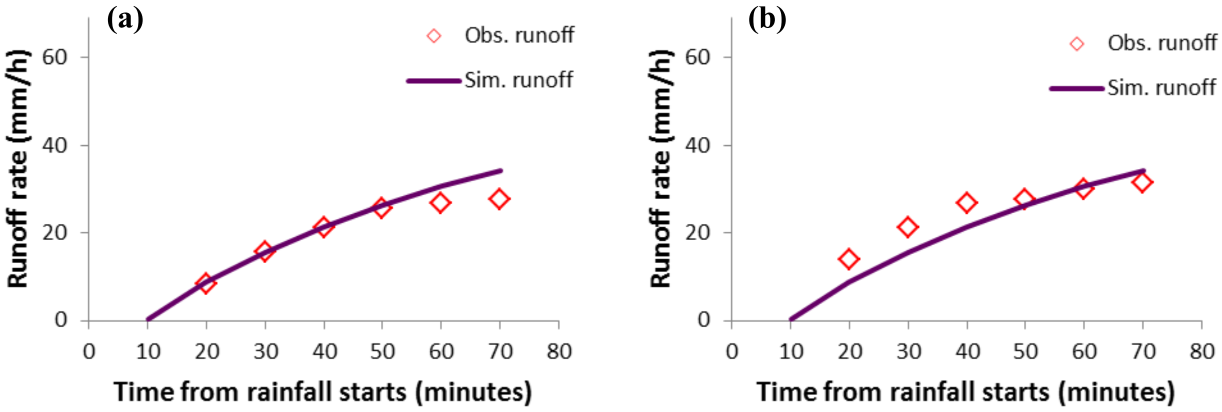


Figure 5.2. Runoff rates in (a) calibration and (b) validation (CN method)

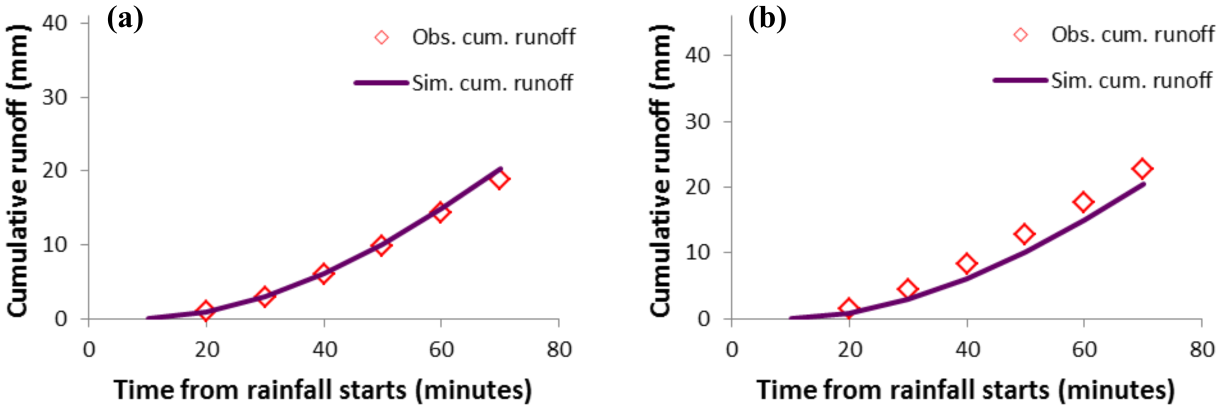


Figure 5.3. Cumulative runoffs in (a) calibration and (b) validation (CN method)

The valid parameters and observed data as well as uncertainty associated with runoff rate and cumulative runoff (in CN method) were checked by using the Monte Carlo simulation for runoff rate and cumulative runoff. The uncertainty results for runoff rate and cumulative runoff with 10%

change of optimal input parameters of *CN* and *λ* are shown in Figure 5.4 and Figure 5.5. The great thicknesses of 95% confidence intervals (difference between high and low values) in calibration and validation of runoff rate simulation highlighted the effects of the two parameters (*CN* and *λ*) to the runoff rate results and were consistent for both calibration and validation (Figure 5.4). However, it seemed to be more uncertainty in validation of runoff rate value because the 95% confidence interval in validation was thicker than that in calibration (Figure 5.4). The similar trend was also found for the uncertainty of cumulative runoff (Figure 5.5). The *CN* and *λ* highlighted their effects to the results of cumulative runoff. As shown in Figure 5.5 that the thicknesses of 95% confidence interval were consistent in both calibration and validation of the cumulative runoff results in which thicker band were found at the last time value of the cumulative runoff.

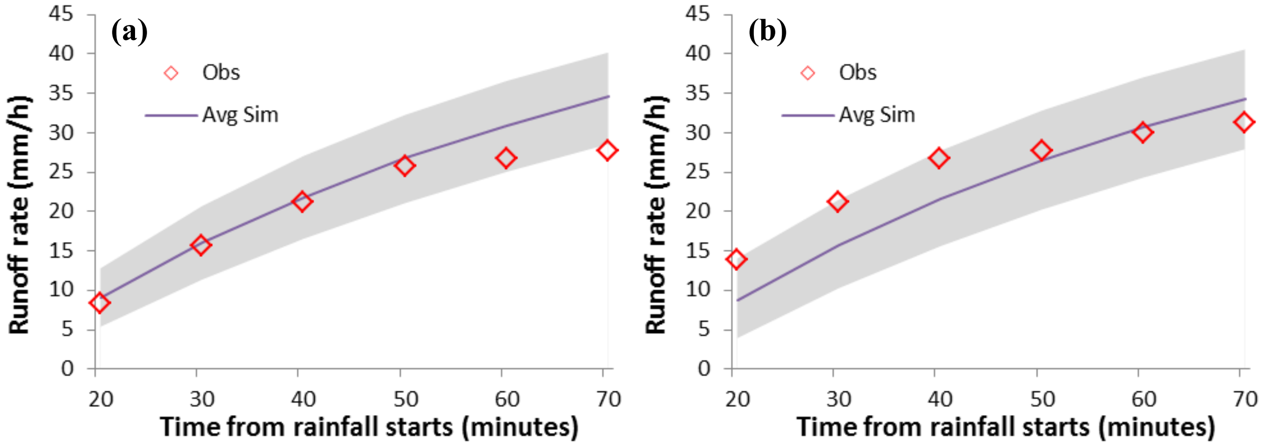


Figure 5.4. Uncertainty results of runoff rate in (a) calibration and (b) validation

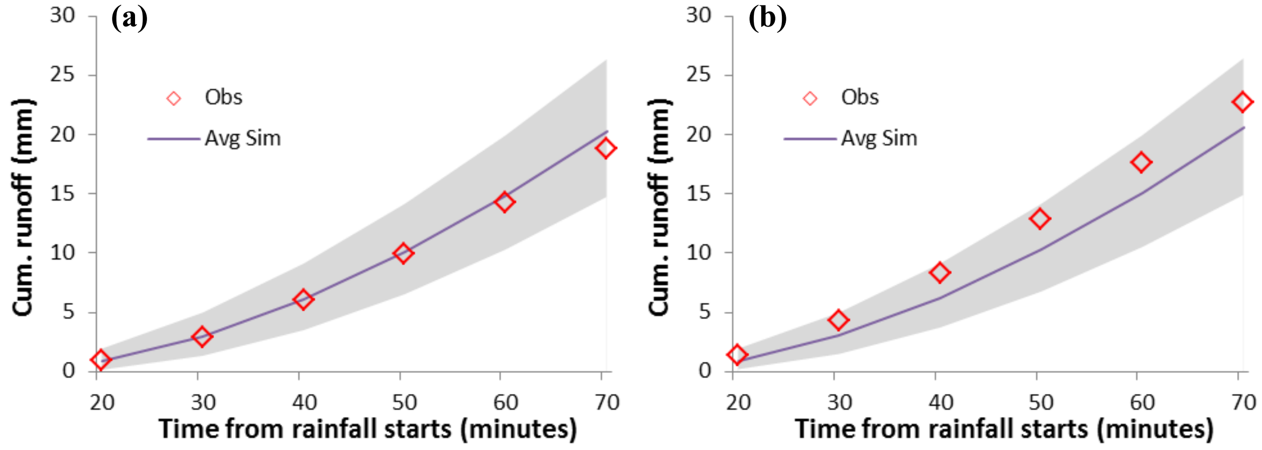


Figure 5.5. Uncertainty results of cumulative runoff in (a) calibration and (b) validation

5.1.2.3 Results for sediment

The cumulative runoff obtained from runoff water simulation was used for the simulations of sediment yield and sediment concentration. For sediment simulation, in the case study of bare soil, the only one parameter is needed for calibration of sediment. The adjustment of erodibility factor, *K* can be conducted through the coefficient of erodibility factor, *K*_coef. The result of calibrated coefficient of erodibility factor is shown in Table 5.5. The calibrated *K* of the study (0.2856) was found within the validated range of *K* (0.1 to 0.5) in the previous study (Sharpley and Williams, 1990).

Table 5.5. Calibrated parameters for runoff and sediment transport

Parameter	**Symbol**	**Unit**	**Initial value**	**Final value**
Coefficient of erodibility factor	*K_coef*	none	0.8 - 1.5	1.3
Erodibility factor	*K*	0.01 ton.acre.h/(acre.ft-ton.in)	0.2197	0.2856

Table 5.6. Average values for pollutant runoff outputs in calibration and validation

Average values	**Unit**	**Calibration**		**Validation**	
		Obs.	Sim.	Obs.	Sim.
Sediment concentration	g/L	16.23	14.38	13.60	17.59
Sediment yield	g	712.97	656.52	713.41	803.00

Notes: Obs.: observed; Sim.: simulated; unit of g specified here is calculated for the plot area of 5m².

Table 5.7. Model performance for pollutant runoff outputs

Statistical results	**Calibration**				**Validation**			
	RMSE (%)	*R²* (-)	*NSE* (-)	*PBIAS* (%)	*RMSE* (%)	*R²* (-)	*NSE* (-)	*PBIAS* (%)
Sediment concentration	14.9	0.8	-0.16*5)*	11.40*1)*	39.50	0.76	-0.47*5)*	-29.30*2)*
Sediment yield	9.9	1	0.98*1)*	7.90*1)*	14.70	1.00	0.97*1)*	-12.6*1)*

Notes: *1)* very good, *2)* good, *3)* satisfactory, *4)* acceptable, *5)* unsatisfactory

The simulated results of sediment transport including sediment yields (from 1m x 5m plot) and concentrations are shown in Table 5.6, Figure 5.6 and Figure 5.7. The *PBIAS* results of sediment yields (7.90% in calibration and -12.60% in validation) and sediment concentrations (11.40% in calibration and -29.30% in validation) indicated that they were underestimated in calibration and overestimated in validation (Table 5.7). This could be due to the smaller runoff coefficient (the observed total runoff was lower than that in validation under the same rainfall amount) in the calibration while the simulated cumulative runoff had the same value for both calibration and validation and vice versa for validation. However, these *PBIAS* values were still in a good level (within ±40%) of statistical indexes for the sediment simulation (Moriasi et al., 2007). It can be seen from Figure 5.6 that the simulated sediment yields were fitted very well with the observed data in both calibration and validation. The statistical indexes for the sediment yields in calibration ($R^2 = 1.00$, $NSE = 0.98$) and in validation ($R^2 = 1.00$, $NSE = 0.97$) indicated a very good model performance (Table 5.7). The simulated sediment concentrations in calibration and validation were fitted reasonably with the observed data (Figure 5.6). Although the negative *NSE* found in calibration (-0.16) and validation (-0.47) for sediment concentrations, the R^2 (0.80 in calbration and 0.76 in validation) indicated a reasonable correlation between the simulated and the obsereved data as well as the trends between them (Table 5.7).

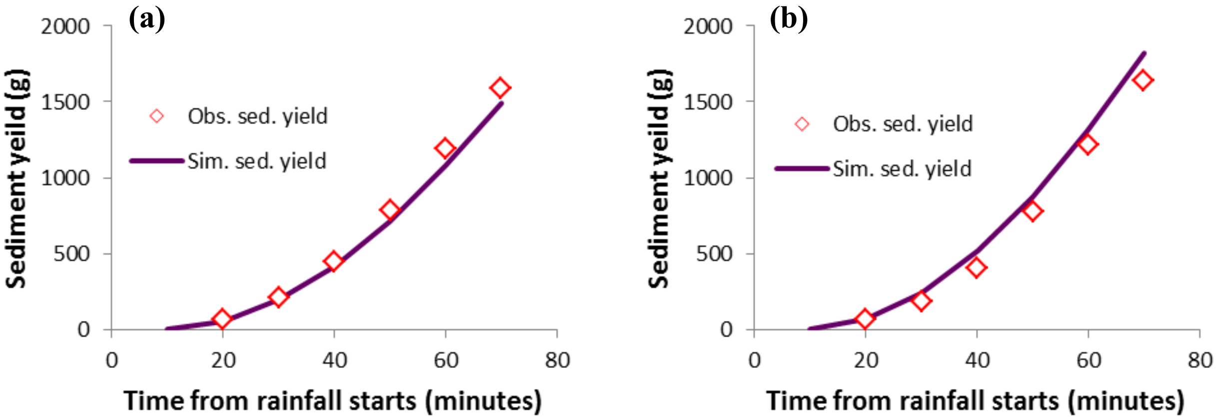


Figure 5.6. Cumulative sediment yields in (a) calibration and (b) validation

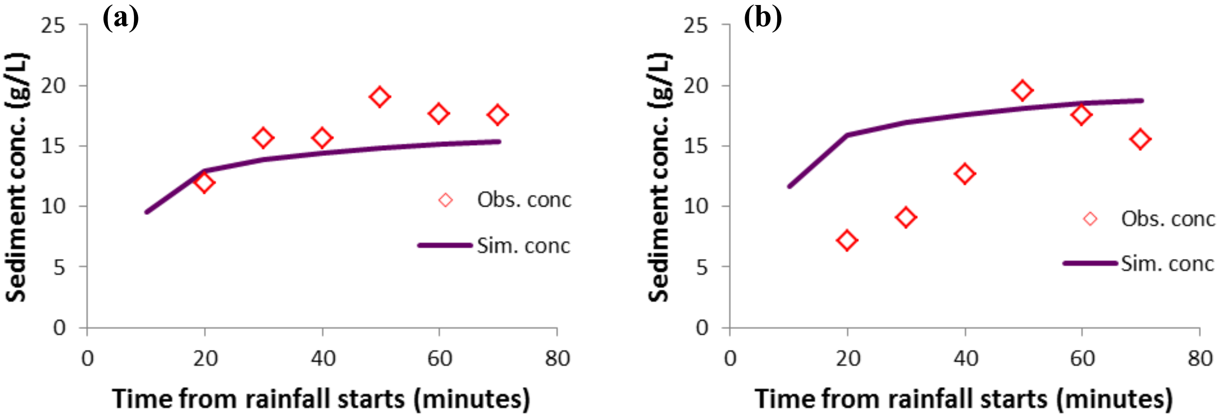


Figure 5.7. Sediment concentrations in (a) calibration and (b) validation

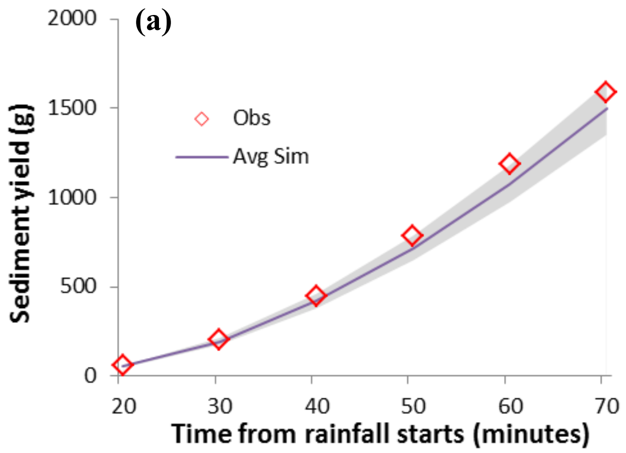


Figure 5.8. Uncertainty results of sediment yield in (a) calibration and (b) validation

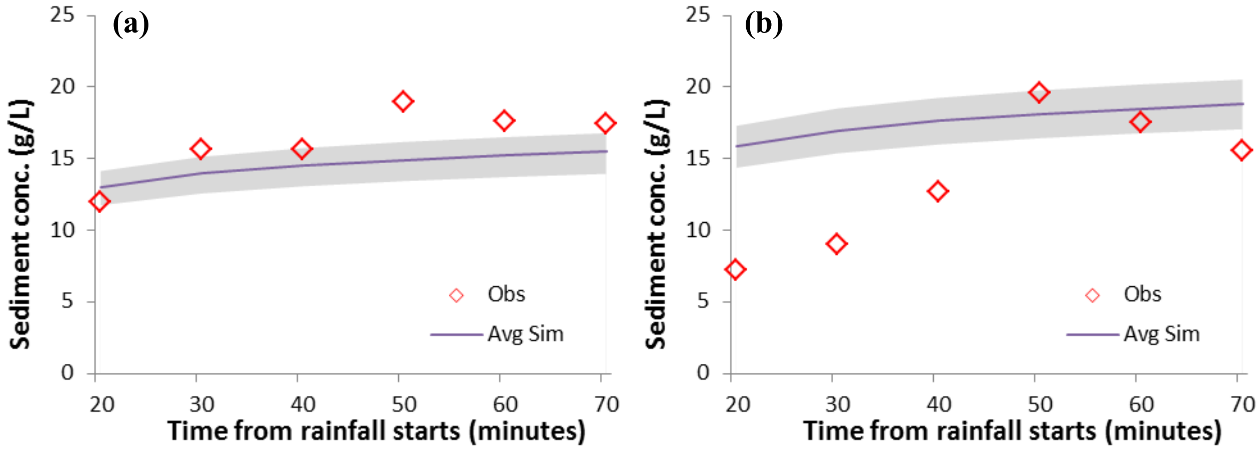


Figure 5.9. Uncertainty results of sediment concentration in (a) calibration and (b) validation

The valid parameter of the erodibility factor was checked by using the Monte Carlo simulation for sediment yield and sediment concentration. The uncertainty results for sediment yield and sediment concentration with 10% change of optimal input parameters of the erodibility factor are shown in Figure 5.8 and Figure 5.9. The great thicknesses of 95% confidence intervals in calibration and validation of sediment yield highlighted the effect of the erodibility factor to the sediment yield results and were consistent for both calibration and validation (Figure 5.8). The higher effect of the erodibility factor at the last time steps values of sediment yield in both calibration and validation indicated more uncertainty of the results or observation data (Figure 5.8). The similar trend was also found for the uncertainty of sediment concentration (Figure 5.9). The erodibility factor highlighted its effect to the results of sediment concentration. As shown in Figure 5.9 that the thicknesses of 95% confidence intervals were consistent in both calibration and validation of the sediment concentration results. However, it seemed to be more uncertainty in validation of sediment concentration because the 95% confidence interval in validation was thicker than that in calibration (Figure 5.9).

5.1.2.4 Results for pesticide runoff

Table 5.8. Calibrated parameters of pesticides

Parameter	**Symbol**	**Unit**	**Clothianidin**	**Imidacloprid**
Coefficient of enrichment ratio	*e_coef*	none	0.78	0.78
Ratio of pesticide concentrations in mobile and static waters	*alpha*	none	1.11	1.28
Ratio of pesticide concentrations in runoff and percolation waters	*beta*	none	0.02	0.06
Q10	*Q10*	none	1¹⁾	1¹⁾
Biodegradation half-life	HL_{bio}	d	149¹⁾	51¹⁾
Partitioning water/ organic matter coefficient	*Koc*	L/kg	86²⁾	158²⁾

Notes: 1) These parameters were found by calculating bio-degradation which assuming no effect of temperature; 2) Yadav and Watanabe, 2018.

For simulation of pesticide concentrations in sediment and in runoff water, there were three sensitive parameters, which were enrichment ratio (*epsilon*) in Eq. 3.65, the ratio of pesticide concentrations in mobile and static water (*alpha*), and the ratio of pesticide concentrations in runoff water and percolation water (*beta*). The calibrated *epsilon* were 0.78 for both clothianidin and imidacloprid (Table 5.8) which were confirmed with that given in Menzel's study (Menzel, 1980). The calibrated *alpha*, were 1.11 and 1.28 for clothianidin and imidacloprid respectively (Table 5.8). The calibrated *beta*, were 0.02 and 0.06 for clothianidin and imidacloprid respectively (Table 5.8). The higher values of *alpha* and *beta* for imidacloprid confirmed the higher observed imidacloprid concentrations in runoff water as compared to those for clothianidin. The higher calibrated values of alpha and beta for imidacloprid as compared to those for clothianidin may be related to higher water solubility of imidacloprid (480 mg/L) as compared to that of clothianidin (327 mg/L) (Yadav and Watanabe, 2018). Comparing to the applied pesticide mass, average percent mass loss (in calibration and validation) of imidacloprid in runoff water (0.68%) was higher than that of clothianidin (0.35%). Higher *Koc* value (Table 5.8) of imidacloprid probably related to the higher concentrations of imidacloprid in sediment as compared to those of clothianidin (Table 5.9).

Comparing to the applied pesticide mass, the average percent mass loss (in calibration and validation) of imidacloprid in sediment (2.32%) were higher than that of clothianidin (2.00%). Simulated concentrations of two types of pesticides in sediment and in runoff water (Table 5.9) were similar to those in observation (Yadav and Watanabe, 2018). Modification of SPEC model with additional parameters (*alpha* and *beta*) allows to generate the concentration differences among three solution components (soil water, percolation water and runoff water) and thus model results of pesticide runoff fitted with the observed data and improved the model performance. It also allows assigning different values for different types of pesticides as in this study.

Table 5.9. Average values for pollutant runoff outputs in calibration and validation

Average values	**Unit**	**Calibration**		**Validation**	
		Obs.	Sim.	Obs.	Sim.
Clothianidin concentration in runoff water	µg/L	11	10	8	9
Clothianidin concentration in sediment	mg/kg	3.53	3.46	3.48	3.26
Imidacloprid concentration in runoff water	µg/L	28	27	19	27
Imidacloprid concentration in sediment	mg/kg	5.30	5.37	4.91	4.99

Notes: Obs.: observed; Sim.: simulated

Table 5.10. Model performance for pollutant runoff outputs

Statistical results	**Calibration**				**Validation**			
	RMSE (%)	R^2 (-)	*NSE* (-)	*PBIAS* (%)	*RMSE* (%)	R^2 (-)	*NSE* (-)	*PBIAS* (%)
Clothianidin concentration in runoff water	42.1	0.92	0.51$^{3)}$	9.5$^{1)}$	41.0	0.72	0.49$^{4)}$	-16.9$^{1)}$
Clothianidin concentration in sediment	22.0	0.98	0.23$^{4)}$	2.0$^{1)}$	13.0	0.95	0.89$^{1)}$	6.2$^{1)}$
Imidacloprid concentration in runoff water	52.2	0.79	0.28$^{4)}$	1.5$^{1)}$	58.0	0.57	-0.16$^{5)}$	-38.4$^{2)}$
Imidacloprid concentration in sediment	13.3	0.88	0.76$^{1)}$	-1.4$^{1)}$	11.5	0.93	0.92$^{1)}$	-1.6$^{1)}$

Notes: *1)* very good, *2)* good, *3)* satisfactory, *4)* acceptable, *5)* unsatisfactory

Next, the results of clothianidin in sediment are shown in Table 5.9. In both calibration and validation, the clothianidin concentrations in sediment were underestimated (Table 5.9). However, it can be seen from Figure 5.10 that the trends of simulated results of clothianidin concentration in sediment were fitted very well with the observed data in both calibration and validation. The clothianidin concentrations were decreased from the start to the end of runoff in both calibration and validation. These trends were confirmed with the previous studies (Watanabe and Grismer, 2003, 2001). The statistical indexes for clothianidin concentration in sediment also confirmed a reasonable agreement in calibration and a good agreement in validation between simulated results and observed data ($R^2 = 0.98$, $NSE = 0.23$, $PBIAS = 2.00\%$ for calibration and $R^2 = 0.95$, $NSE = 0.89$, $PBIAS = 6.20\%$ for validation).

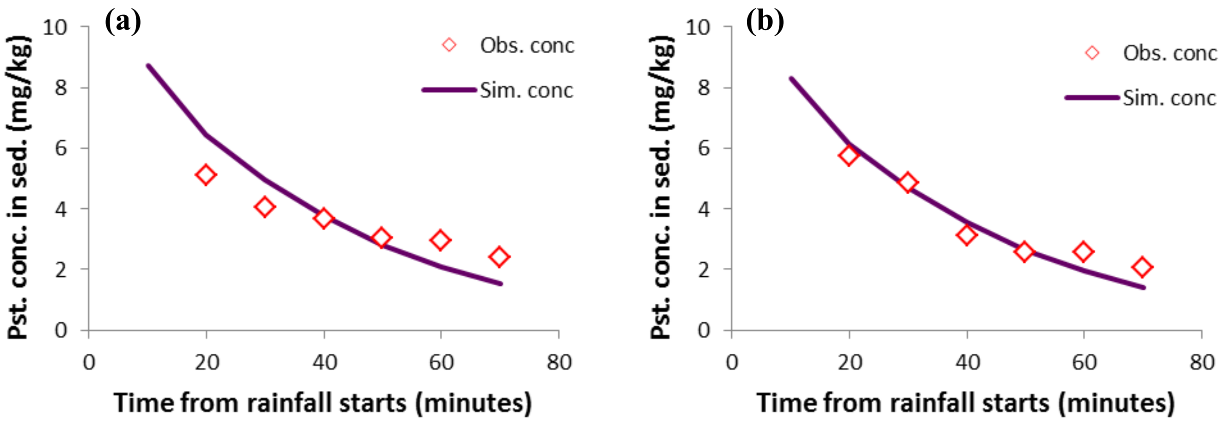


Figure 5.10. Clothianidin concentrations in sediment in (a) calibration and (b) validation

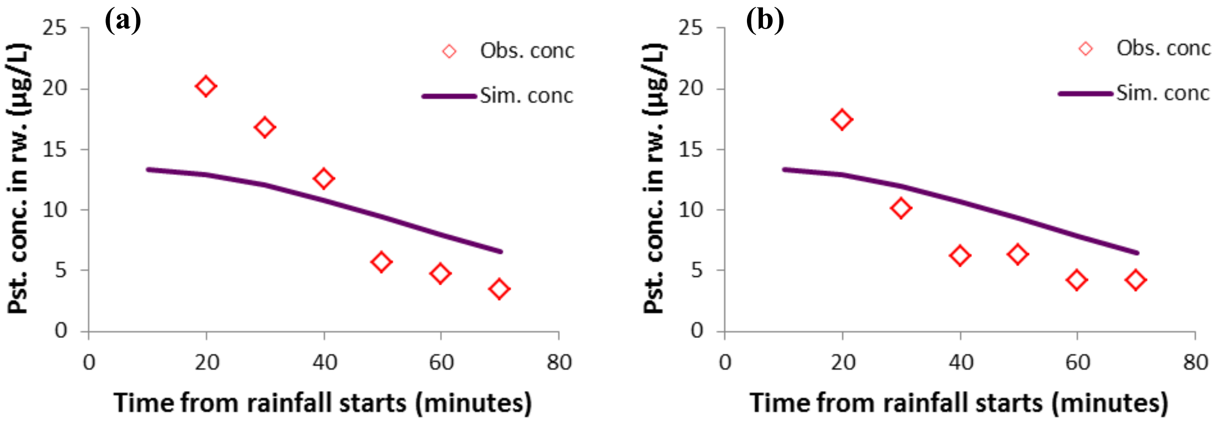


Figure 5.11. Clothianidin concentrations in runoff water in (a) calibration and (b) validation

The average values of clothianidin concentrations in runoff water were underestimated in calibration but overestimated in validation (Table 5.9). However, the statistical indexes for clothianidin concentrations in runoff water in calibration (R^2 = 0.92, *NSE* = 0.51, *PBIAS* = 9.50%) and in validation (R^2 = 0.72, *NSE* = 0.49, *PBIAS* = -16.90%) indicated an acceptable model performance (Table 5.10). Compared to the simulated clothianidin concentrations in sediment, those in runoff water were fitted reasonably with the observed data in both calibration and validation (Figure 5.11). As seen in Figure 5.11, the clothianidin concentrations in runoff water were higher at the beginning and declined at the end of the runoff in both calibartion and validation. These trends were similar to the observed data and model results of presticde runoff in the previous studies (Watanabe and Grismer, 2003, 2001).

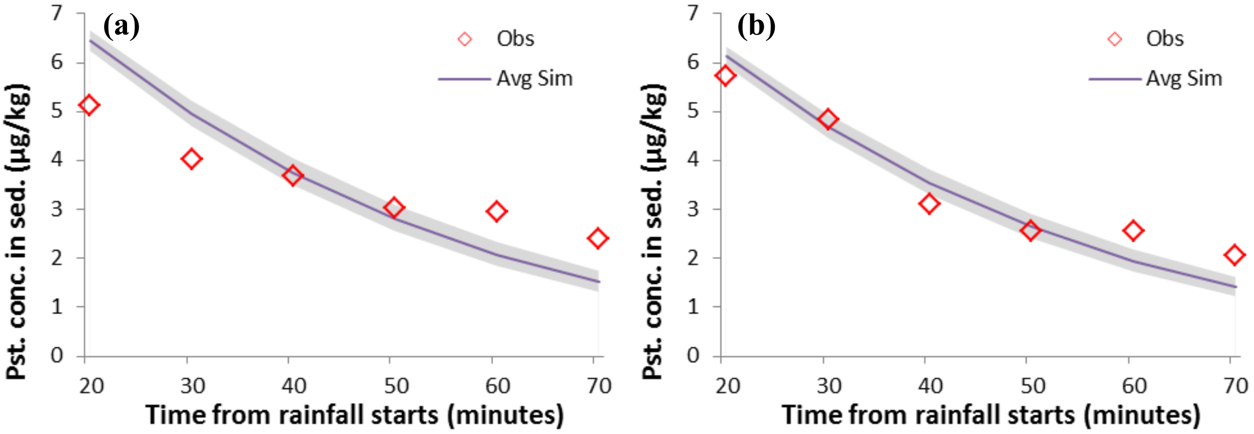


Figure 5.12. Uncertainty results of clothianidin in sediment in (a) calibration and (b) validation

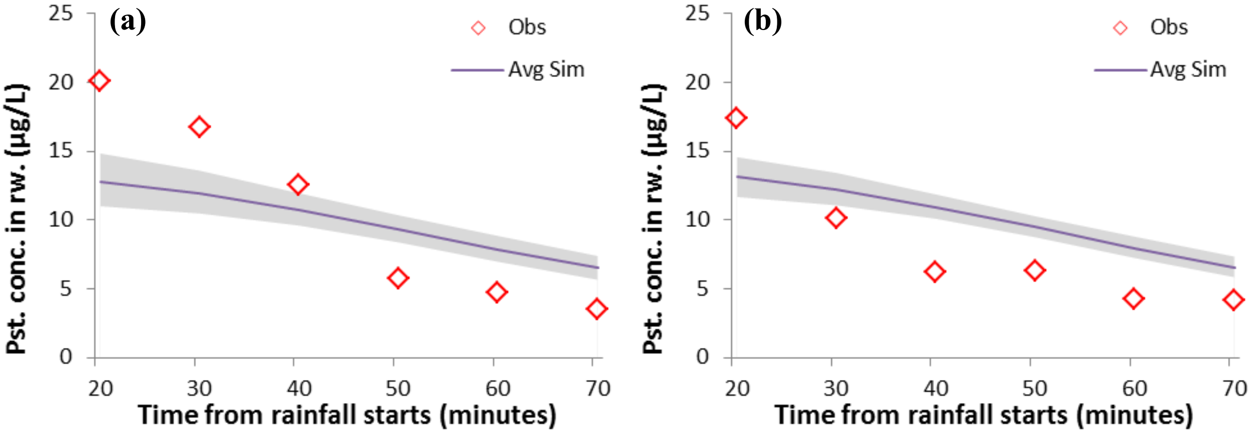


Figure 5.13. Uncertainty results of clothianidin in runoff water in (a) calibration and (b) validation

The valid parameters and observed data as well as uncertainty associated with clothianidin in sediment and in runoff water were checked by using the Monte Carlo simulation for clothianidin in sediment and in runoff water. The uncertainty results for clothianidin in sediment and in runoff water with 10% change of optimal input parameters of *alpha* and *beta* are shown in Figure 5.12 and

Figure 5.13. The thicknesses of 95% confidence intervals in calibration and validation of clothianidin in sediment highlighted the effect of the *alpha* and *beta* to the clothianidin in sediment results and were consistent for both calibration and validation (Figure 5.12). The similar trend was also found for the uncertainty of clothianidin in runoff water (Figure 5.13). The *alpha* and *beta* also highlighted their effects to the results of clothianidin in runoff water. As shown in Figure 5.13 that the thicknesses of 95% confidence intervals were consistent with the clothianidin in runoff water results for both calibration and validation. However, the higher effect of *alpha* and *beta* at the earlier time steps values of clothianidin in runoff water for both calibration and validation indicated more uncertainty of the simulated results or the observation data (Figure 5.13).

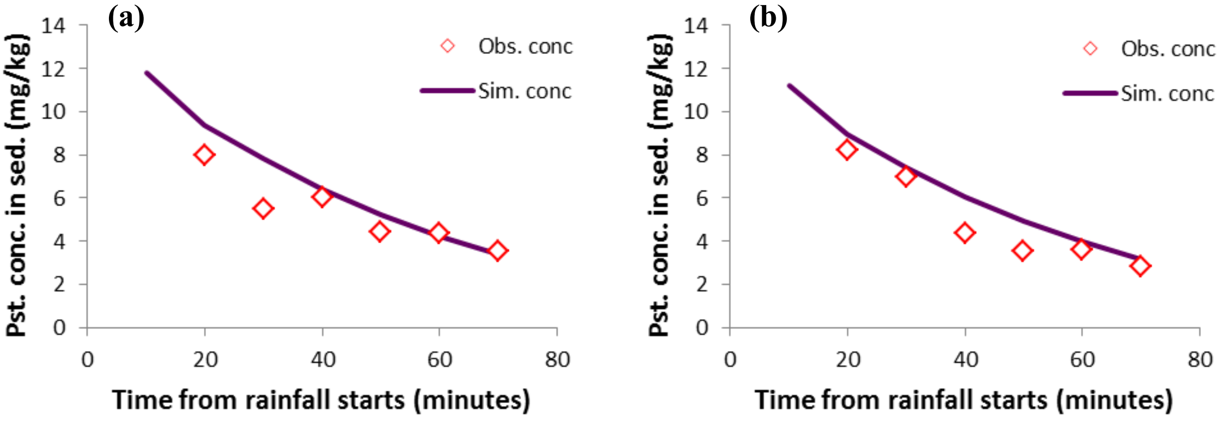


Figure 5.14. Imidacloprid concentrations in sediment in (a) calibration and (b) validation

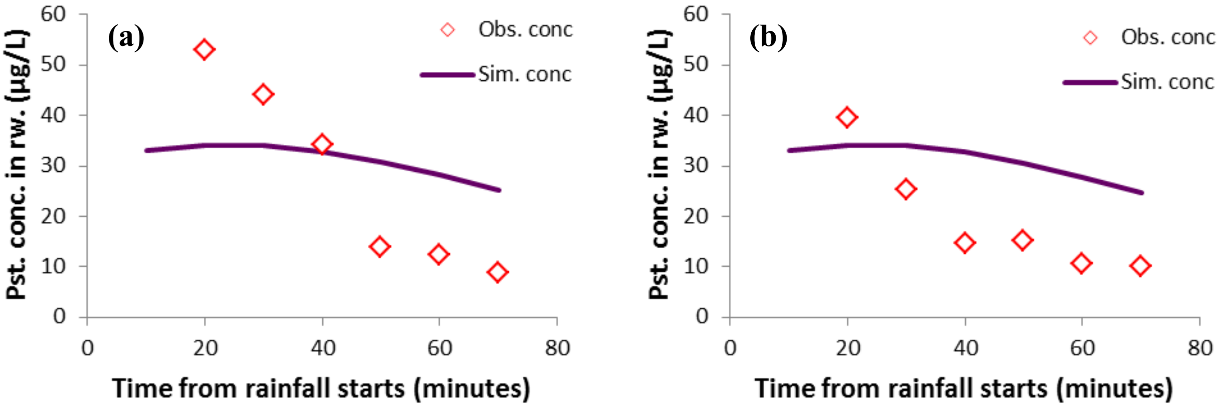


Figure 5.15. Imidacloprid concentrations in runoff water in (a) calibration and (b) validation

Finally, the simulation results of imidacloprid runoff are shown in Table 5.9. The simulated average imidacloprid concentrations in sediment were slightly higher than the observed data (in calibration, *PBIAS* = -1.40% and in validation, *PBIAS* = -1.60%). However, other statistical indexes of imidacloprid concentrations in sediment in calibration (R^2 = 0.88, *NSE* = 0.76) and in validation (R^2 = 0.93, *NSE* = 0.92) indicated a very good agreement between the simulated results and the observed data. The confirmation of good agreement can be seen in Figure 5.14. Compared to imidacloprid in sediment, the results of imidacloprid in runoff water were less accurate (the *NSE* values in calibration and validation were 0.28 and -0.16, respectively). The positive *NSE* in calibrated indicated an acceptable prediction; while the negative *NSE* found in validation indicated a failure prediction (Table 5.10). However, the other statistical indexes in validation (R^2 = 0.57, *PBIAS* = -38.4%) indicated that the mean values and the trends of simulated results were still agreed reasonably with the observed data (Table 5.10). As shown in Figure 5.14 and Figure 5.15, the simulated concentrations of imidacloprid in sediment as well as in runoff water were higher at the start and were lower at the end of the runoff. These simulated trends were fitted with those in the observed data. The imidacloprid concentrations in sediment agreed the observed data better than those in runoff water. Both of them had higher values at the start and lower values at the end of the runoff. These trends were found similar to those of clothianidin and were agreed with the previous studies on pesticide runoff (Watanabe and Grismer, 2003, 2001).

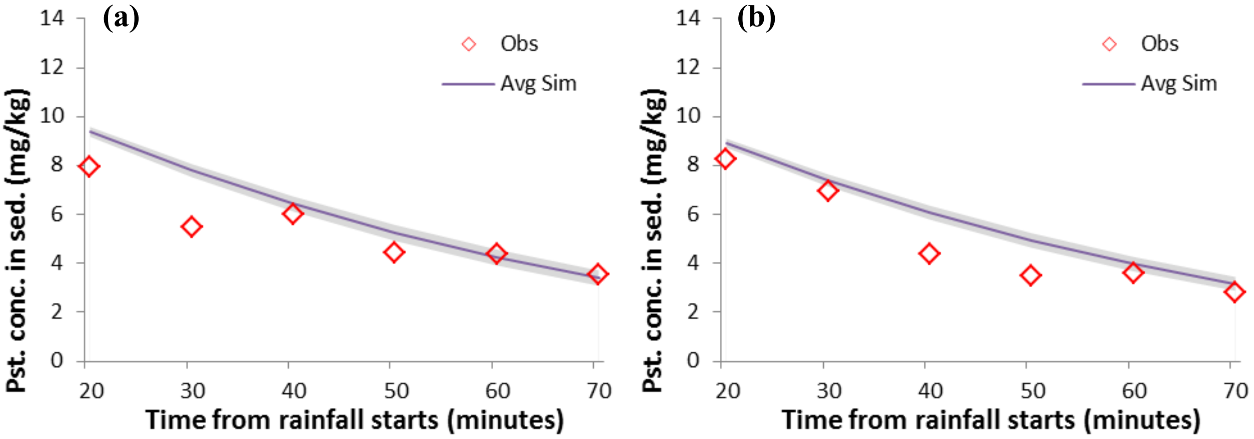


Figure 5.16. Uncertainty results of imidacloprid in sediment in (a) calibration and (b) validation

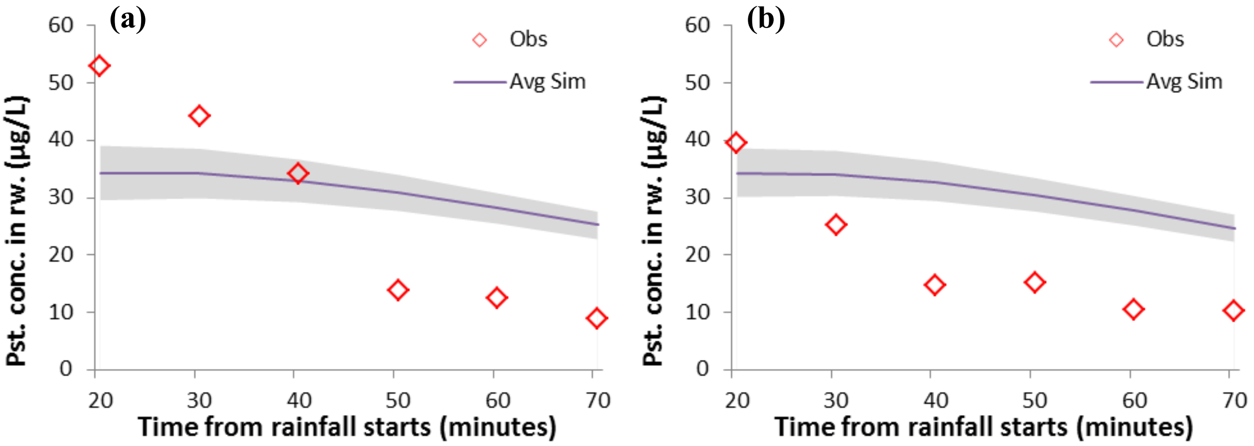


Figure 5.17. Uncertainty results of imidacloprid in runoff water in (a) calibration and (b) validation

The valid parameters and observed data as well as uncertainty associated with imidacloprid in sediment and in runoff water were checked by using the Monte Carlo simulation for imidacloprid in sediment and in runoff water. The uncertainty results for imidacloprid in sediment and in runoff water with 10% change of optimal input parameters of *alpha* and *beta* are shown in Figure 5.16 and Figure 5.17. The thicknesses of 95% confidence intervals in calibration and validation of imidacloprid in sediment highlighted the effect of the *alpha* and *beta* to the results of imidacloprid in sediment and were consistent for both calibration and validation (Figure 5.16). The similar trend was also found for the uncertainty of imidacloprid in runoff water (Figure 5.17). The *alpha* and *beta* also highlighted their effects to the results of imidacloprid in runoff water. As shown in Figure 5.17 that the thicknesses of 95% confidence intervals were consistent with the imidacloprid in runoff water results for both calibration and validation. However, the higher effect of *alpha* and *beta* at the earlier time steps values of imidacloprid in runoff water were found in both calibration and validation indicated more uncertainty of the simulated results or the observation data (Figure 5.17).

5.1.2.5 Results for Green-Ampt infiltration

In this section, the Green-Ampt infiltration was used to simulate runoff in plot 1 (calibration) and plot 2 (validation) under the first rainfall event (October 2nd, 2017) for Sakaecho upland field.

The sensitivity analysis result for runoff rate simulation in Green-Ampt method showed that the saturated water content, the field capacity and the saturated hydraulic conductivity (*Ks*) were the most sensitive parameters, in which the standardized regression rank coefficients were -0.24, 0.13 and -0.97 for the saturated water content, the field capacity and the saturated hydraulic conductivity, respectively. The similar trend was also found for cumulative runoff simulation in which the standardized regression rank coefficients were -0.21, 0.13 and -0.95 for the saturated water content, the field capacity and the saturated hydraulic conductivity, respectively. However, to maintain the values of water content (the saturated water content and the field capacity) similar to those used in CN method, *Ks* was the only parameter which was used for calibration and validation in this simulation. The calibrated value of *Ks* was found to be 68 mm/h. This *Ks* value was smaller than that used in CN runoff method; however the intention for this simulation was to check the model capacity to simulate runoff using Green-Ampt method.

The results of runoff rates for calibration and validation are shown in Figure 5.18. The *NSE* for runoff rates which are shown in Table 5.12 indicated a very good performance for calibration (0.81) and a good performance of the model for validation (0.72). Compared to those simulated in

CN runoff method, the Green-Ampt method performed better the simulated runoff rates.

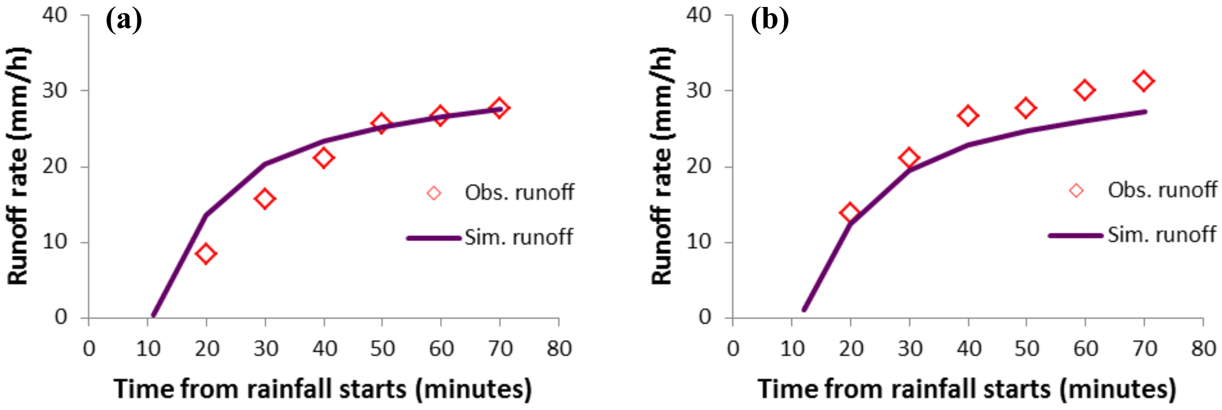


Figure 5.18. Runoff rates in (a) calibration and (b) validation (Green-Ampt method)

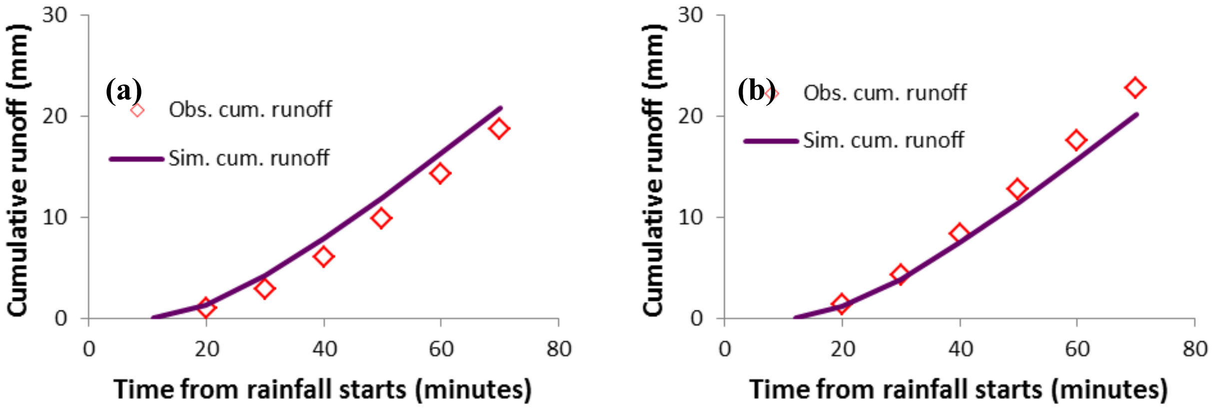


Figure 5.19. Cumulative runoffs in (a) calibration and (b) validation (Green-Ampt method)

Table 5.11. Average values for surface runoff using Green-Ampt method

Average values	**Unit**	**Calibration**		**Validation**	
		Obs.	Sim.	Obs.	Sim.
Time to first runoff	min	10	11	10	12
Runoff rate	mm/h	20.88	20.00	25.11	19.00
Cumulative runoff	mm	8.80	9.00	11.21	9.00

The results of cumulative runoff for calibration and validation are shown in Figure 5.19. The *NSE* for cumulative runoffs which are shown in Table 5.12 indicated a very good performance for both calibration (0.92) and validation (0.96). For simulating the cumulative runoff, the Green-Ampt method performed as well as CN runoff method.

Table 5.12. Model performance for surface runoff using Green-Ampt method

Statistical results	Calibration				Validation			
	RMSE (%)	*R²* (-)	*NSE* (-)	*PBIAS* (%)	*RMSE* (%)	*R²* (-)	*NSE* (-)	*PBIAS* (%)
Time to first runoff				-10				-20
Runoff rate	14.36	0.98	0.81 *1)*	-9.08 *1)*	12.53	0.99	0.72 *2)*	11.81 *2)*
Cumulative runoff	20.12	1.00	0.92 *1)*	-18.81 *2)*	13.20	1.00	0.96 *1)*	11.05 *2)*

Notes: *1)* very good, *2)* good, *3)* satisfactory, *4)* acceptable, *5)* unsatisfactory

The valid parameters and observed data as well as uncertainty associated with runoff rate and cumulative runoff (in Green-Ampt method) were checked by using the Monte Carlo simulation for runoff rate and cumulative runoff. The uncertainty results for runoff rate and cumulative runoff with 10% change of optimal input parameter of *Ks* are shown in Figure 5.20 and Figure 5.21. The great thicknesses of 95% confidence intervals in calibration and validation of runoff rate simulation highlighted the effect of *Ks* to the runoff rate results and were consistent in both calibration and validation (Figure 5.20). The similar trend was also found for the uncertainty of cumulative runoff (Figure 5.21). The *Ks* also highlighted its effect to the results of cumulative runoff. As shown in Figure 5.21 that the thicknesses of 95% confidence intervals were consistent in both calibration and validation of the cumulative runoff results in which the thicker bands were found at the last time values of the cumulative runoff.

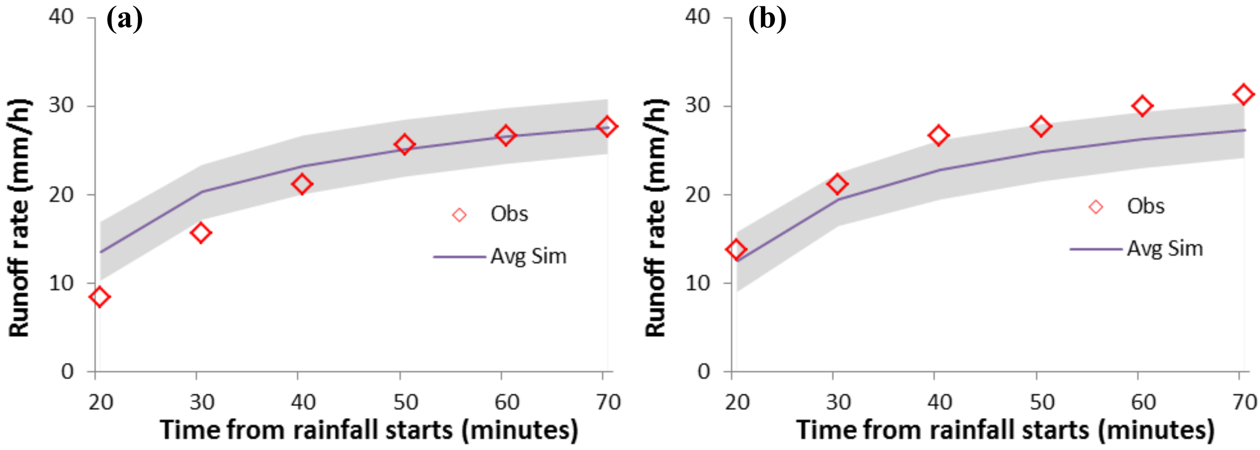


Figure 5.20. Uncertainty results for runoff rates in (a) calibration and (b) validation (Green-Ampt method)

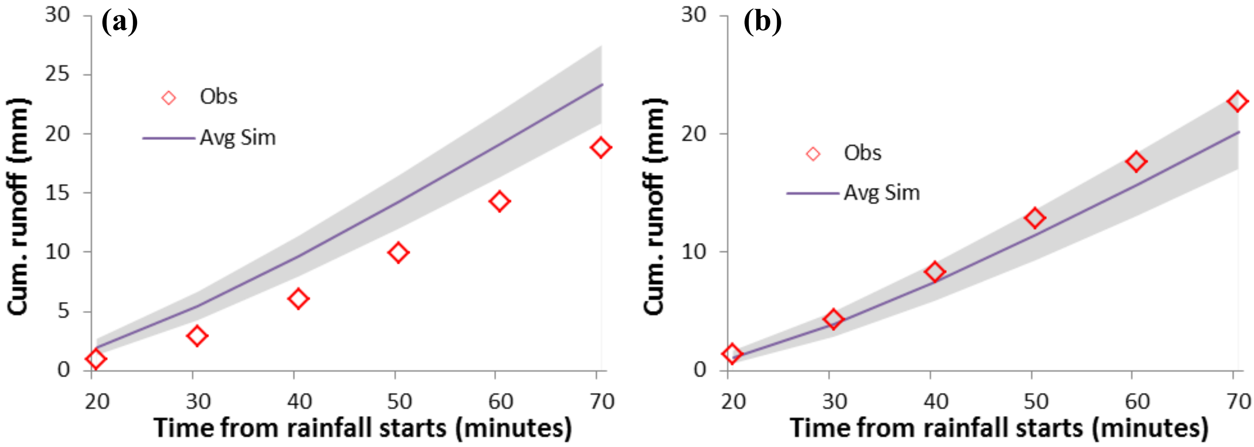


Figure 5.21. Uncertainty results for cumulative runoffs in (a) calibration and (b) validation (Green-Ampt method)

5.2 Case study in Sakaecho in 2017 - a continuous simulation

5.2.1 Input data

This simulation was a continued case from the above single event simulation. The observed data in details can be found in the previous study (Yadav and Watanabe, 2018). In the experiment condition, the plots were covered by the plastic from the application day to the first rainfall event, thus the rainfall data in that period were excluded from data input. The rainfall time step was modified into 10 minutes. The time step for temperature was 1 hour, and those for evaporation and solar radiation were one day which was similar to those in the single event simulation. The duration of simulation was 65 days from Sep 26th to November 30th, 2017.

The observed data included pesticide (clothianidin, imidacloprid) concentrations for 3 plots and water contents data for plot 1 and plot 2 in 4 layers of soils (0-1 cm, 1-5 cm, 5-10 cm, 10-15 cm). However, the water contents in plot 2 were resulted to have errors, thus data for plot 1 were only data available for water content calibration. The time step for observed water data was daily.

The average concentrations of pesticide in 15 cm depth were calculated for 3 plots to find the half-lives of biodegradation. For clothiadindin, the negative value of half-life biodegradation was found in plot 3 indicated a significant error for observed data of clothianidin concentration in soil in plot 3. For imidacloprid, the half-life biodegradation in plot 3 had very low R^2 (0.08) and that half-life value was quite different from the average values of those in plot 1 and 2. Thus, the average values of half-life biodegradation in plot 1 and plot 2 were used for 2 types of insecticides. The average concentration in 15 cm for clothianidin in plot 1 on 0, 6, 14, 22, 35, 64 days after application days were 0.241, 0.196, 0.142, 0.238, 0.285, 0.168 mg/kg, respectively. Those for clothianidin in plot 2 on 0, 6, 14, 22, 35, 64 days after application days were 0.188, 0.322, 0.187, 0.262, 0.220, 0.165 mg/kg, respectively. It can be seen from these data that the average concentrations of clothianidin were increased at some days. This indicated there must be certain errors in data collection and/or data analysis. The similar cases were also found for average imidacloprid in plots 1 and 2. Another error was also found for the average pesticide concentrations on the application day. Based on the results of pesticide concentrations in 15 cm depth, the application rates of pesticides of observation were calculated and compared with the application rates. The calculated application rates in plot 1 and plot 2 occupied 84.9% and 66.1% of the given application rate of clothianidin (256 g/ha) and occupied 92.3% and 65.1% of the given application rate of imidacloprid (320 g/ha), respectively.

In this simulation, data from plot 1 and 2 of clothianidin and imidacloprid concentrations in four layers of soil (0-1 cm, 1-5 cm, 5-10 cm, 10-15 cm) were used. The time steps for output and simulation were 10 minutes.

5.2.2 Results and discussion

5.2.2.1 Results for water content in soil layers

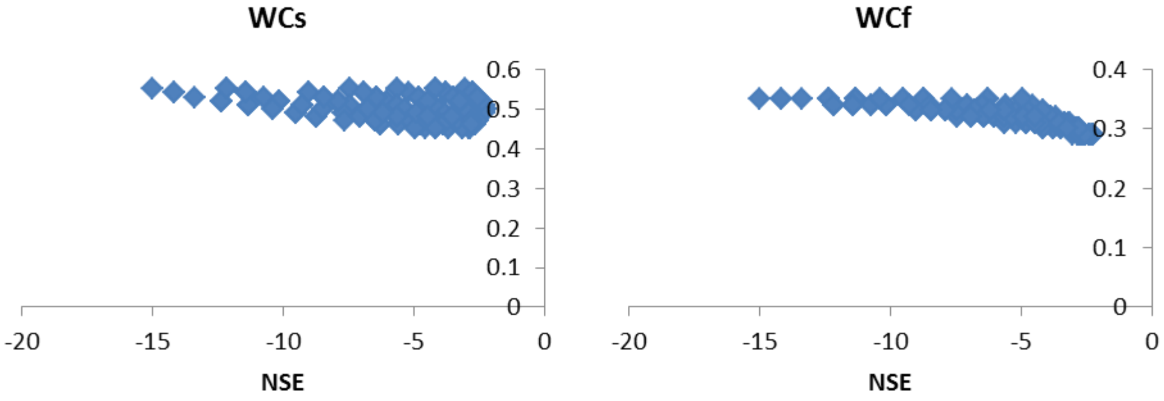


Figure 5.22. Ranges of saturated water content (*WCs*) and field capacity (*WCf*) in finding optimal solution for average water content in 15 cm for plot 1

In this simulation, the CN method was used and the option for *CN* varies with water content was selected. The initial abstraction ratio (0.06) was obtained from surface runoff simulation for the single rainfall event. The calibrated initial *CN* was found to be 44, in which the *PBIAS* of the cumulative runoff was -17.77%. In sensitivity analysis for water content, the saturated water content and the field capacity were found to be the most sensitive parameters. The standardized rank regression coefficients for the saturated water content and the field capacity were found to be 0.5 and 0.87, respectively. The MCS for water content output with optimal option for *WCs* and *WCf* is shown in Figure 5.22. It can be seen from Figure 5.22 that there were no values of the saturated water content and the field capacity that gave the positive *NSE* for water content. The calibrated values for saturated water content and field capacity were 0.5 and 0.32, respectively. The *NSE* for water content (-10.95) indicated an unsatisfactory model performance; however, the *PBIAS* for water content (-17.51%) indicated a satisfactory model performance (Table 5.13).

Table 5.13. Model performance for water content in 15cm in plot 1 (2 layers simulation)

Water content	**Obs. mean (mm^3/m^3)**	**Sim. mean (mm^3/mm^3)**	***RMSE* (%)**	**R^2 (-)**	***NSE* (-)**	***PBIAS* (%)**
In 15 cm	0.351	0.413	21.92	0.42	-10.95 5)	-17.51 3)

Notes: *1)* very good, *2)* good, *3)* satisfactory, *4)* acceptable, *5)* unsatisfactory

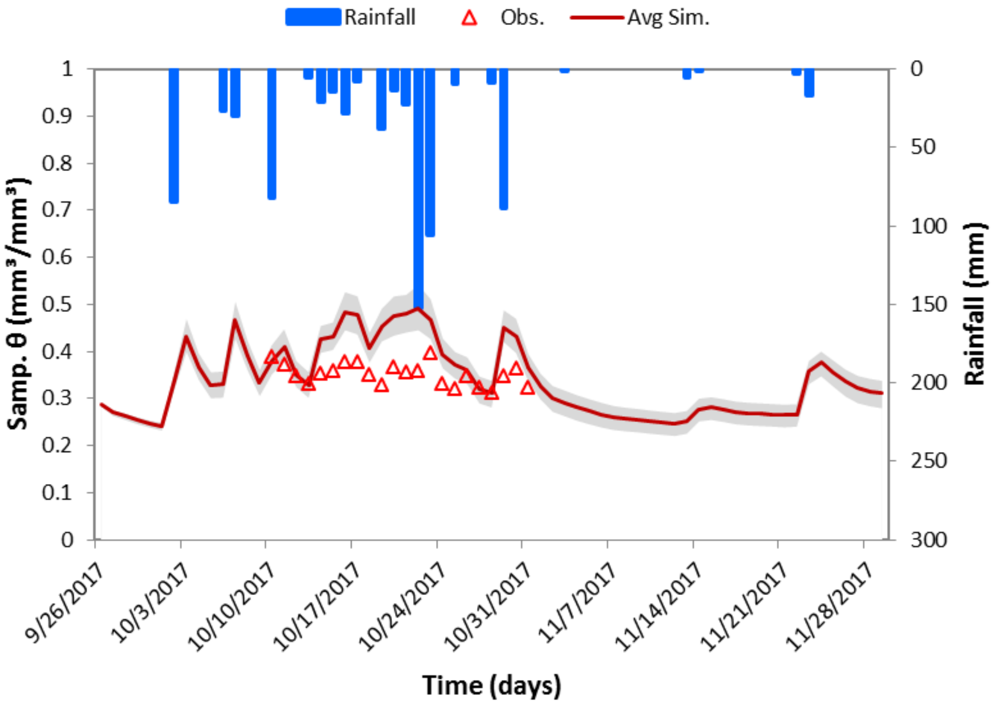


Figure 5.23. Average water content in 15 cm for plot 1

Figure 5.23 shows the average simulated and observed water contents in 15 cm. It can be seen from Figure 5.23 that, the observed water content values were very low as compared to the saturated water contents in the same period. There could be certain errors in water content observation or the limitation of the codes inside the model. The uncertainty of water content and its related parameters are also found from Figure 5.23. The thickness of 95% confidence interval around the average values of water contents highlighted the effects of sensitive parameters (the saturated water content and the field capacity) to the simulated water contents. The effect of rainfall to the simulated water contents was found. As shown in Figure 5.23, the simulated water contents increased significantly when high rainfall occurred, however there was a higher uncertainty of simulated water contents in the period of high rainfall which was indicated by the thicker band.

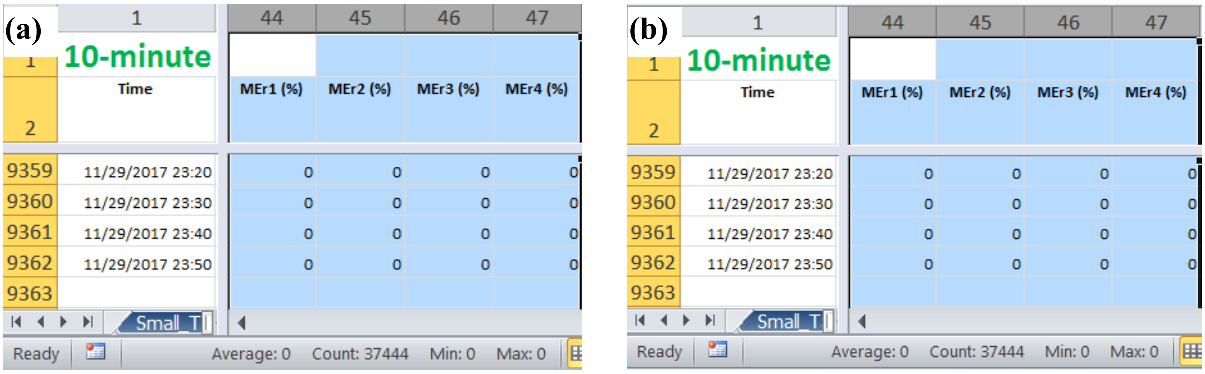
5.2.2.2 Calibrated parameters for pesticide concentrations in soil layers

It was found from the sensitivity analysis for clothianidin concentrations in soil that the field capacity and the bulk density were the most sensitive parameters. However, to inherit the parameters obtained from water content simulation, the saturated water content and the field capacity were kept as they were (WCs = 0.5 mm³/mm³, WCf = 0.32 mm³/mm³). The calibrated bulk density was 0.6 g/cm³ for both clothianidin and imiacloprid concentrations in soil layers. The other parameters were kept as they were as reported in Table 5.8.

5.2.2.3 Results for clothianidin concentrations in soil layers

The simulated results of clothianidin in soil layers are presented for 4 depths of 0-1 cm, 1-5 cm, 5-10 cm, 10-15 cm and the average value of clothianidin for the whole depth of 15 cm which was calculated from those four layers.

The mass balances of clothianidin concentrations in all layers for both plots were performed in Figure 5.24. There was no error for mass balances of clothianidin concentrations in all four layers for both plots (Figure 5.24.a and Figure 5.24.b).



(a)

	1	44	45	46	47
1	10-minute				
2	Time	MEr1 (%)	MEr2 (%)	MEr3 (%)	MEr4 (%)
9359	11/29/2017 23:20	0	0	0	0
9360	11/29/2017 23:30	0	0	0	0
9361	11/29/2017 23:40	0	0	0	0
9362	11/29/2017 23:50	0	0	0	0
9363					

Small_T

Ready Average: 0 Count: 37444 Min: 0 Max: 0

(b)

	1	44	45	46	47
1	10-minute				
2	Time	MEr1 (%)	MEr2 (%)	MEr3 (%)	MEr4 (%)
9359	11/29/2017 23:20	0	0	0	0
9360	11/29/2017 23:30	0	0	0	0
9361	11/29/2017 23:40	0	0	0	0
9362	11/29/2017 23:50	0	0	0	0
9363					

Small_T

Ready Average: 0 Count: 37444 Min: 0 Max: 0

Figure 5.24. Mass balance errors of clothianidin concentrations in 4 soil layers in (a) plot 1 and in (b) plot 2

The simulated results of clothianidin in layer 1 (0-1 cm) for plots 1 and 2 are shown in Figure 5.25 and Figure 5.26, respectively. The model performances for those results are shown in Table 5.14. It can be seen from Table 5.14 that the *NSE* results for plots 1 (0.63) and 2 (0.77) indicated a satisfactory and a very good performance of the model in predicting the clothianidin concentrations in 0-1 cm. The *PBIAS* results ($\pm 25\% \le PBIAS < \pm 40\%$) for clothianidin concentrations in 0-1 cm in both plots indicated a good performance of model (Table 5.14). The R^2 for plot 1 (0.75) and plot 2 (0.95) indicated that the trends of simulated results performed rather well with the observed data for both plots (Table 5.14). As shown in Figure 5.25 and Figure 5.26, the observed concentrations of clothiadin in 0-1 cm were lower than those in simulation. This can be explained by the lower calculated application rate as compared to the given application rate (on the application day, the pesticide concentration was found only in 0-1 cm). The simulated trends of clothinidin performed quite well with the observed data in both plots (Figure 5.25 and Figure 5.26). It can be seen from Figure 5.26 that there could be certain errors in the observed data in 0-1 cm for plot 2 because the second time series value was higher than the first time series value.

Table 5.14. Model performance for clothianidin concentration in layer 1 for 2 plots

Clothianidin concentration in 0-1 cm	**Obs. mean (mg/kg)**	**Sim. mean (mg/kg)**	***RMSE* (%)**	**R^2 (-)**	***NSE* (-)**	***PBIAS* (%)**
Plot 1	1.221	0.900	58.15	0.75	0.63*3)*	26.32*2)*
Plot 2	1.385	0.963	39.28	0.95	0.77*1)*	30.47*2)*

Notes: *1)* very good, *2)* good, *3)* satisfactory, *4)* acceptable, *5)* unsatisfactory

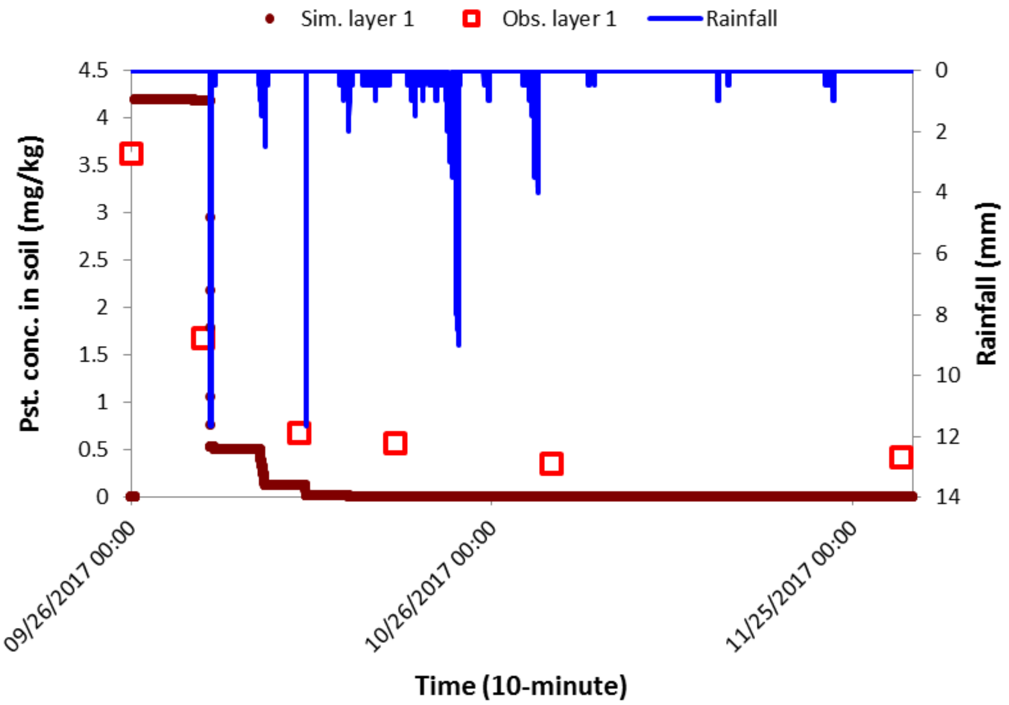


Figure 5.25. Result of clothianidin concentration in 0-1 cm (plot 1)

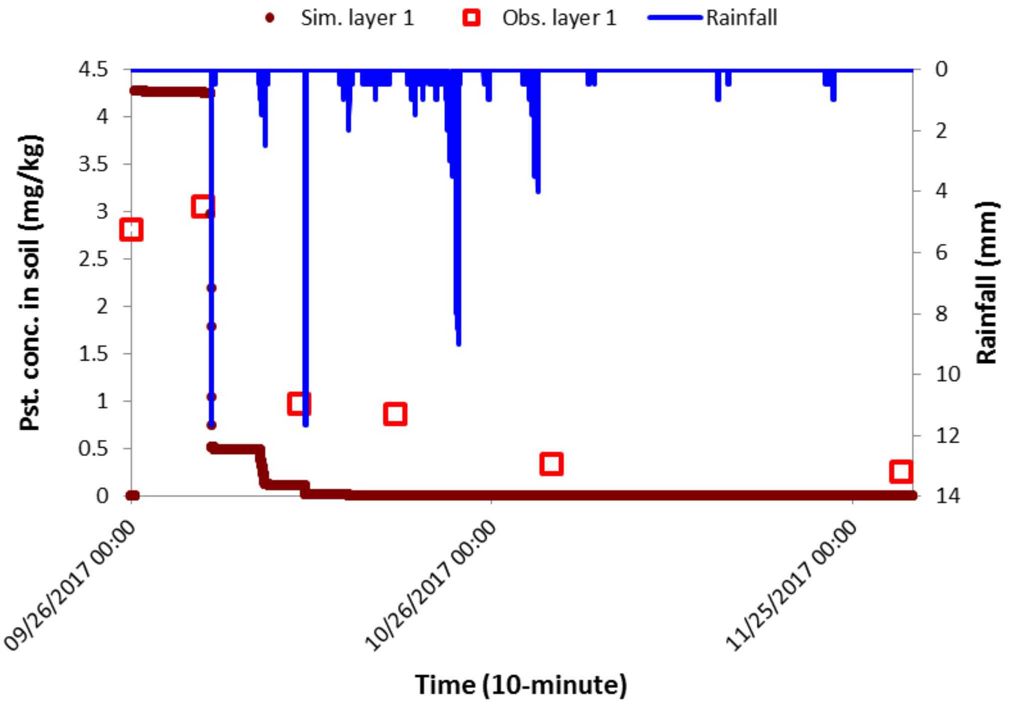


Figure 5.26. Result of clothianidin concentration in 0-1 cm (plot 2)

The simulated results of clothianidin in layer 2 (1-5 cm) for plots 1 and 2 are shown in Figure

5.27 and Figure 5.28, respectively. The model performances for those results are shown in Table 5.15. It can be seen from Table 5.15 that the *NSE* results for both plots were negative indicated an unsatisfactory model performance. The *PBIAS* results (< ±25%) for clothianidin concentrations in 1-5 cm in both plots indicated a very good performance of the model (Table 5.15). The R^2 for plot 1 (0) and plot 2 (0.11) were very low indicated that the trends of simulated results were not performed well with the observed data for both plots (Table 5.15). There could be the limitation from the codes or the error in the observation data.

Table 5.15. Model performance for clothianidin concentration in layer 2 for 2 plots

Clothianidin concentration in 1-5 cm	**Obs. mean (mg/kg)**	**Sim. mean (mg/kg)**	***RMSE* (%)**	**R^2 (-)**	***NSE* (-)**	***PBIAS* (%)**
Plot 1	0.232	0.218	108.78	0	-2.44*5)*	6.38*1)*
Plot 2	0.259	0.204	82.65	0.11	-1.22*5)*	21.07*1)*

Notes: *1)* very good, *2)* good, *3)* satisfactory, *4)* acceptable, *5)* unsatisfactory

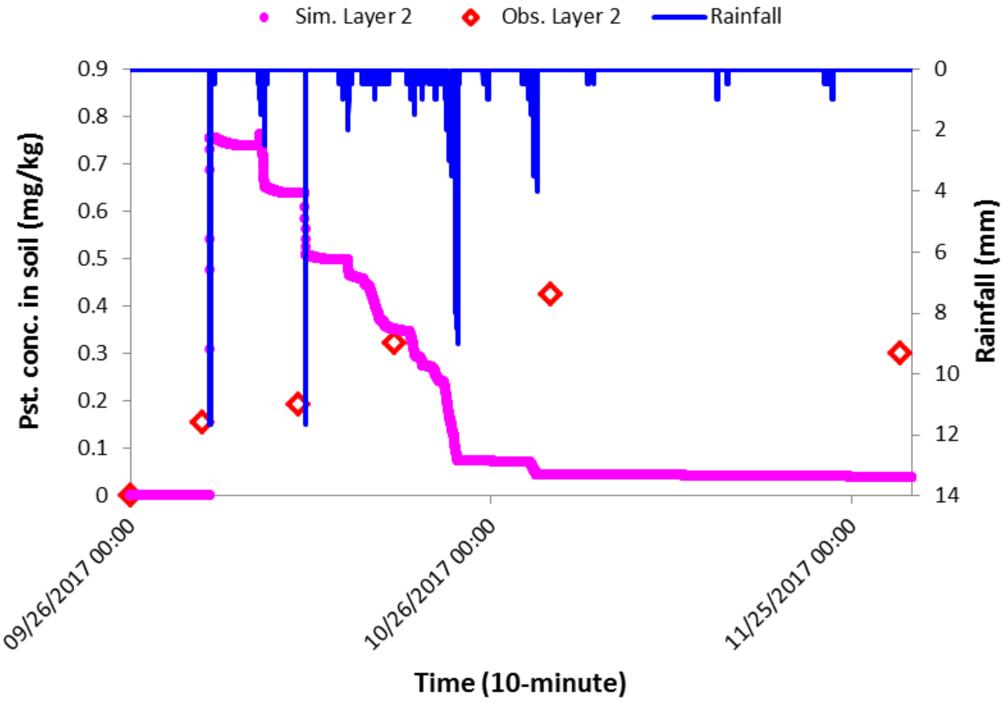


Figure 5.27. Result of clothianidin concentration in 1-5 cm (plot 1)

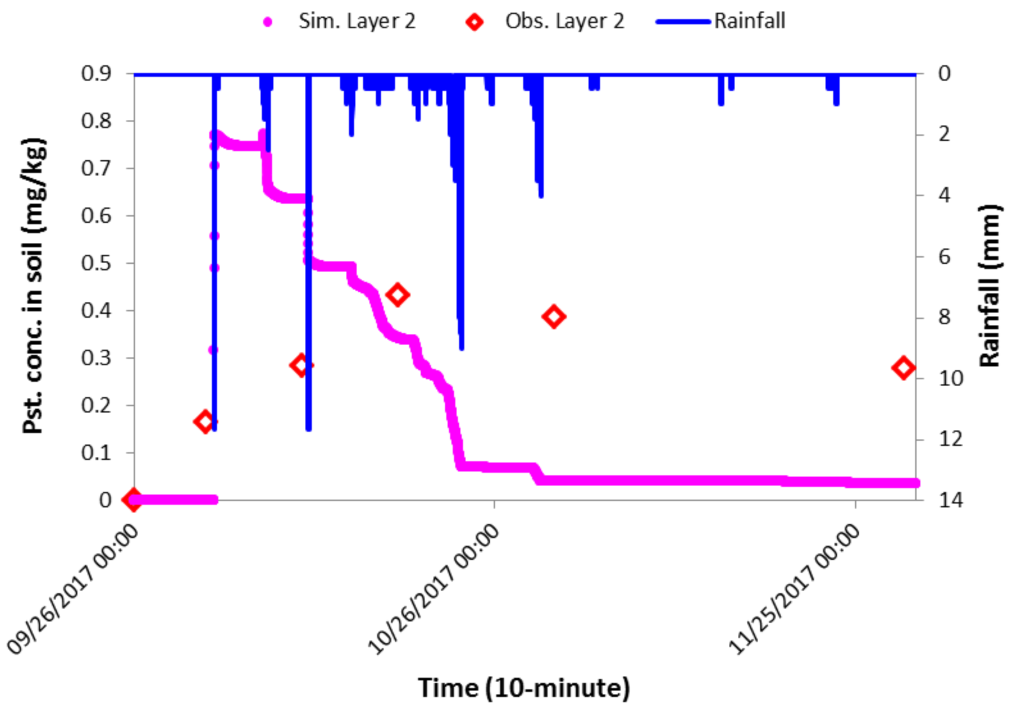


Figure 5.28. Result of clothianidin concentration in 1-5 cm (plot 2)

The simulated results of clothianidin in layer 3 (5-10 cm) for plots 1 and 2 are shown in Figure 5.29 and Figure 5.30, respectively. The model performances for those results are shown in Table 5.16. It can be seen from Table 5.16 that the *NSE* results for both plots were negative indicated an unsatisfactory model performance. The *PBIAS* results for clothianidin concentrations in 5-10 cm indicated a good model performance for plot 1 (*PBIAS* < ±25%) and a satisfactory performance for plot 2 (±25% ≤ *PBIAS* < ±40%) (Table 5.16). As shown in Figure 5.29 and Figure 5.30, the simulated trend of clothianidin concentration in plot 1 matched rather well with the observed data ($R^2 = 0.51$) but that for plot 2 did not perform well ($R^2 = 0.11$). It can be seen from Figure 5.29 and Figure 5.30, the trends of two observed data of clothianidin in layer 3 for both plots were not consistent indicated that there was possible error in the observation data.

Table 5.16. Model performance for clothianidin concentration in layer 3 for 2 plots

Clothianidin concentration in 5-10 cm	**Obs. mean (mg/kg)**	**Sim. mean (mg/kg)**	***RMSE* (%)**	**R^2 (-)**	***NSE* (-)**	***PBIAS* (%)**
Plot 1	0.123	0.162	74.51	0.51	-0.17$^{5)}$	-32.22$^{2)}$
Plot 2	0.110	0.162	114.95	0.11	-4.19$^{5)}$	-47.15$^{3)}$

Notes: *1)* very good, *2)* good, *3)* satisfactory, *4)* acceptable, *5)* unsatisfactory

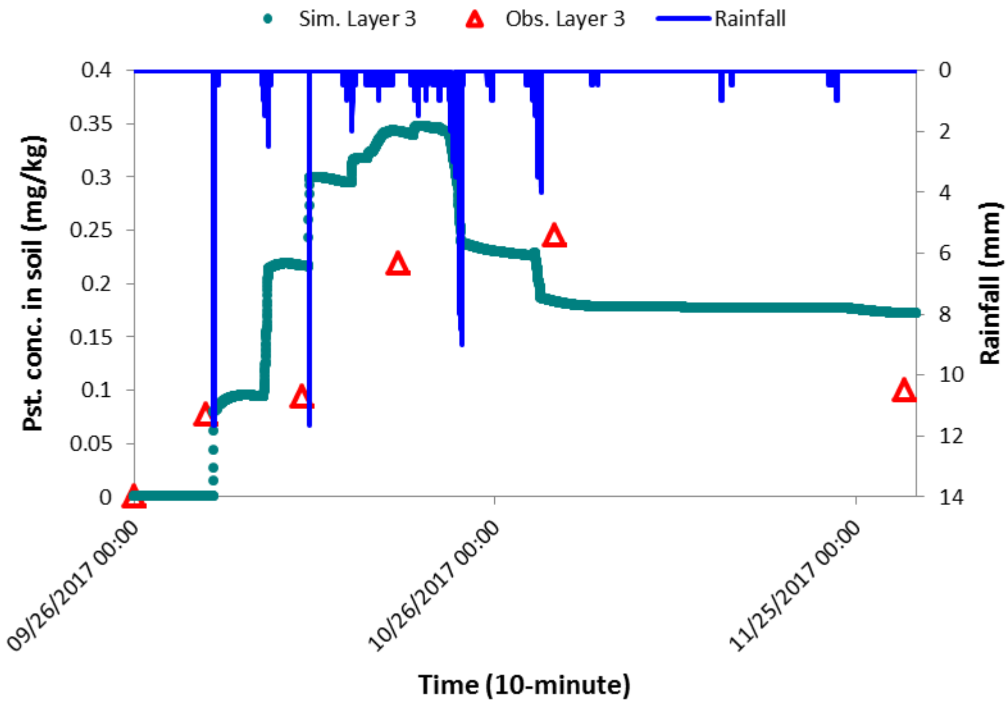


Figure 5.29. Result of clothianidin concentration in 5-10 cm (plot 1)

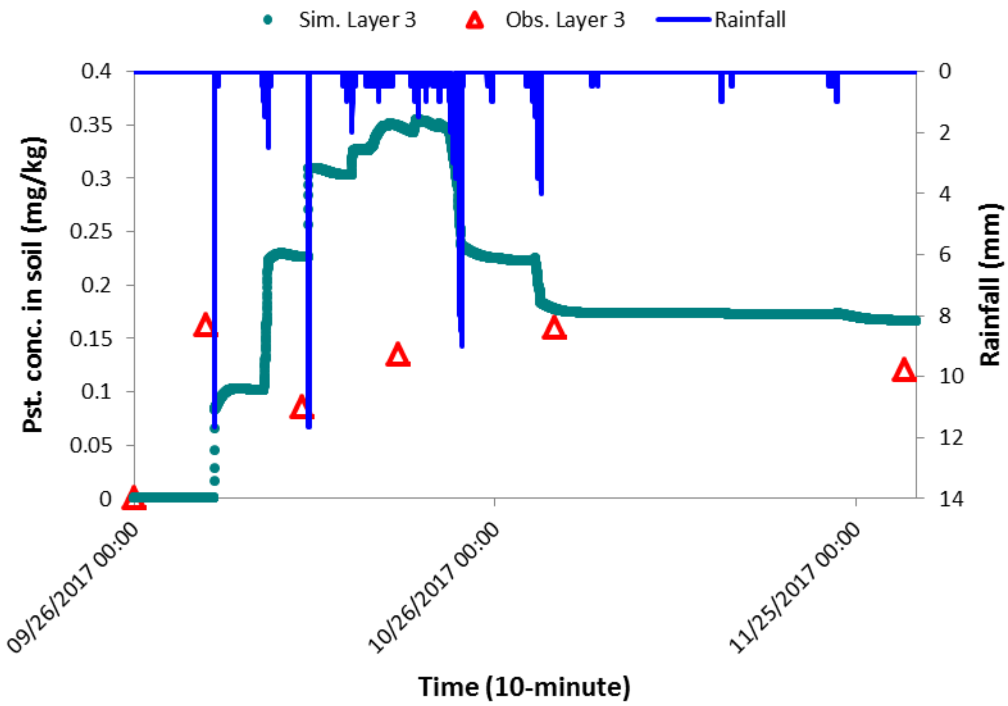


Figure 5.30. Result of clothianidin concentration in 5-10 cm (plot 2)

The simulated results of clothianidin in layer 4 (10-15 cm) for plots 1 and 2 are shown in Figure 5.31 and Figure 5.32, respectively. The model performances for those results are shown in Table 5.17. The *NSE* results for both plots were negative (Table 5.17) indicated an unsatisfactory model performance. The *PBIAS* results for clothianidin concentrations in 10-15 cm indicated a good model performance for plot 1 (±25% ≤ *PBIAS* < ±40%) and a satisfactory performance for plot 2 (±40% ≤ *PBIAS* < ±70%) (Table 5.17). The R^2 for plot 1 (0.64) and plot 2 (0.65) indicated the trends of simulated results performed rather well with the observed data for both plots (Table 5.17). As shown in Figure 5.31 and Figure 5.32, the simulated trend of clothianidin concentration in plot 1 matched quite well with the observed data and performed better than the trend in plot 2. As shown in Figure 5.29 to Figure 5.32, in the observed data the last values of clothianidin in layer 4 were decreased but those in layer 3 were also decreased for both plots. This was not reasonable because in the same day, the decreasing of pesticide concentration in the above layer (layer 3) would increase the pesticide concentration to the right below layer (layer 4). In addition, the trends of clothianidin concentrations in layer 4 for both plots were not consistent (Figure 5.31 and Figure 5.32). From these reasons, there could be some errors in the observation of clothianidin concentrations in layer 4. Therefore, it was difficult for the model to match with such low quality of data.

Table 5.17. Model performance for clothianidin concentration in layer 4 for 2 plots

Clothianidin concentration in 10-15 cm	**Obs. mean (mg/kg)**	**Sim. mean (mg/kg)**	***RMSE* (%)**	**R^2 (-)**	***NSE* (-)**	***PBIAS* (%)**
Plot 1	0.083	0.113	86.50	0.64	-0.25 *5)*	-35.91 *2)*
Plot 2	0.077	0.115	105.29	0.66	-2.27 *5)*	-49.34 *3)*

Notes: *1)* very good, *2)* good, *3)* satisfactory, *4)* acceptable, *5)* unsatisfactory

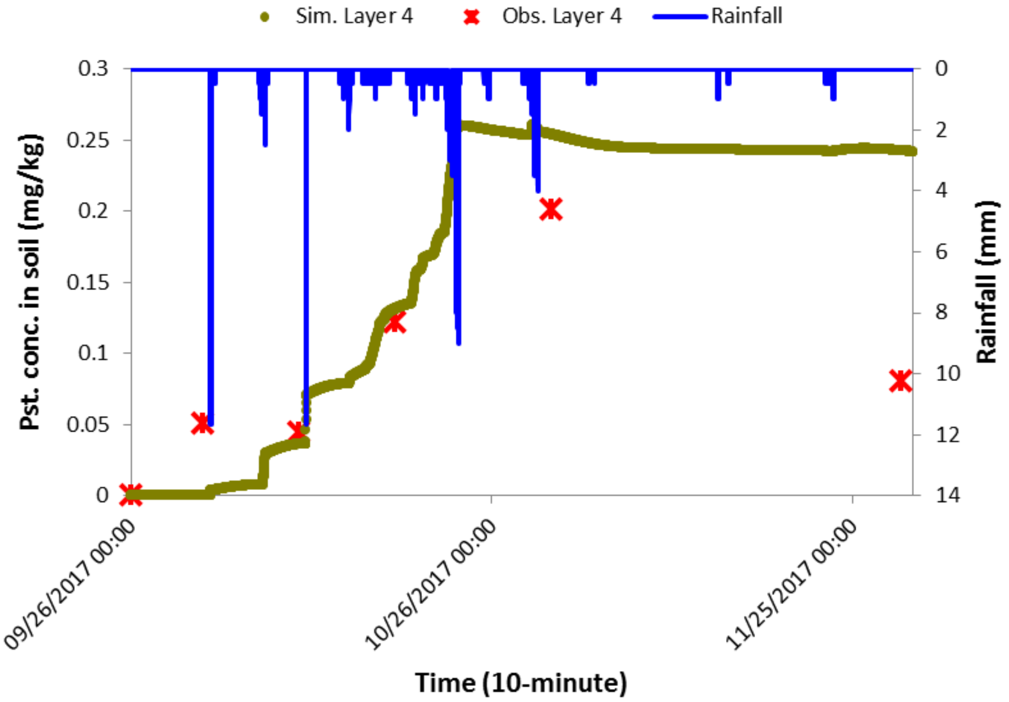


Figure 5.31. Result of clothianidin concentration in 10-15 cm (plot 1)

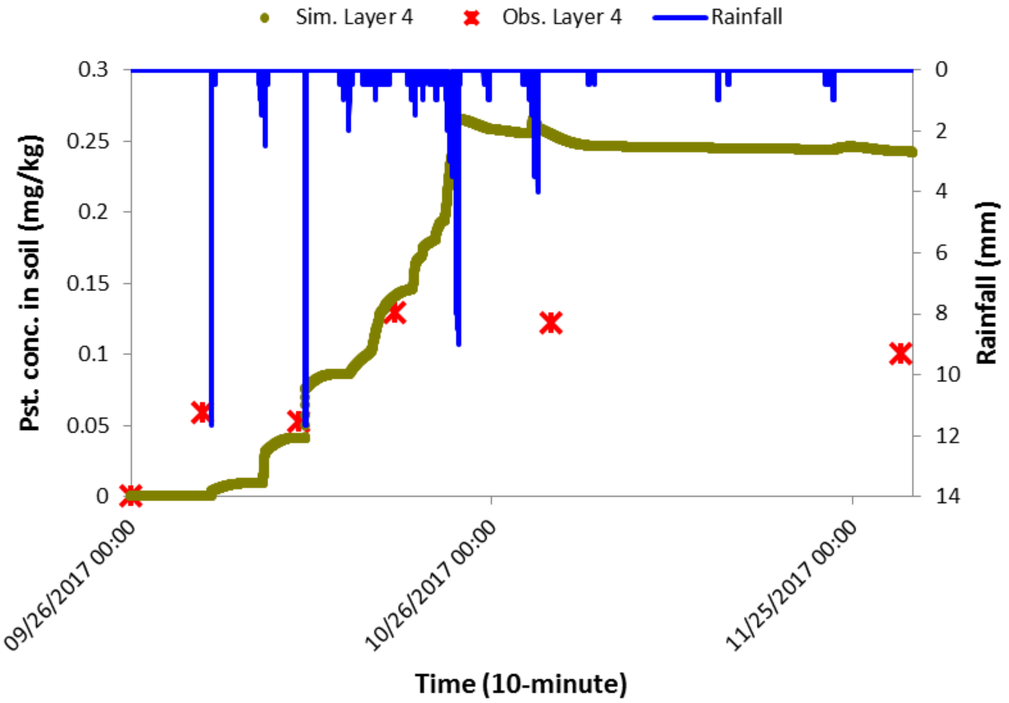


Figure 5.32. Result of clothianidin concentration in 10-15 cm (plot 2)

The simulated results of average clothianidin concentration in 0-15 cm for plots 1 and 2 are shown in Figure 5.33 and Figure 5.34, respectively. The model performances for those results are shown in Table 5.18. It can be seen from Table 5.18 that the *NSE* result for plot 1 was negative (-1.96) indicated an unsatisfactory model performance while the *NSE* value for plot 2 (0.24) indicated an acceptable model performance. The *PBIAS* results for clothianidin concentrations in 0-15 cm for both plots (< 25%) indicated a very good model performance (Table 5.18). As shown in Figure 5.33 and Figure 5.34 the observed data went up and down; in addition, the trends of two series of observation data in two plots were quite different or inconsistent indicated a great uncertainty of data observation (R^2 were 0.15 and 0.43 for plot 1 and plot 2, respectively). Therefore, it was difficult for the model to generate the simulated results to fit such a data series.

Table 5.18. Model performance for clothianidin concentration in 15 cm for 2 plots

Clothianidin concentration in 15 cm	**Obs. mean (mg/kg)**	**Sim. mean (mg/kg)**	***RMSE* (%)**	**R^2 (-)**	***NSE* (-)**	***PBIAS* (%)**
Plot 1	0.212	0.210	39.17	0.15	-1.96⁵⁾	1.08¹⁾
Plot 2	0.224	0.211	20.75	0.43	0.24⁴⁾	5.64¹⁾

Notes: *1)* very good, *2)* good, *3)* satisfactory, *4)* acceptable, *5)* unsatisfactory

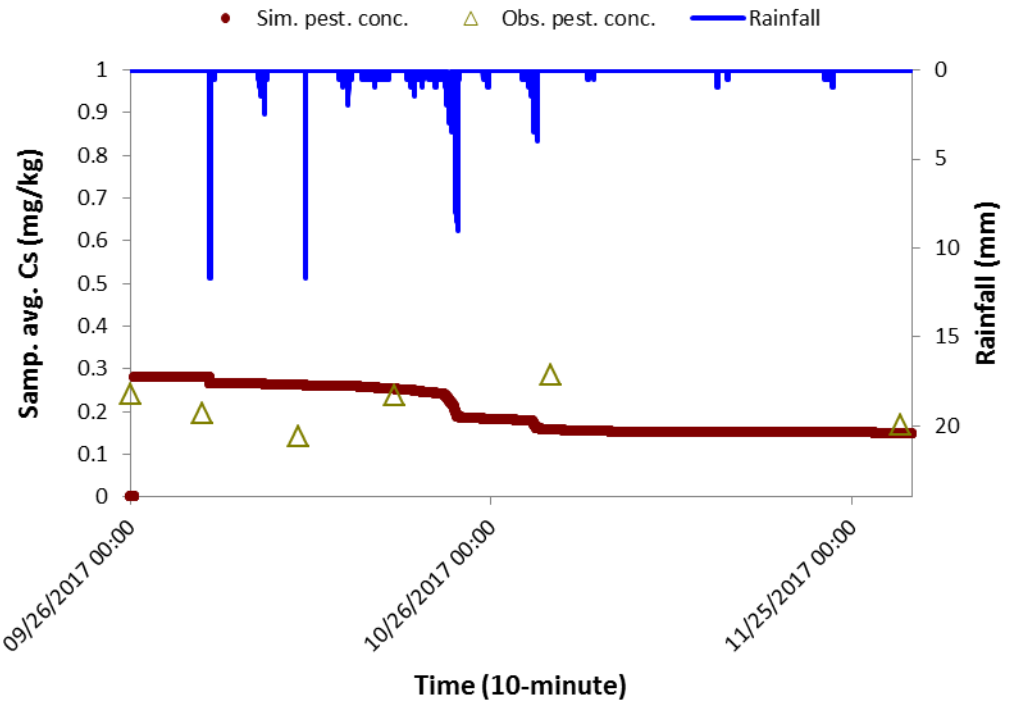


Figure 5.33. Result of clothianidin concentration in 15 cm (plot 1)

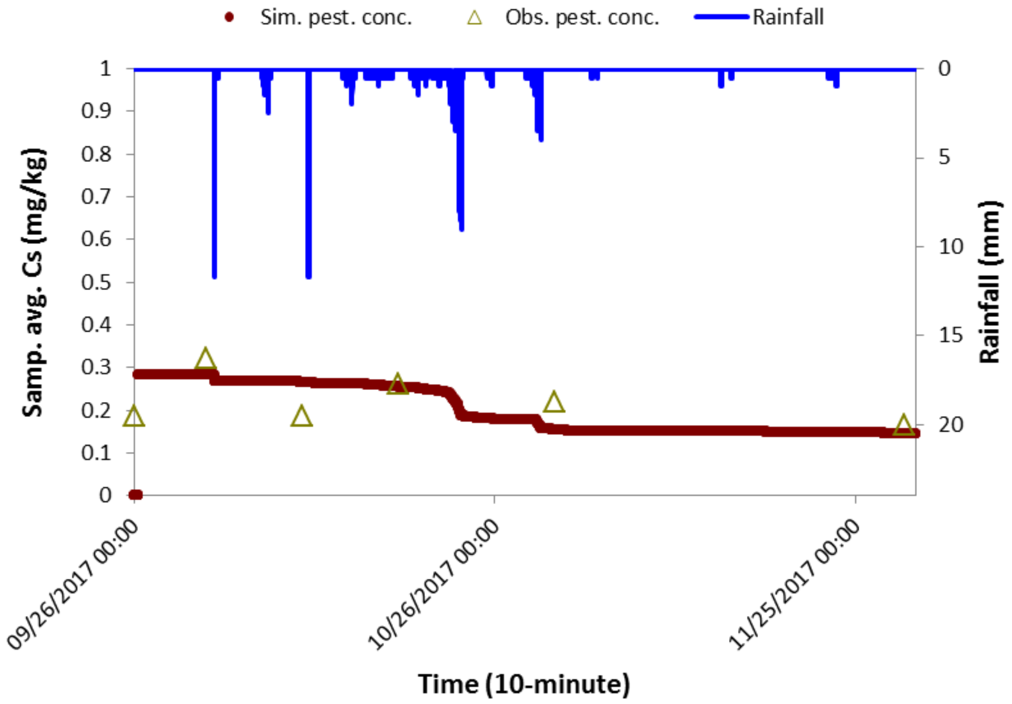


Figure 5.34. Result of clothianidin concentration in 15 cm (plot 2)

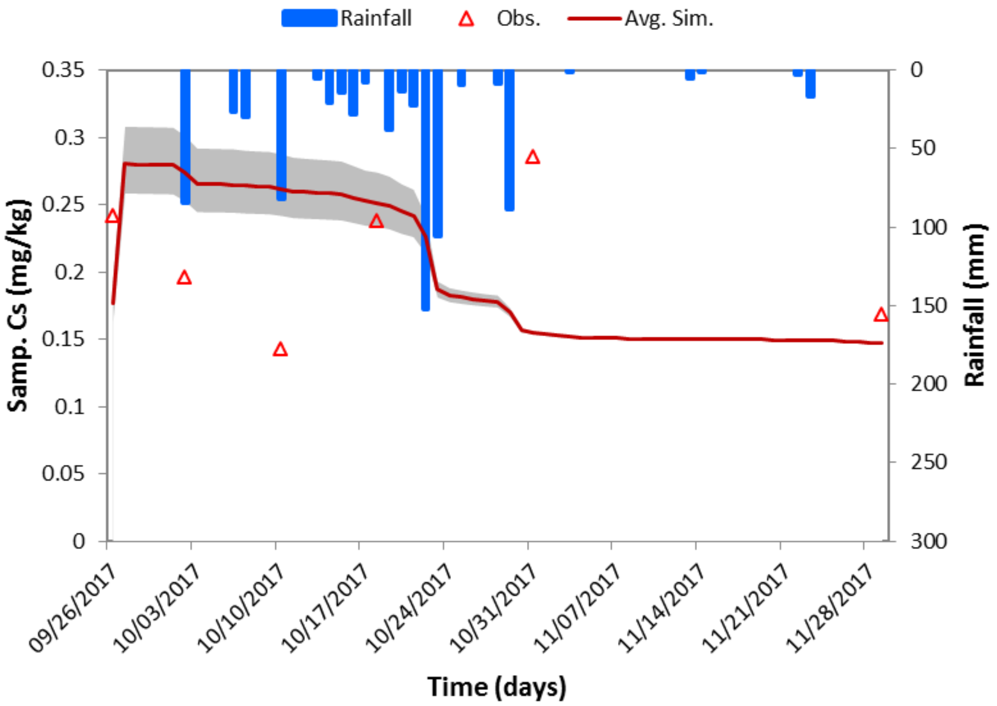


Figure 5.35. Uncertainty result of clothianidin concentration in 15 cm (plot 1)

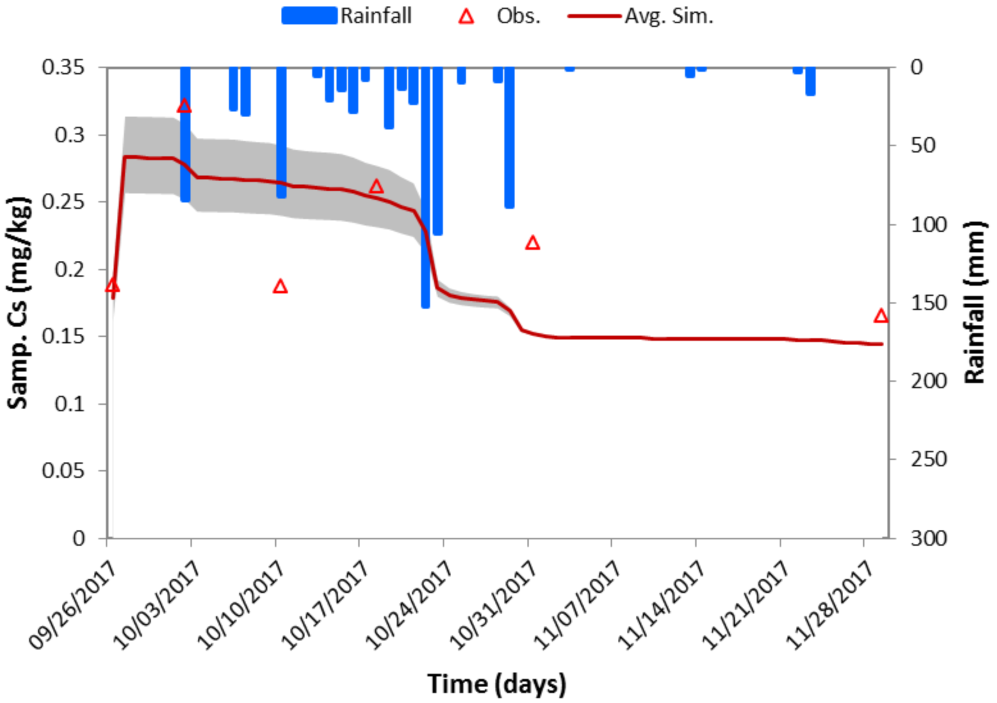
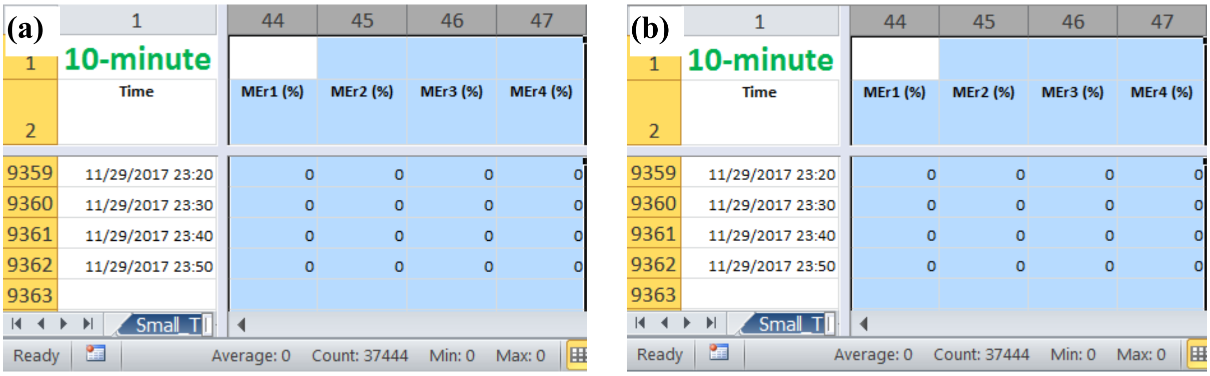


Figure 5.36. Uncertainty result of clothianidin concentration in 15 cm (plot 2)

The uncertainty results of average clothianidin concentration in 0-15 cm for plots 1 and 2 are shown in Figure 5.35 and Figure 5.36, respectively. The great thickness of 95% confidence interval of the average clothianidin concentration in 0-15 cm for both plots highlighted the effect of *Rb* to those concentration results as well as the high uncertainty of the clothianidin concentration results.

5.2.2.4 Results for imidacloprid concentrations in soil layers



(a)

	1	44	45	46	47
1	10-minute				
2	Time	MEr1 (%)	MEr2 (%)	MEr3 (%)	MEr4 (%)
9359	11/29/2017 23:20	0	0	0	0
9360	11/29/2017 23:30	0	0	0	0
9361	11/29/2017 23:40	0	0	0	0
9362	11/29/2017 23:50	0	0	0	0
9363					

Average: 0 Count: 37444 Min: 0 Max: 0

(b)

	1	44	45	46	47
1	10-minute				
2	Time	MEr1 (%)	MEr2 (%)	MEr3 (%)	MEr4 (%)
9359	11/29/2017 23:20	0	0	0	0
9360	11/29/2017 23:30	0	0	0	0
9361	11/29/2017 23:40	0	0	0	0
9362	11/29/2017 23:50	0	0	0	0
9363					

Average: 0 Count: 37444 Min: 0 Max: 0

Figure 5.37. Mass balance errors of clothianidin concentrations in 4 soil layers in (a) plot 1 and in (b) plot 2

Similar to the case of clothianidin, the simulated results of imidacloprid in soil layers are presented for 4 depths of 0-1 cm, 1-5 cm, 5-10 cm, 10-15 cm and the average value of imidacloprid for the whole depth of 15 cm which was calculated from those four layers.

The mass balances of clothianidin concentrations in all layers for both plots were performed in Figure 5.37. There was no error for mass balances of imidacloprid concentrations in all four layers for both plots (Figure 5.37.a and Figure 5.37.b).

Table 5.19. Model performance for imidacloprid concentration in layer 1 for 2 plots

Imidacloprid concentration in 0-1 cm	**Obs. mean (mg/kg)**	**Sim. mean (mg/kg)**	***RMSE*** **(%)**	**R^2 (-)**	***NSE*** **(-)**	***PBIAS*** **(%)**
Plot 1	1.707	1.255	60.48	0.69	0.56*3)*	26.47*2)*
Plot 2	1.868	1.299	40.06	0.95	0.71*2)*	30.46*2)*

Notes: *1)* very good, *2)* good, *3)* satisfactory, *4)* acceptable, *5)* unsatisfactory

The simulated results of imidacloprid in layer 1 (0-1 cm) for plots 1 and 2 are shown in Figure 5.38 and Figure 5.39, respectively. The model performances for those results are shown in Table 5.19. It can be seen from Table 5.19 that the *NSE* results for plots 1 (0.56) and 2 (0.71) indicated a satisfactory performance and a good performance of the model in predicting the imidacloprid concentrations in 0-1 cm. The *PBIAS* results for imidacloprid concentrations in 0-1 cm in both plots indicated a good performance of model (±25% ≤ *PBIAS* < ±40%) (Table 5.19). The R^2 for plot 1 (0.69) and plot 2 (0.95) indicated that the trends of simulated results performed rather well with the observed data for both plots (Table 5.19). As shown in Figure 5.38 and Figure 5.39, the observed concentrations of imidacloprid in 0-1 cm were lower than those in simulation. This can be explained by the lower calculated application rate as compared to the given application rate (on the application day, the pesticide concentration was found only in 0-1 cm). The simulated trends of imidacloprid performed quite well with the observed data in both plots (Figure 5.38 and Figure 5.39). It can be seen from Figure 5.38 that there could be certain errors in the observed data in 0-1 cm for plot 1 because the fourth time series value was higher than the third time series value. Similar to the case of plot 1, it can be seen from Figure 5.39 that there could be certain errors in the observed data in 0-1 cm for plot 2 because the second time series value was higher than the first time series value.

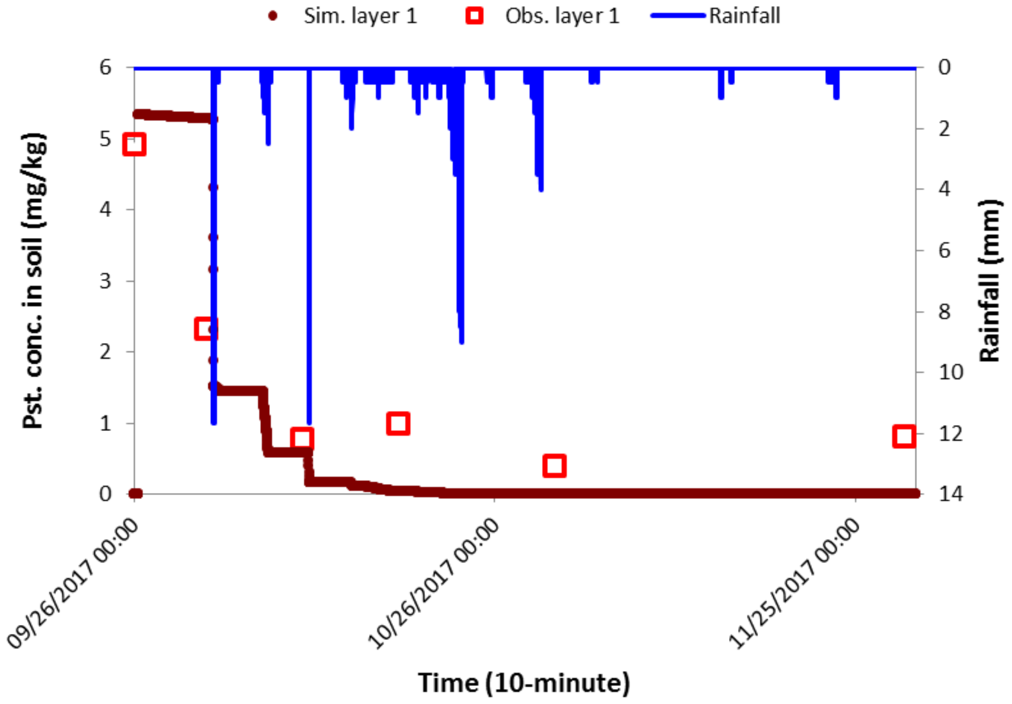


Figure 5.38. Result of imidacloprid concentration in 0-1 cm (plot 1)

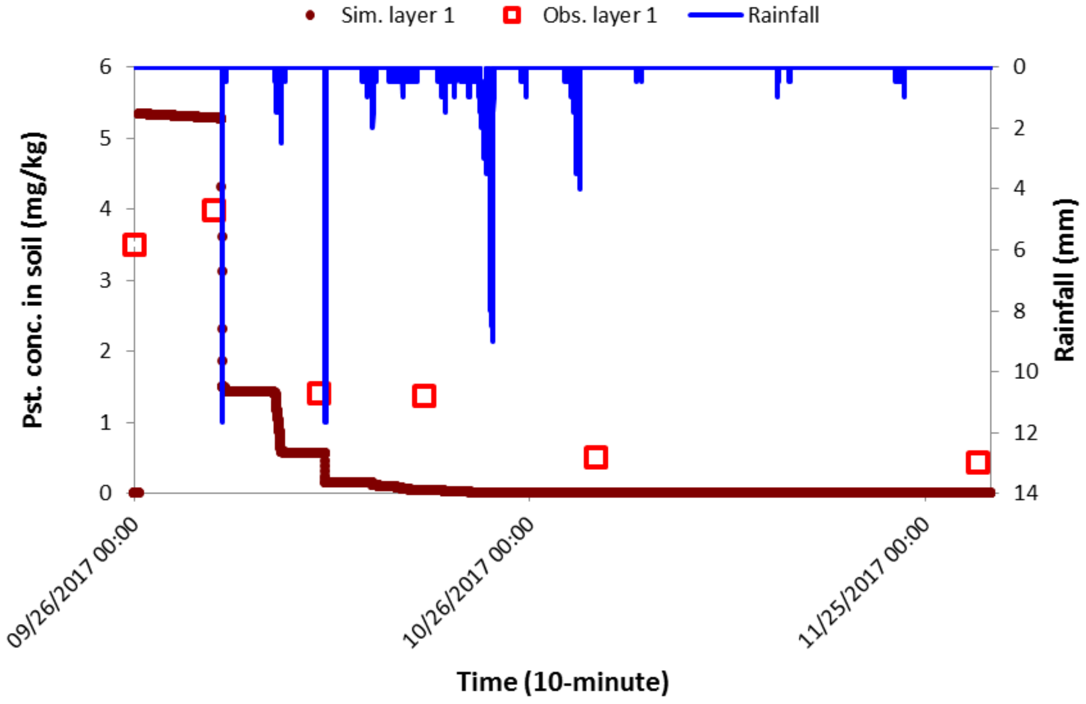


Figure 5.39. Result of imidacloprid concentration in 0-1 cm (plot 2)

The simulated results of imidacloprid in layer 2 (1-5 cm) for plots 1 and 2 are shown in Figure 5.40 and Figure 5.41, respectively. The model performances for those results are shown in Table

5.20. It can be seen from Table 5.20 that the *NSE* results for both plots were negative indicated an unsatisfactory model performance. The *PBIAS* result for imidacloprid concentrations in 1-5 cm indicated an unsatisfactory model performance for plot 1 (*PBIAS* > ±70%) and a satisfactory model performance for plot 2 (±40% ≤ *PBIAS* <±70%) (Table 5.20). The R^2 for plot 1 (0.22) and plot 2 (0.31) were very low indicated that the trends of simulated results were not performed well with the observed data for both plots (Table 5.20). There could be the limitation from the codes or the error in the observation data.

Table 5.20. Model performance for imidacloprid concentration in layer 2 for 2 plots

Imidacloprid concentration in 1-5 cm	**Obs. mean (mg/kg)**	**Sim. mean (mg/kg)**	***RMSE* (%)**	**R^2 (-)**	***NSE* (-)**	***PBIAS* (%)**
Plot 1	0.190	0.328	149.01	0.22	-8.58$^{5)}$	-72.82$^{5)}$
Plot 2	0.213	0.313	117.95	0.31	-3.27$^{5)}$	-47.01$^{3)}$

Notes: *1)* very good, *2)* good, *3)* satisfactory, *4)* acceptable, *5)* unsatisfactory

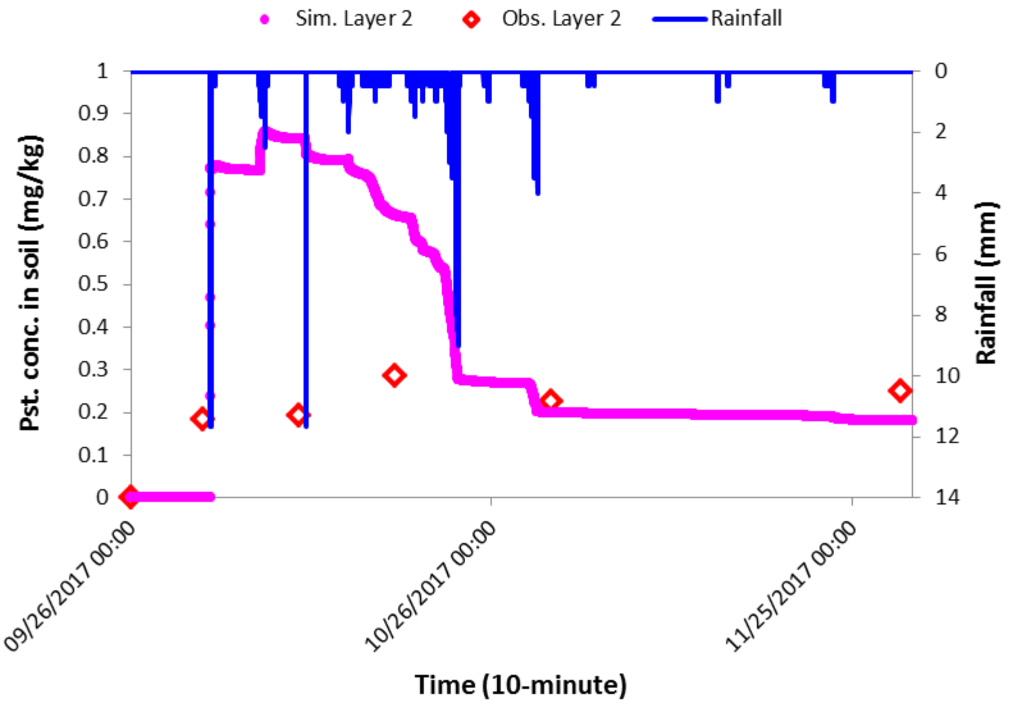


Figure 5.40. Result of imidacloprid concentration in 1-5 cm (plot 1)

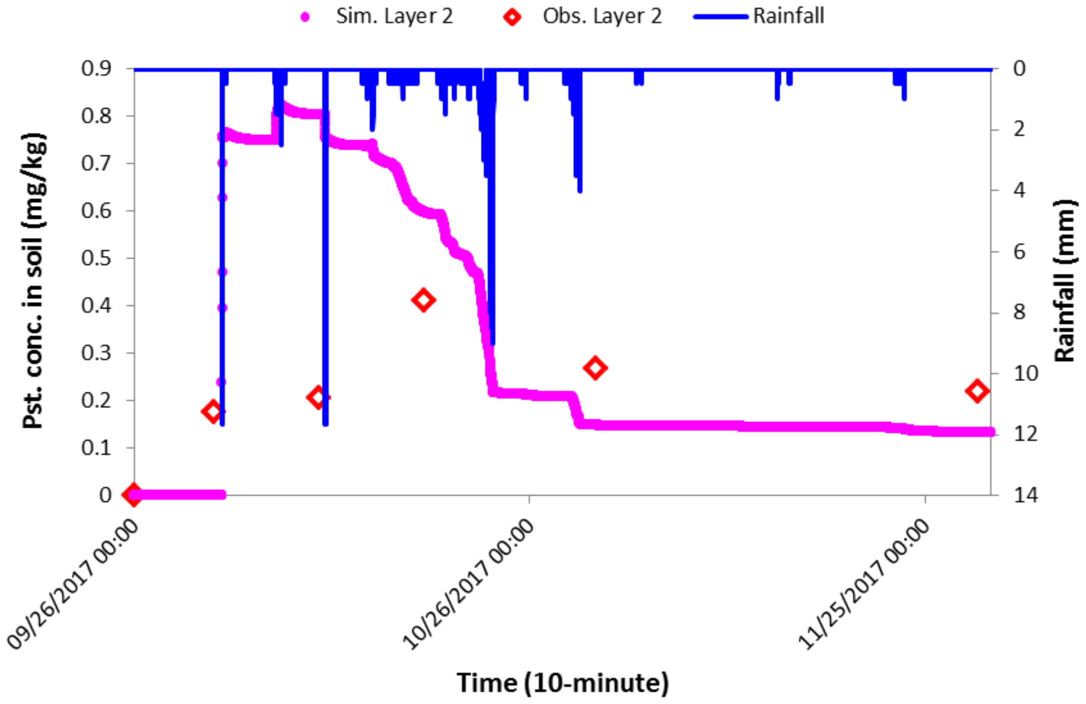


Figure 5.41. Result of imidacloprid concentration in 1-5 cm (plot 2)

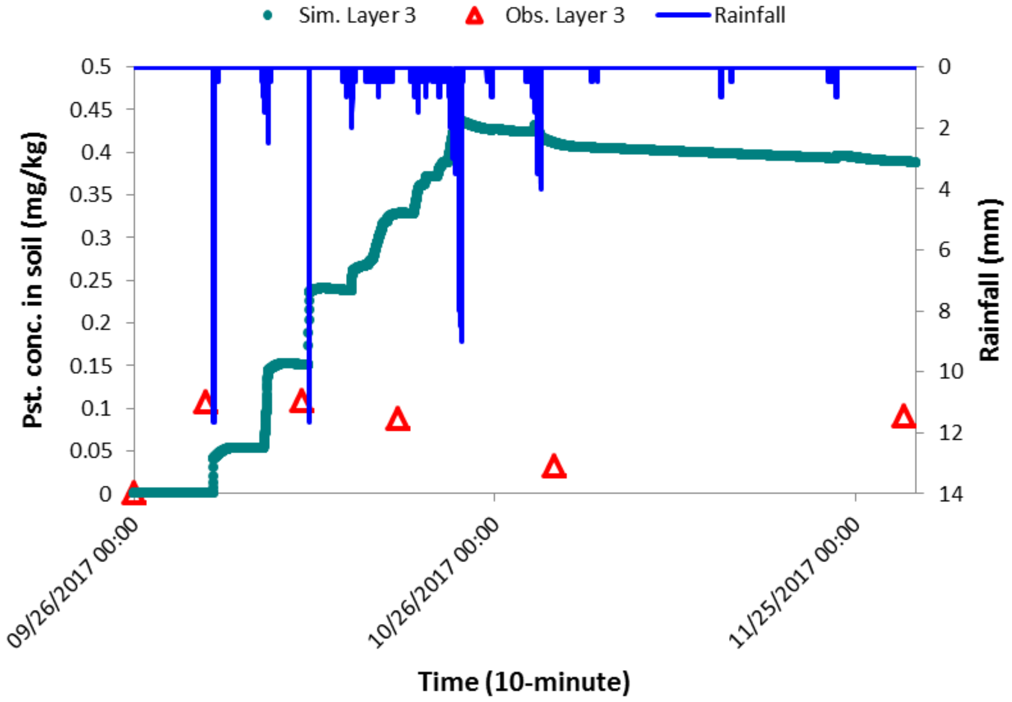


Figure 5.42. Result of imidacloprid concentration in 5-10 cm (plot 1)

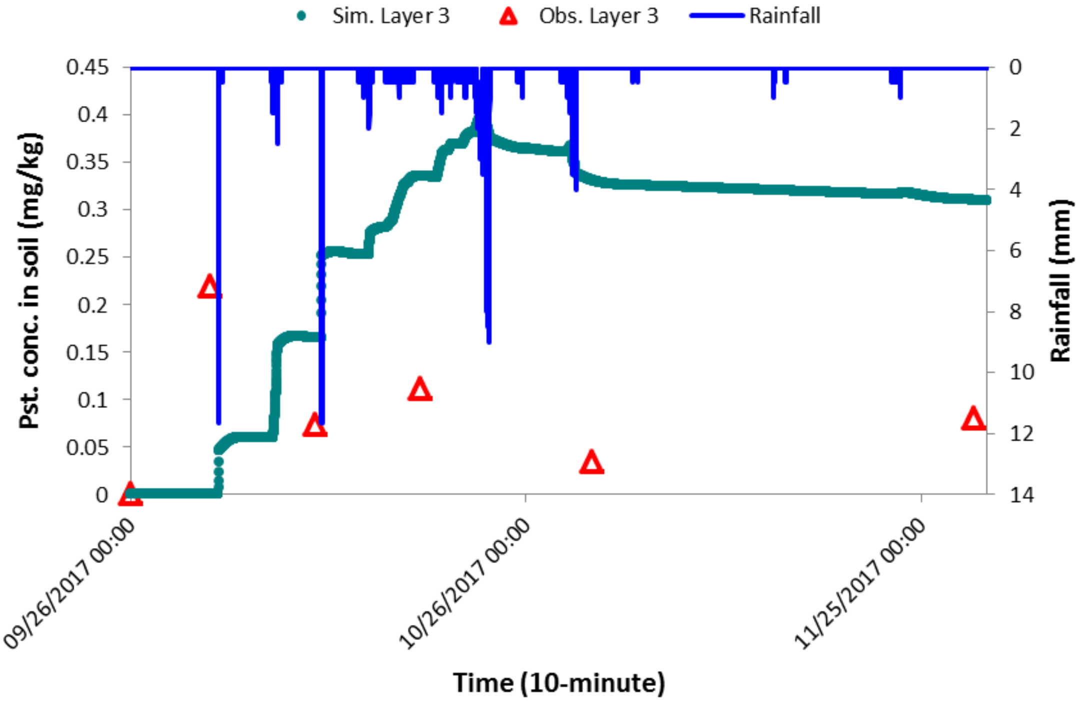


Figure 5.43. Result of imidacloprid concentration in 5-10 cm (plot 2)

The simulated results of imidacloprid in layer 3 (5-10 cm) for plots 1 and 2 are shown in Figure 5.42 and Figure 5.43, respectively. The model performances for those results are shown in Table 5.21. It can be seen from Table 5.21 that the *NSE* results for both plots were negative indicated an unsatisfactory model performance. Similar to *NSE*, the *PBIAS* results for imidacloprid concentrations in 5-10 cm for both plots (*PBIAS* > ±70%) indicated an unsatisfactory model performance (Table 5.21). The R^2 for both plots (0.04) were very low indicated that the trends of simulated results were not performed well with the observed data for both plots (Table 5.21). There could be some errors from the observed data or the codes of the model. However, it can be seen from Figure 5.42 and Figure 5.43, the trends of two observed data of imidacloprid in layer 3 for both plots were not consistent indicated that there was possible error in the observation data.

Table 5.21. Model performance for imidacloprid concentration in layer 3 for 2 plots

Imidacloprid concentration in 5-10 cm	**Obs. mean (mg/kg)**	**Sim. mean (mg/kg)**	***RMSE* (%)**	**R^2 (-)**	***NSE* (-)**	***PBIAS* (%)**
Plot 1	0.071	0.201	270.28	0.04	-21.08*5)*	-183.87*5)*
Plot 2	0.087	0.198	233.94	0.04	-7.57*5)*	-128.94*5)*

Notes: *1)* very good, *2)* good, *3)* satisfactory, *4)* acceptable, *5)* unsatisfactory

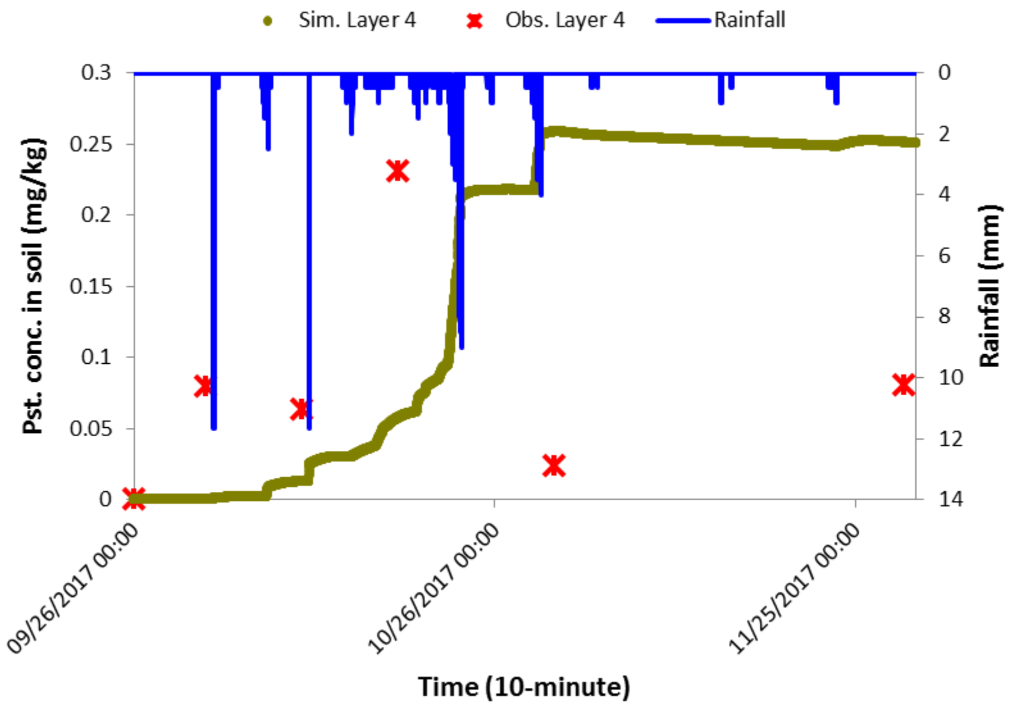


Figure 5.44. Result of imidacloprid concentration in 10-15 cm (plot 1)

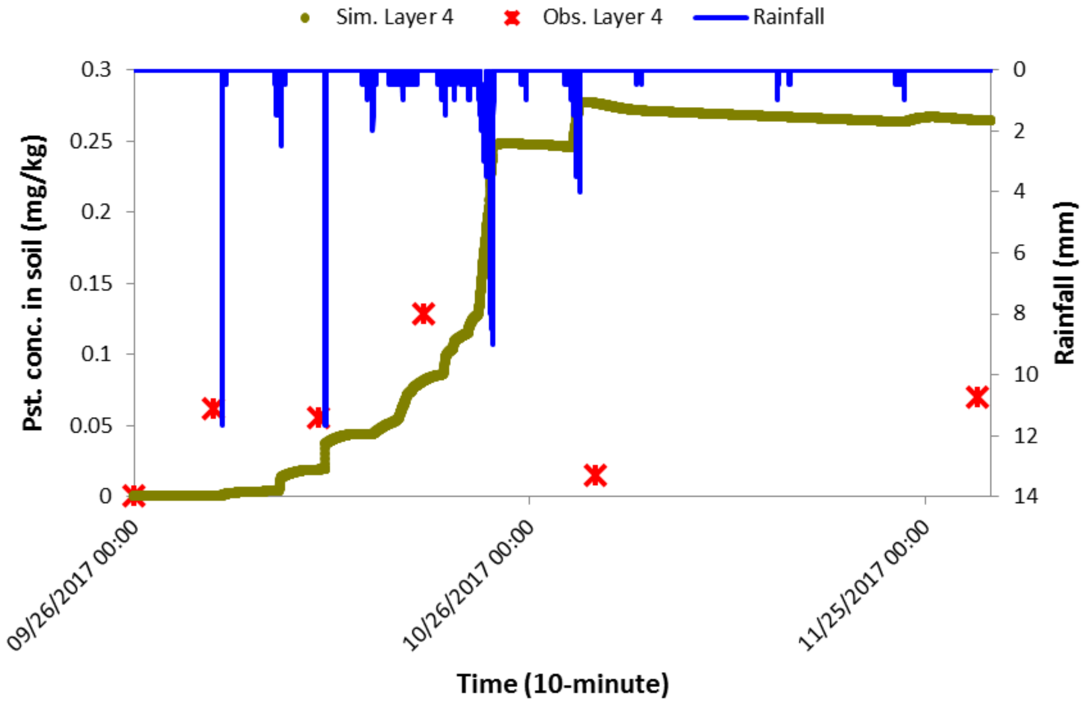


Figure 5.45. Result of imidacloprid concentration in 10-15 cm (plot 2)

The simulated results of imidacloprid in layer 4 (10-15 cm) for plots 1 and 2 are shown in Figure 5.44 and Figure 5.45, respectively. The model performances for those results are shown in Table 5.22. It can be seen from Table 5.22 that the *NSE* results for both plots were negative indicated an unsatisfactory model performance. The *PBIAS* results for imidacloprid concentrations in 10-15 cm indicated a good model performance for plot 1 (±25% ≤ *PBIAS* < ±40%) and an unsatisfactory performance for plot 2 (*PBIAS* > ±70%) (Table 5.22). The R^2 for both plots (0) were very low indicated that there was no match between the trends of simulated results and the observed data for both plots (Table 5.22).

Table 5.22. Model performance for imidacloprid concentration in layer 4 for 2 plots

Imidacloprid concentration in 10-15 cm	**Obs. mean (mg/kg)**	**Sim. mean (mg/kg)**	***RMSE* (%)**	**R^2 (-)**	***NSE* (-)**	***PBIAS* (%)**
Plot 1	0.080	0.109	183.68	0	-2.93 *5)*	-36.87 *2)*
Plot 2	0.055	0.108	247	0	-9.81 *5)*	-96.32 *5)*

Notes: *1)* very good, *2)* good, *3)* satisfactory, *4)* acceptable, *5)* unsatisfactory

The simulated results of average imidacloprid concentration in 0-15 cm for plots 1 and 2 are shown in Figure 5.46 and Figure 5.47, respectively. The model performances for those results are shown in Table 5.23. It can be seen from Table 5.23 that the *NSE* result for plot 1 was negative (-0.93) indicated an unsatisfactory model performance while the *NSE* value for plot 2 (0.28) indicated an acceptable model performance. The *PBIAS* results for imidacloprid concentrations in 0-15 cm indicated a good model performance for plot 1 (±25% ≤ *PBIAS* < ±40%) and a very good model performance for plot 2 (*PBIAS* < ±25%) (Table 5.23). As shown in Figure 5.46 and Figure 5.47 the observed data went up and down indicated a very uncertainty of data observation, thus it was difficult to match the simulated results with such a data series.

Table 5.23. Model performance for imidacloprid concentration in 15 cm for 2 plots

Imidacloprid concentration in 15 cm	**Obs. mean (mg/kg)**	**Sim. mean (mg/kg)**	***RMSE* (%)**	**R^2 (-)**	***NSE* (-)**	***PBIAS* (%)**
Plot 1	0.215	0.274	47.96	0.01	-0.93 *5)*	-27.91 *2)*
Plot 2	0.228	0.272	35.78	0.56	0.28 *4)*	-19.09 *1)*

Notes: *1)* very good, *2)* good, *3)* satisfactory, *4)* acceptable, *5)* unsatisfactory

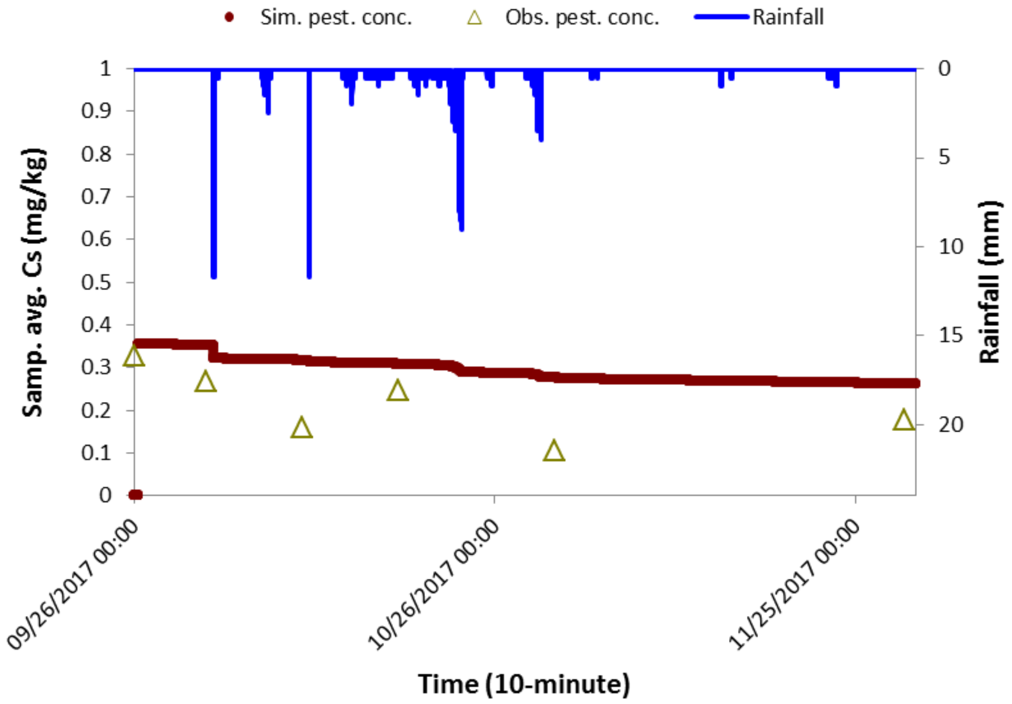


Figure 5.46. Result of imidacloprid concentration in 15 cm (plot 1)

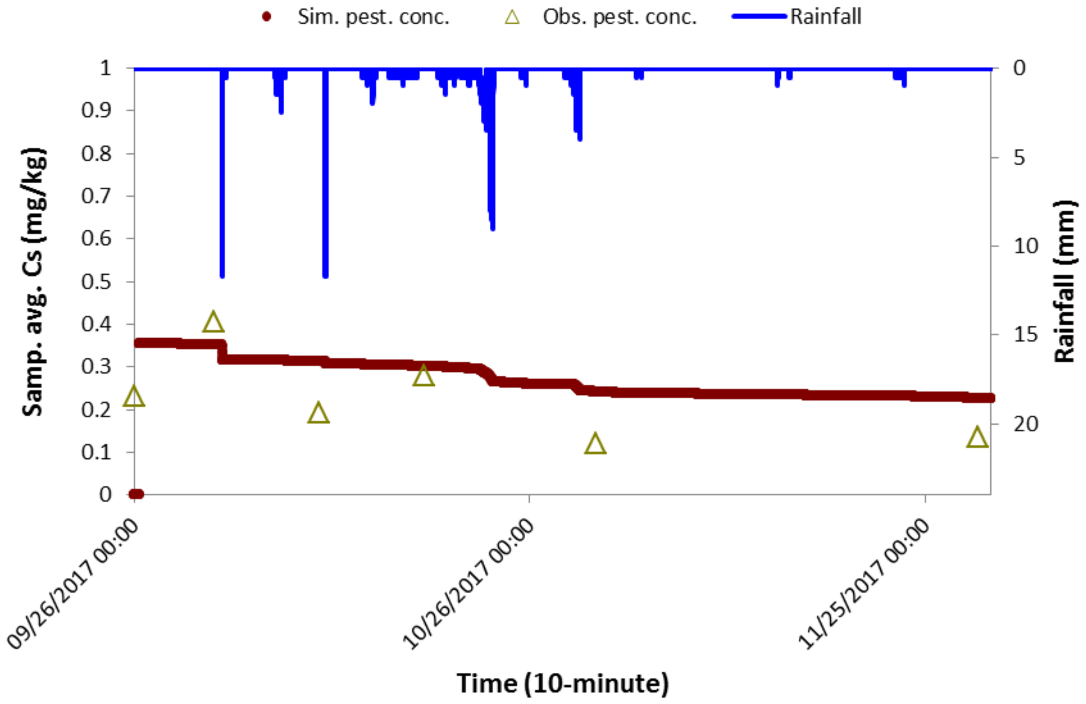


Figure 5.47. Result of imidacloprid concentration in 15 cm (plot 2)

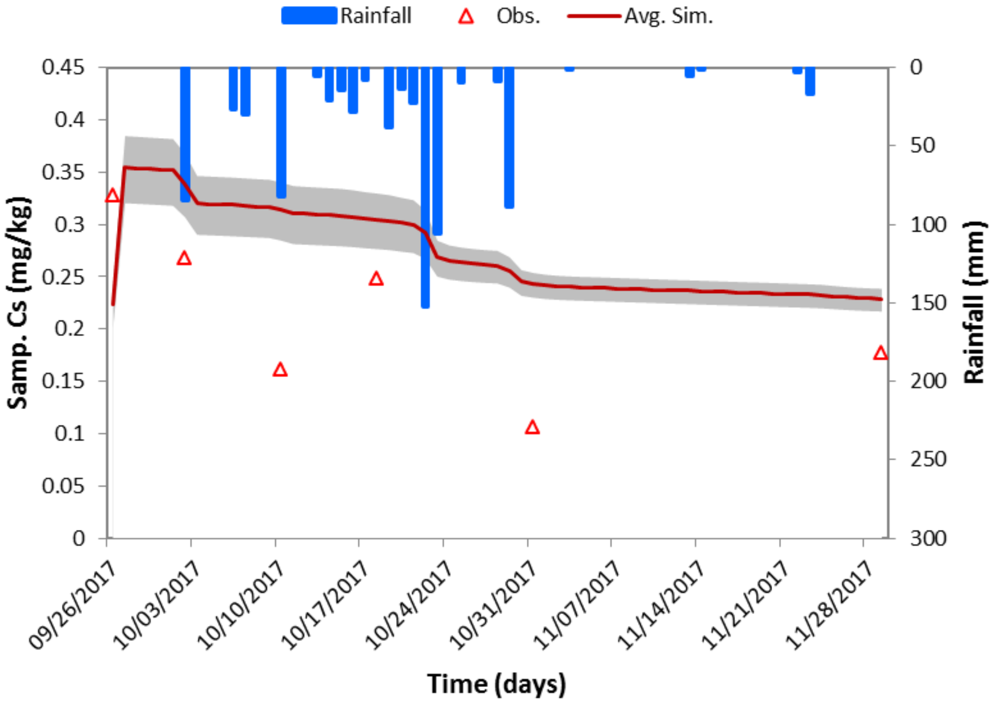


Figure 5.48. Uncertainty result of imidacloprid concentration in 15 cm (plot 1)

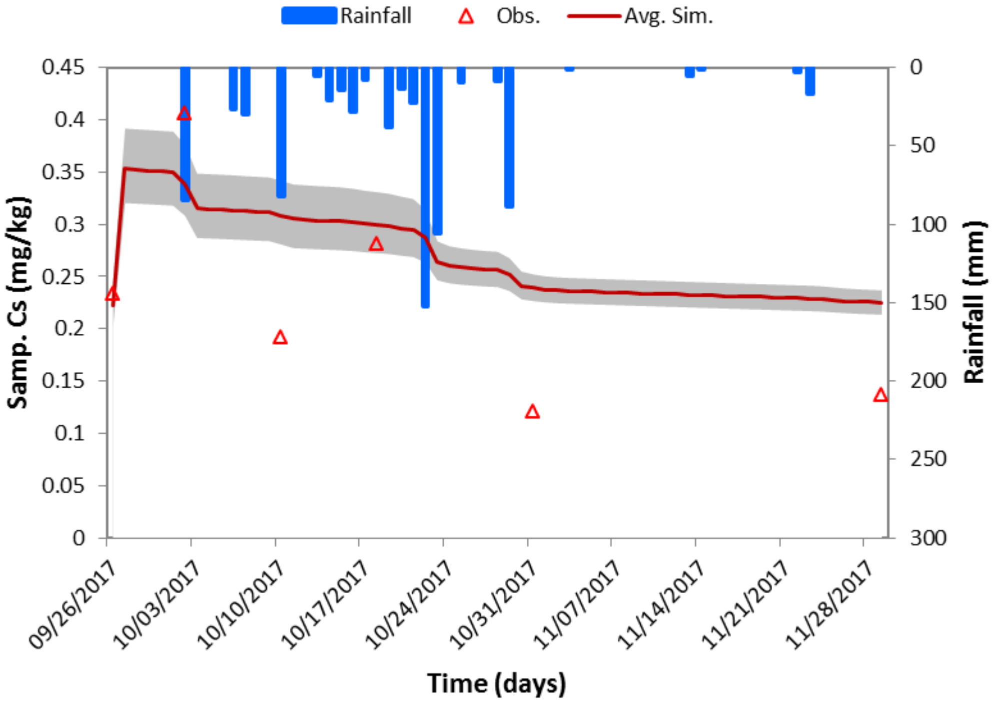


Figure 5.49. Uncertainty result of imidacloprid concentration in 15 cm (plot 2)

The uncertainty results of average imidacloprid concentration in 0-15 cm for plots 1 and 2 are shown in Figure 5.48 and Figure 5.49, respectively. Similar to the case of clothinidin, the great thickness of 95% confidence interval of the average imidacloprid concentration in 0-15 cm for both plots highlighted the effect of *Rb* to those concentration results as well as the high uncertainty of the imidacloprid concentration results.

5.3 Case sudy in Sakaecho in 2013-2014 - a continuous simulation

5.3.1 Study area and data input

The study area was in Sakaecho field, Fuchu campus, Tokyo University of Agriculture and Technology, Tokyo, Japan. The soil condition was bare soil upland field. The details were shown in the previous study (Boulange et al., 2016).

The weather data including rainfall, temperature were collected from the weather station website for Fuchu, which nearby the study area. The evaporation and solar radiation were computed from related weather data that were also obtained from the weather station website for Fuchu, which nearby the study area. The time steps for rainfall and temperatures were hourly and those for evaporation and solar radiation were daily (Boulange et al., 2016).

Two types of pesticides (atrazine and metolachlor) were used for pesticide measurement in the depth of 5 cm. In the previous SPEC application, 2 layers of soil (depths of 1 cm and 4 cm) were used as numbers of layers input for the model. The first and the second application rates of pesticides for atrazine and metolachlor were 771.3 g/ha and 732.5 g/ha, respectively. The first and the second application days for atrazine and metolachlor were conducted on June 10th, 2013 and December 06th, 2013, respectively (Boulange et al., 2016).

The observed data included daily water content, pesticide concentrations (atrazine and metolachlor) in 5 cm depth. During field experiments conducted, plastic wall borders were installed surrounding the plots to avoid the potential cross-contamination of pesticides; as a result the surface runoff of each plot was confined within the plots (Boulange et al., 2016). Therefore, the data of pollutant runoff were not available in this case study.

The quality of observed data is very important to the modelling works. Therefore, the possible errors of observed atrazine concentrations in soil were checked by calculating the application rates of atrazine based on the average concentrations of atrazine concentration in 5 cm sampling depth. The calculated application rates were found for the first and the second days of application to be 1050.6 g/ha and 1036.6 g/ha, respectively. Comparing these values to the given application rates which were 771.3 g/ha, these values were 36.2% and 34.4% higher than application rates on the first and the second day. This indicated that there could be certain errors in data collection or data analysis. The actual observed atrazine concentrations in soil should be lower than they were.

Similar to the case of atrazine, the application rates of metolachlor were calculated to check the possible errors in data observation. Based on the average concentration of metolachlor concentrations in 5 cm sampling depth, the calculated application rates were found for the first and the second days of application to be 996.8 g/ha and 1030.4 g/ha, respectively. Comparing these values to the given application rates which were 732.5 g/ha, these values were 36.1% and 40.7% higher than the given application rates on the first and the second days. This indicated that there could be certain errors in data collection or data analysis. The actual observed metolachlor concentrations in soil should be lower than they were.

The output and simulation time steps were daily. The simulation duration was 329 days from June 10th, 2013 to May 4th, 2014. In this improved SPEC model, 2 layers (0-1 cm, 1-9 cm) and 3 layers (0-1 cm, 1-5 cm, 5-10 cm) were used to test the effect of numbers of soil layers on the model performance for simulating the pesticide concentrations in multiple soil layers.

5.3.2 Results and discussion

5.3.2.1 Results for water content in soil layers

In this simulation, the initial abstraction ratio of 0.06 and the *CN* value of 86 in the previous study, were used. In sensitivity analysis for water content simulation, it was found that the saturated water content and the field capacity were the most sensitive parameters. The standardized rank regression coefficients for the saturated water content and the field capacity were 0.55 and 0.84, respectively. The graphic display in MCS is shown in Figure 5.50.

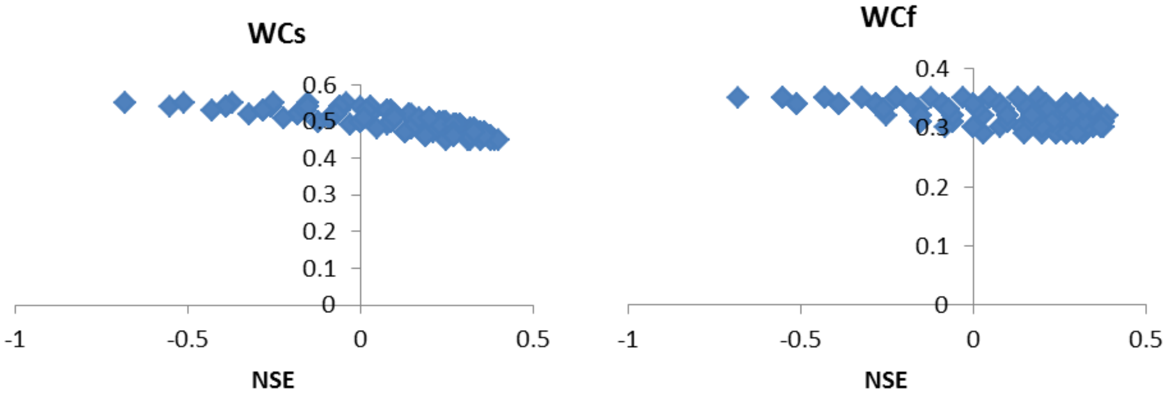


Figure 5.50. Ranges of saturated water content (*WCs*) and field capacity (*WCf*) in finding optimal solution for average water content in 5 cm

The final calibrated saturated water content and field capacity were 0.5 and 0.32 mm^3/mm^3, respectively. The simulated result of water content at 5 cm depth was improved in which the *NSE* had positive value (0.29) and the *PBIAS* was only 3.2% (Table 5.24). The result of average water content in 5 cm sampling depth is shown in Figure 5.51. In the simulation using previous version of SPEC model, the *NSE* of water content 5 cm sampling depth was negative (-1.06) (Boulange et al., 2016). Comparing to the previous study (Boulange et al., 2016), the simulated water content in 5 cm was improved.

Table 5.24. Model performance for water content in 5 cm

Water content	**Obs. mean (mm^3/mm^3)**	**Sim. mean (mm^3/mm^3)**	***RMSE* (%)**	**R^2 (-)**	***NSE* (-)**	***PBIAS* (%)**
In 5 cm sampling depth	0.326	0.315	10.71	0.53	0.29 *4)*	3.2 *1)*

Notes: *1)* very good, *2)* good, *3)* satisfactory, *4)* acceptable, *5)* unsatisfactory

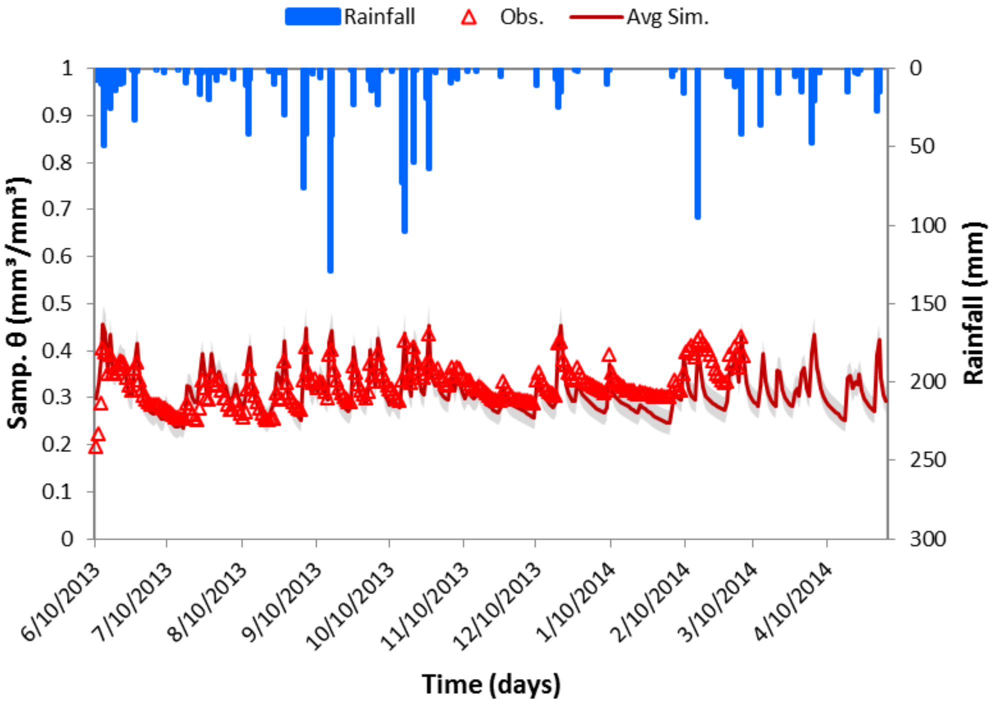


Figure 5.51. The result of average water content in 5 cm

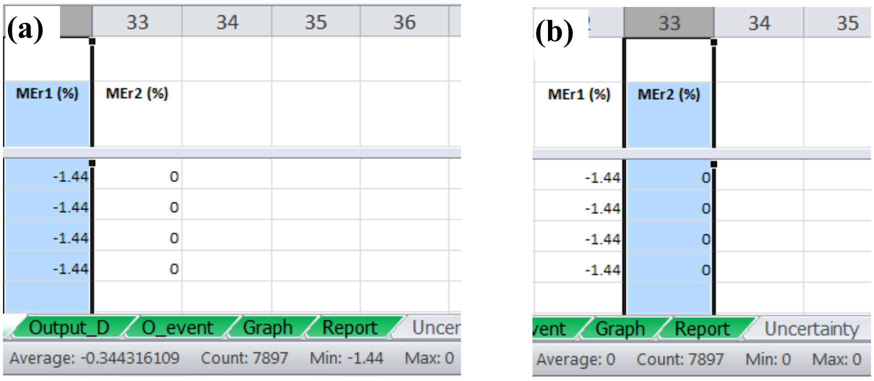
The uncertainty of water content was conducted to check the validated values of saturated water content and field capacity. By changing ±10% of saturated water content and field capacity from its calibrated values, the uncertainty of water content is shown in Figure 5.51. The thickness of

95% confidence interval around the average values of water contents highlighted the effects of the saturated water content and the field capacity to the simulated water contents (Figure 5.51). The effect of rainfall to the simulated water content was also found. As seen in Figure 5.51 that in the dry period (no rainfall), the simulated water contents were reduced and increased significantly when rainfall occurred.

5.3.2.2 *Results for atrazine concentrations in soil layers*

The sensitivity analysis of atrazine concentrations in sampling depth of soil indicated that the *Q10*, *Rb* and *Koc* were the most sensitive parameters, the standardized rank regression coefficients of which were 0.74, -0.68 and 0.21 respectively. The negative sign of *Rb* indicated the reduction of *Rb* would increase *NSE* of atrazine concentration in soil; however to minimize the change of parameters that given in the previous study (Boulange et al., 2016), the simulation was conducted with the previous values of parameters (*Rb* = 0.5 g/cm^3, *Q10* = 1.35, *HLpho* = 100 d, *HLbio* = 23.5 d, *Koc* = 100 L/kg).

In 2-layer simulation, the max, min and average errors for mass balance of atrazine concentration in layer 1 were found to be 0%, -1.44% and -0.344%, respectively (Figure 5.52.a) indicated that there was very small mass balance error in simulating pesticide concentrations in layer 1. There was no error for mass balance of atrazine concentration in layer 2 (Figure 5.52.b).



(a)

MEr1 (%)	MEr2 (%)
-1.44	0
-1.44	0
-1.44	0
-1.44	0

Average: -0.344316109 Count: 7897 Min: -1.44 Max: 0

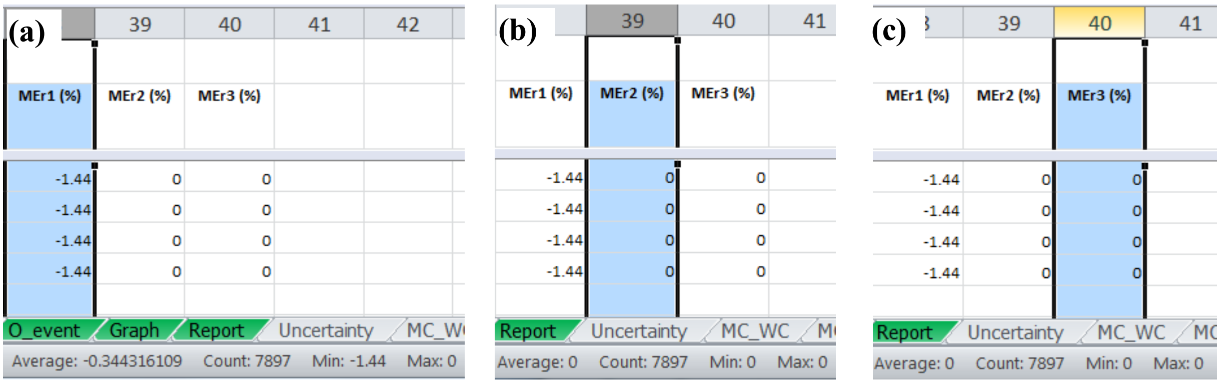
(b)

MEr1 (%)	MEr2 (%)
-1.44	0
-1.44	0
-1.44	0
-1.44	0

Average: 0 Count: 7897 Min: 0 Max: 0

Figure 5.52. Mass balance errors of atrazine concentrations in (a) layer 1 and (b) layer 2 (for 2-layer simulation)

In 3-layer simulation, the max, min and average errors for mass balance of atrazine concentration in layer 1 were found to be 0%, -1.44% and -0.344%, respectively (Figure 5.53.a) indicated that there was very small mass balance error in simulating pesticide concentrations in layer 1. There was no error for mass balances of atrazine concentrations in layer 2 (Figure 5.53.b) and layer 3 (Figure 5.53.c).



(a)

	39	40	41	42
MEr1 (%)	MEr2 (%)	MEr3 (%)		
-1.44	0	0		
-1.44	0	0		
-1.44	0	0		
-1.44	0	0		

Average: -0.344316109 Count: 7897 Min: -1.44 Max: 0

(b)

	39	40	41
MEr1 (%)	MEr2 (%)	MEr3 (%)	
-1.44	0	0	
-1.44	0	0	
-1.44	0	0	
-1.44	0	0	

Average: 0 Count: 7897 Min: 0 Max: 0

(c)

	39	40	41
MEr1 (%)	MEr2 (%)	MEr3 (%)	
-1.44	0	0	
-1.44	0	0	
-1.44	0	0	
-1.44	0	0	

Average: 0 Count: 7897 Min: 0 Max: 0

Figure 5.53. Mass balance errors of atrazine concentrations in (a) layer 1, (b) layer 2 and (c) layer 3 (for 3-layer simulation)

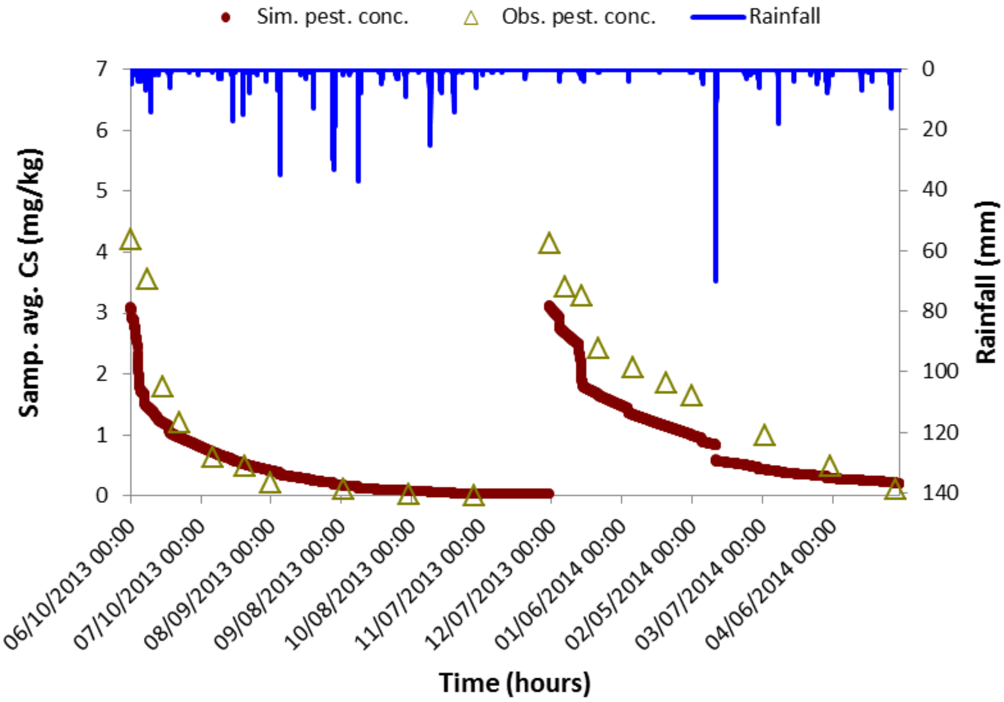


Figure 5.54. Result of atrazine concentration in 5 cm (2 layers simulation)

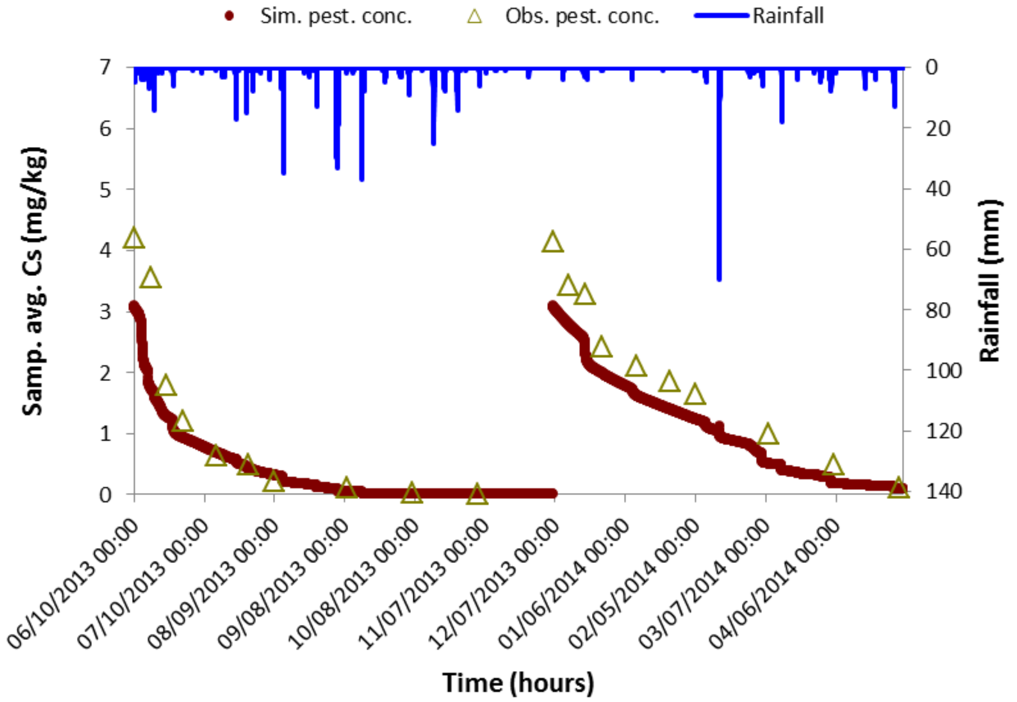


Figure 5.55. Result of atrazine concentration in 5 cm (3 layers simulation)

The results of atrazine concentrations in 5 cm sampling depth of soil simulated by 2 and 3 layers are shown in Table 5.25. For both simulation cases, the average values of atrazine concentration were underestimated with the *PBIAS* were 46.29% and 30.88% for 2-layer and 3-layer simulations, respectively. These underestimated results were possible due to the errors of data observation. As discussed previously, the actual observed concentrations of atrazine in soil should be lower than they were. It was found from Table 5.25 that the result of atrazine concentration in 5 cm depth calculated by 3 layers of soils was better than that simulated by 2 layers. The *NSE* for 3 layers simulation was 0.74 indicated a good model performance; while *NSE* for 2 layers simulation was 0.47 indicated an acceptable model performance. This confirmed that the increasing of numbers of soil layers would improve the model performance. The time series results of atrazine concentrations in 5 cm depth simulated by 2 layers and 3 layers are shown in Figure 5.54 and Figure 5.55, respectively. The results of atrazine concentration in 5 cm simulated by 3 layers (in Figure 5.55) was found to match with the observed values better than those simulated by 2 soil layers (Figure 5.54). As compared to atrazine concentration in 5 cm sampling depth simulated from the previous SPEC model (before adjustment), the result from improved SPEC model (3-layer simulation) performed better (*NSE* for atrazine concentration in 5 cm in the improved and in the previous SPEC models were 0.74 and 0.57, respectively). It is noticed that the results of atrazine concentrations in 5 cm shown in the previous study were adjusted into dry soil condition (outside the SPEC model).

Table 5.25. Model performance for atrazine concentrations in 5 cm (*Q10* = 1.35)

SPEC simulation	**Obs. mean (mg/kg)**	**Sim. mean (mg/kg)**	***RMSE* (%)**	***R²* (-)**	***NSE* (-)**	***PBIAS* (%)**
2 layers (0-1 cm, 1-10 cm)	1.637	0.879	62.51	0.85	0.47*3)*	46.29*3)*
3 layers (0-1 cm, 1-5 cm, 5-10 cm)	1.637	1.131	43.75	0.95	0.74*2)*	30.88*2)*

Notes: *1)* very good, *2)* good, *3)* satisfactory, *4)* acceptable, *5)* unsatisfactory

The Monte Carlo simulation for atrazine concentrations in 5 cm were conducted for 2 and 3 layers simulation with the calibrated *Q10* of 1.35 and 10% change from its value to check the uncertainty of *Q10* and observed data. The uncertainty results of atrazine concentration in 5 cm simulated by 2 layers and 3 layers are shown in Figure 5.56 and Figure 5.57, respectively. It can be seen that the *Q10* was not sensitive to atrazine concentrations in soil in the summer season but it was sensitive to atrazine concentrations in winter season for both cases of simulations (Figure 5.56 and Figure 5.57). The uncertainty results of atrazine concentration in 5 cm simulated by 3 layers (in Figure 5.57) were found to match with the observed values better than those simulated by 2 soil layers (Figure 5.56).

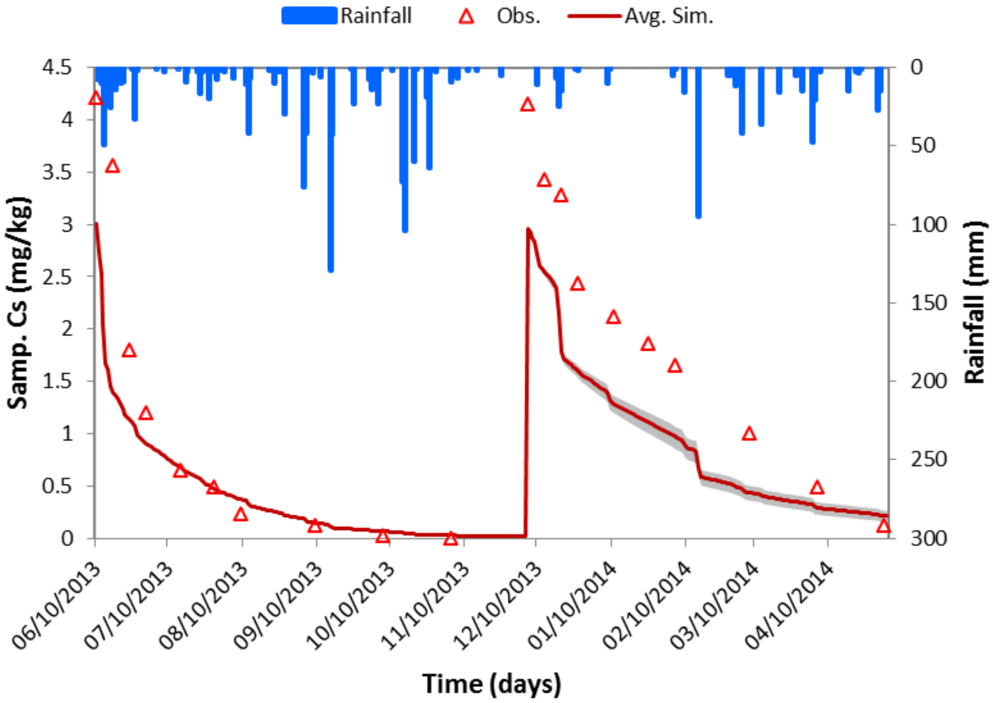


Figure 5.56. Uncertainty result of atrazine in 5 cm (2 layers simulation)

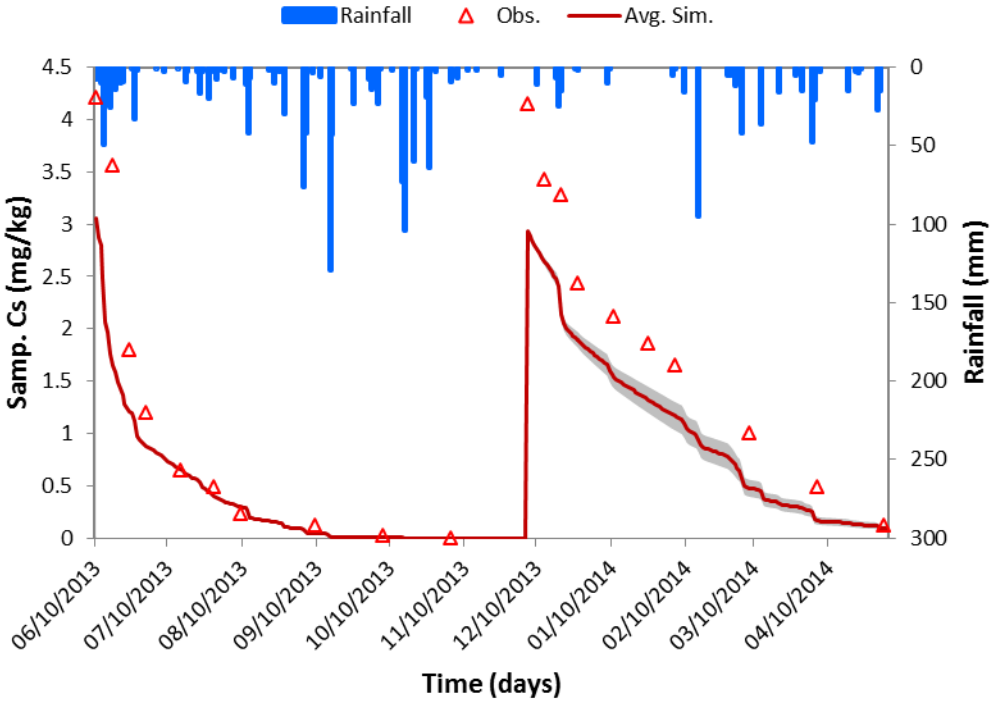


Figure 5.57. Uncertainty result of atrazine in 5 cm (3 layers simulation)

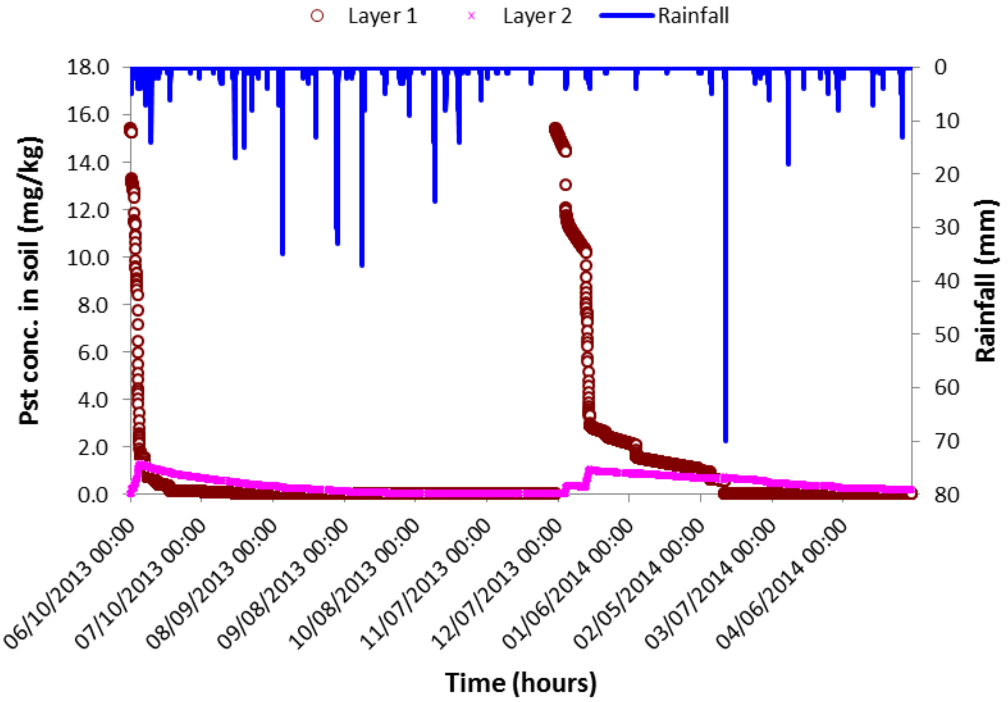


Figure 5.58. Result of atrazine concentrations in 2 soil layers (0-1 cm, 1-10 cm)

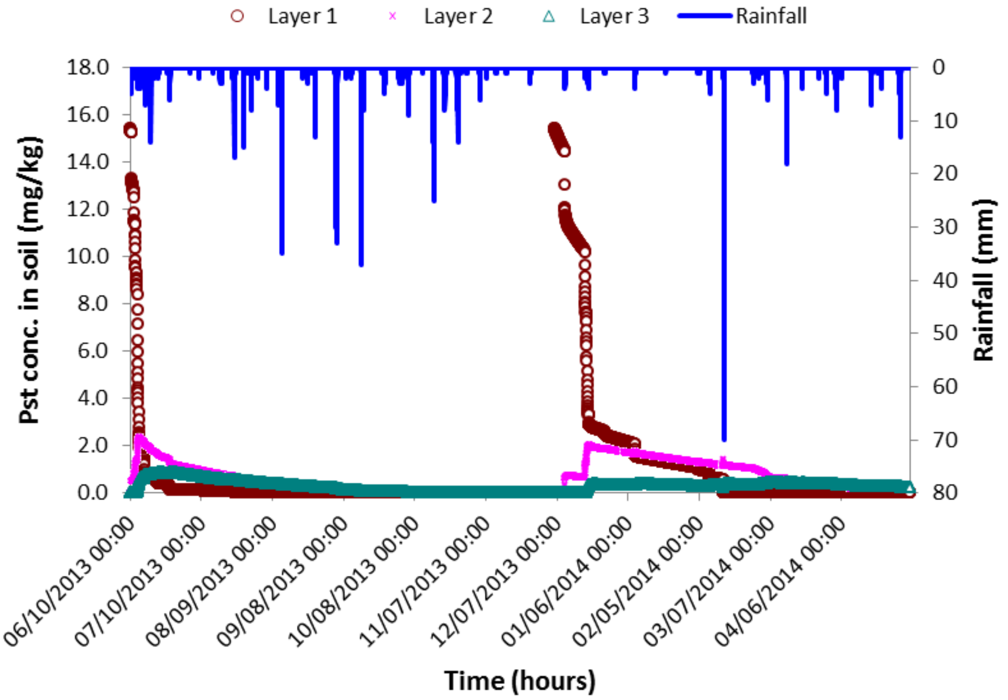


Figure 5.59. Result of atrazine concentrations in 3 soil layers (0-1 cm, 1-5 cm, 5-10 cm)

The results of atrazine in every soil layer are shown in Figure 5.58 for 2 layers simulation and in Figure 5.59 for 3 layer simulation to give more information on atrazine concentrations at different depths. It can be seen from Figure 5.58 and Figure 5.59 that the atrazine concentration in layer 2 in 2 layers simulation was lower than that in 3 layers simulation, this could be explained why the average value of atrazine concentrations in 5 cm calculated from 3 layers simulation having a higher value.

The model performance for atrazine concentrations in 5 cm can be improved if the adjustment has been made for *Q10* and *Koc*. With the calibrated *Q10* of 2.0 and *Koc* of 150 L/kg, the simulated results of atrazine were improved. As shown in Table 5.26 the *NSE* results for atrazine concentrations in 5 cm using *Q10* of 2 and *Koc* of 150 L/kg in both simulations were higher than those simulated using *Q10* of 1.35 and *Koc* of 100 L/kg.

Table 5.26. Model performance for atrazine concentrations in 5 cm (*Q10* = 2.0, *Koc* = 150 L/kg)

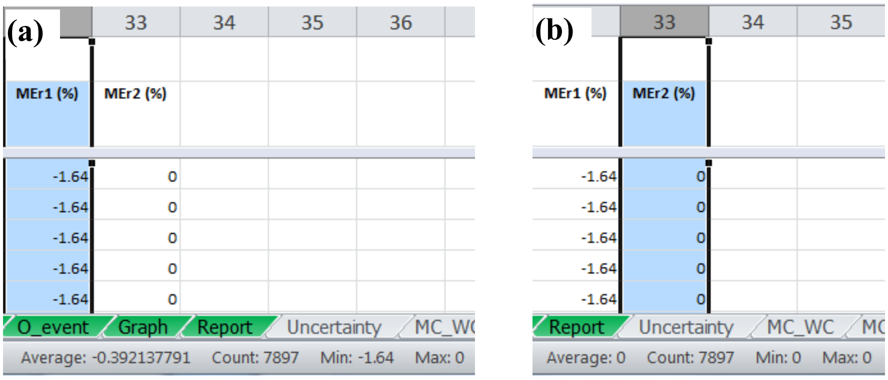
SPEC simulation	**Obs. mean (mg/kg)**	**Sim. mean (mg/kg)**	***RMSE* (%)**	**R^2 (-)**	***NSE* (-)**	***PBIAS* (%)**
2 layers (0-1 cm, 1-10 cm)	1.637	1.069	51.98	0.89	0.63$^{2)}$	34.68$^{2)}$
3 layers (0-1 cm, 1-5 cm, 5-10 cm)	1.637	1.408	34.85	0.93	0.84$^{1)}$	14.01$^{1)}$

Notes: *1)* very good, *2)* good, *3)* satisfactory, *4)* acceptable, *5)* unsatisfactory

5.3.2.3 Results for metolachlor concentrations in soil layers

The sensitivity analysis results of metolachlor concentration in sampling depth of soil indicated that the *Q10*, *Rb* and *Koc* were the most sensitive parameters, the standardized rank regression coefficients of which were 0.69, -0.66 and 0.21 respectively. The negative sign of *Rb* indicated the reduction of *Rb* would increase *NSE* of metolachlor concentration; however to minimize the change of parameters that given in the previous study (Boulange et al., 2016), the simulation was conducted with previous values of parameters (*Rb* = 0.5 g/cm³, *Q10* = 1.42, *HLpho* = 199 d, *HLbio* = 24.7 d, *Koc* = 120 L/kg).

The mass balances for metolachlor concentrations in soil layers in the case of 2-layer simulation were performed and shown in Figure 5.60. The max, min and average errors for mass balance of metolachlor concentration in layer 1 were found to be 0%, -1.64% and -0.392%, respectively (Figure 5.60.a) indicated that there was very small error in simulating pesticide concentrations in layer 1. There was no error for mass balance of metolachlor concentration in layer 2 (Figure 5.60.b).



(a)

	33	34	35	36
MEr1 (%)	MEr2 (%)			
-1.64	0			
-1.64	0			
-1.64	0			
-1.64	0			
-1.64	0			

Average: -0.392137791 Count: 7897 Min: -1.64 Max: 0

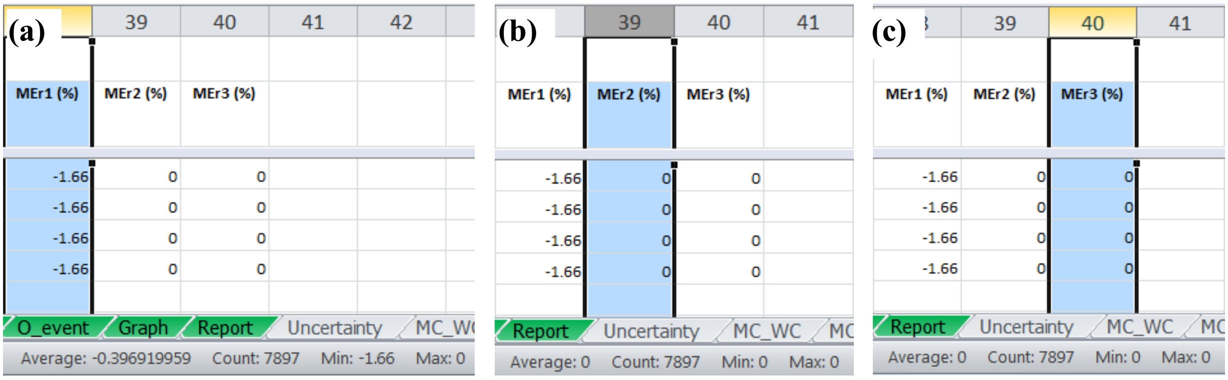
(b)

	33	34	35
MEr1 (%)	MEr2 (%)		
-1.64	0		
-1.64	0		
-1.64	0		
-1.64	0		
-1.64	0		

Average: 0 Count: 7897 Min: 0 Max: 0

Figure 5.60. Mass balance errors of metolachlor concentrations in (a) layer 1 and (b) layer 2 (for 2-layer simulation)

The mass balances for metolachlor concentrations in soil layers in the case of 3-layer simulation were performed and shown in Figure 5.61. The max, min and average errors for mass balance of metolachlor concentration in layer 1 were found to be 0%, -1.66% and -0.397%, respectively (Figure 5.61.a) indicated that there was very small error in simulating pesticide concentrations in layer 1. There was no error for mass balances of metolachlor concentrations in layer 2 (Figure 5.61.b) and layer 3 (Figure 5.61.c).



(a)

	39	40	41	42
MEr1 (%)	MEr2 (%)	MEr3 (%)		
-1.66	0	0		
-1.66	0	0		
-1.66	0	0		
-1.66	0	0		

Average: -0.396919959 Count: 7897 Min: -1.66 Max: 0

(b)

	39	40	41
MEr1 (%)	MEr2 (%)	MEr3 (%)	
-1.66	0	0	
-1.66	0	0	
-1.66	0	0	
-1.66	0	0	

Average: 0 Count: 7897 Min: 0 Max: 0

(c)

	39	40	41
MEr1 (%)	MEr2 (%)	MEr3 (%)	
-1.66	0	0	
-1.66	0	0	
-1.66	0	0	
-1.66	0	0	

Average: 0 Count: 7897 Min: 0 Max: 0

Figure 5.61. Mass balance errors of metolachlor concentrations in (a) layer 1, (b) layer 2 and (c) layer 3 (for 3-layer simulation)

The results of metolachlor concentrations in 5 cm of soil simulated by 2 and 3 layers are shown in Table 5.27. For both simulation cases, the average values of metolachlor concentration were underestimated with the *PBIAS* were 34.55% and 14.59% for 2-layer and 3-layer simulations, respectively. However, the *PBIAS* result in 3 layers simulation indicated a very good model performance while the *PBIAS* in 2 layers simulation indicated a good model performance. The underestimated results were possible due to the errors of data observation. As discussed previously, the actual observed concentrations of metolachlor in soil should be lower than they were. It was found from Table 5.27 that the result of metolachlor concentration in 5 cm calculated by 3 layers of soils was performed better than that simulated by 2 layers. The *NSE* for 3 layers simulation was 0.87 indicated a very good model performance, while *NSE* for 2 layers simulation was 0.73 indicated a good model performance. This confirmed that the increasing of numbers of soil layers would improve the model performance. As compared to metolachlor concentration in 5 cm sampling depth simulated from the previous SPEC model (before adjustment), the result from improved SPEC model (3-layer simulation) performed better (*NSE* for metolachlor concentration in 5 cm in the improved and in the previous SPEC models were 0.87 and 0.72, respectively). It is noticed that the results of metolachlor concentrations in 5 cm shown in the previous study were adjusted into dry soil condition (outside the SPEC model).

Table 5.27. Model performance for metolachlor concentrations in 5 cm (*Q10* = 1.42)

SPEC simulation	**Obs. mean (mg/kg)**	**Sim. mean (mg/kg)**	***RMSE* (%)**	***R²* (-)**	***NSE* (-)**	***PBIAS* (%)**
2 layers (0-1 cm, 1-10 cm)	1.388	0.908	47.64	0.97	0.73 *2)*	34.55 *2)*
3 layers (0-1 cm, 1-5 cm, 5-10 cm)	1.388	1.185	32.95	0.95	0.87 *1)*	14.59 *1)*

Notes: *1)* very good, *2)* good, *3)* satisfactory, *4)* acceptable, *5)* unsatisfactory

The time series results of metolachlor concentrations in 5 cm simulated by 2 layers and 3 layers are shown in Figure 5.62 and Figure 5.63, respectively. The results of metolachlor concentration in 5 cm simulated by 3 layers (in Figure 5.63) were found to match better than those simulated by 2 soil layers (Figure 5.62).

The Monte Carlo simulation for metolachlor concentrations in 5 cm were conducted for 2 and 3 layers simulation with the calibrated *Q10* value of 1.42 and 10% change from its value to check the uncertainty of *Q10* and observed data. The uncertainty results of metolachlor concentration in 5 cm simulated by 2 layers and 3 layers are shown in Figure 5.64 and Figure 5.65, respectively. It can be seen that the *Q10* was not sensitive to metolachlor concentration in soil in the summer season but it was sensitive to metolachlor concentration in winter season for both cases of simulation (Figure 5.64 and Figure 5.65). The uncertainty results of metolachlor concentration in 5 cm simulated by 3 layers (Figure 5.65) were found to match with the observed values better than those simulated by 2 soil layers (Figure 5.65).

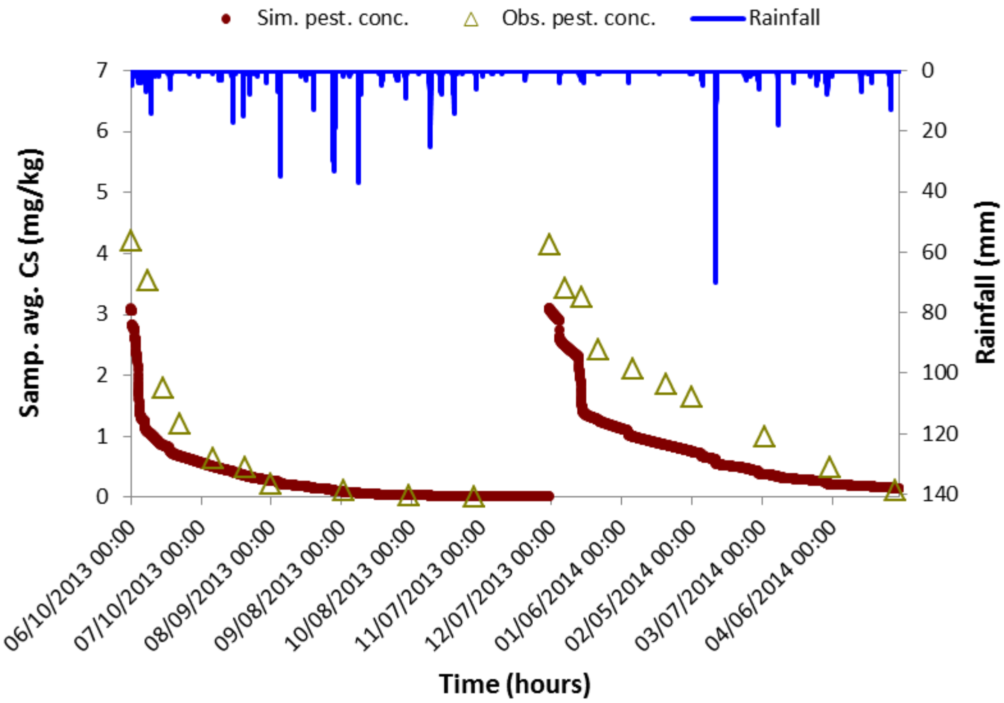


Figure 5.62. Result of metolachlor concentration in 5 cm soil (2 layers simulation)

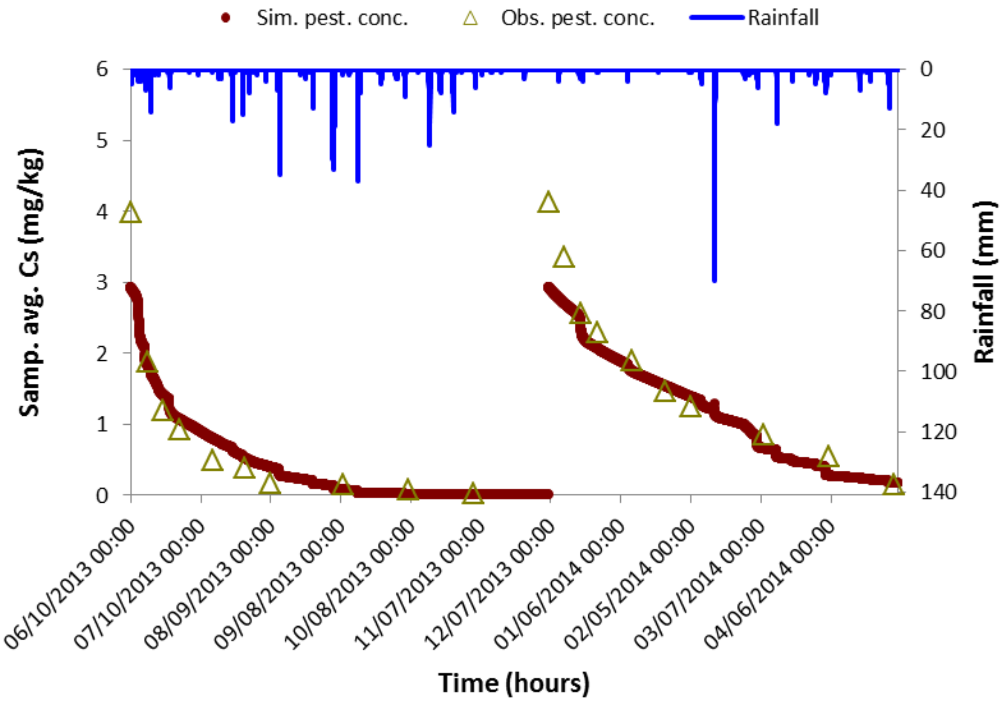


Figure 5.63. Result of metolachlor concentration in 5 cm soil (3 layers simulation)

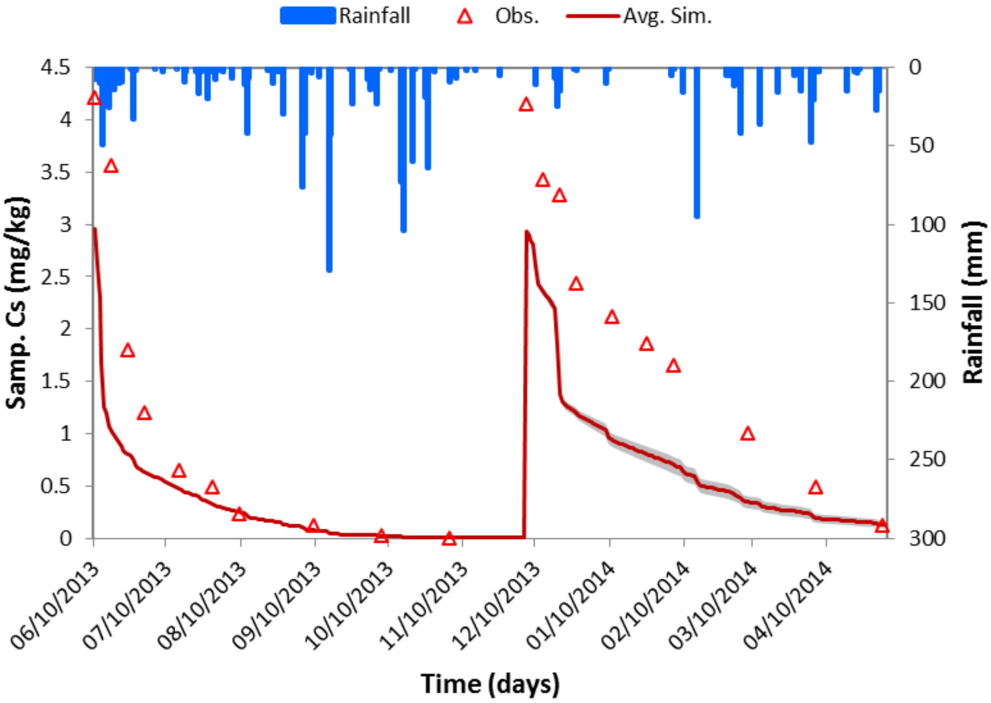


Figure 5.64. Uncertainty result of metolachlor concentration in 5 cm soil (2 layers simulation)

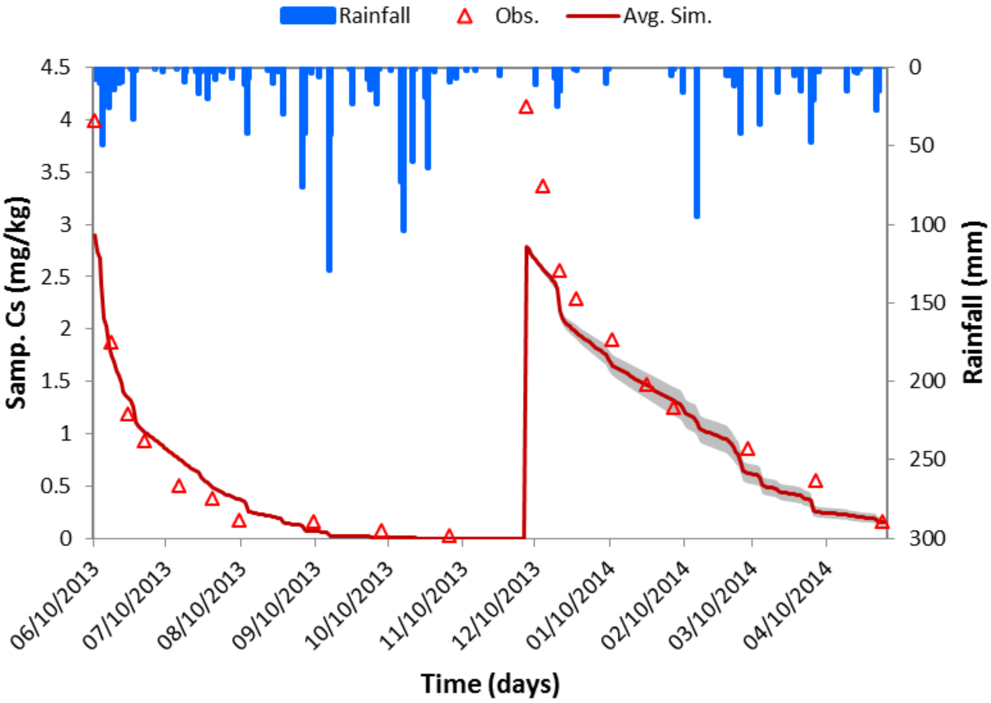


Figure 5.65. Uncertainty result of metolachlor concentration in 5 cm soil (3 layers simulation)

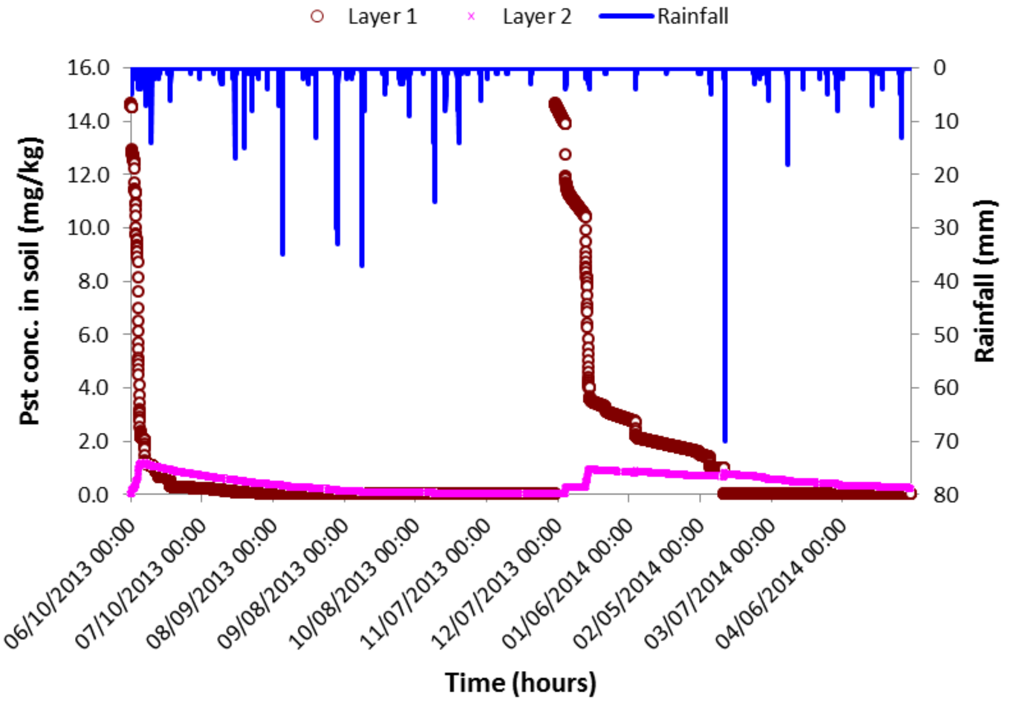


Figure 5.66. Result of metolachlor concentrations in 2 soil layers (0-1 cm, 1-10 cm)

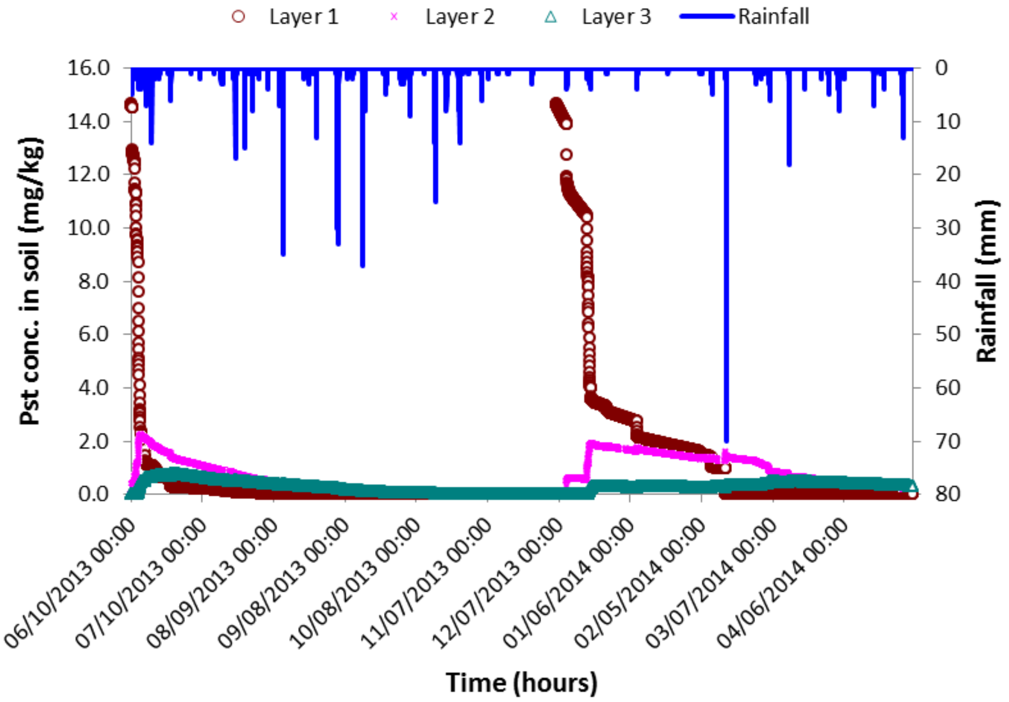


Figure 5.67. Result of metolachlor concentrations in 3 soil layers (0-1 cm, 1-5 cm, 5-10 cm)

Similar to the results of atrazine, the results of metolachlor in every soil layer are shown in Figure 5.66 for 2 layers simulation and in Figure 5.67 for 3 layer simulation to give more information on metolachlor concentrations at different depths. It can be seen from Figure 5.66 and

Figure 5.67 that the metolachlor concentrations in layer 2 (in 2 layers simulation) were lower than those in 3 layers simulation, this explained why the average value of metolachlor concentrations in 5 cm calculated from 3 layers simulation having a higher value.

The performance of the model for metolachlor concentration in 5 cm soil was improved using the calibrated *Q10* of 2.0. As shown in Table 5.28 the *NSE* results for metolachlor concentration in 5 cm soil using *Q10* of 2 in both simulations were higher than those simulated using *Q10* of 1.42.

Table 5.28. Model performance for metolachlor concentrations in 5 cm (*Q10* = 2.0)

SPEC simulation	**Obs. mean (mg/kg)**	**Sim. mean (mg/kg)**	***RMSE* (%)**	**R^2 (-)**	***NSE* (-)**	***PBIAS* (%)**
2 layers (0-1 cm, 1-10 cm)	1.388	0.983	43.39	0.98	0.77*1)*	29.18*2)*
3 layers (0-1 cm, 1-5 cm, 5-10 cm)	1.388	1.286	32.37	0.92	0.87*1)*	7.31*1)*

Notes: *1)* very good, *2)* good, *3)* satisfactory, *4)* acceptable, *5)* unsatisfactory

Chapter 6. Summary and conclusions

The new module was developed and integrated in SPEC model to simulate the pollutant runoff. The improvement was made in SPEC model to simulate pesticide fate and transport in multiple soil layers. The improvements allow users to simulate pollutant runoff as well as pesticides in multiple soil layers not only in a single event but also a continuous simulation. The addition of shorter time steps for input and output enable the capability for modeling pollutant runoff during single rainfall events. This allows the simulation of the time to first runoff for single events. The improvement was made not only in the simulation codes but also in output display. It allows displaying dynamically in both tables and graphs.

The simulation of pesticides in soil layers was improved which allows predicting pesticides at deeper soil depths as well as in multiple depths at the same time. Dividing the soil depth into multiple small depths improved the pesticide simulation in soil because it could model in more details the variable distribution of pesticide concentrations along the soil depth.

The pollutant runoff module allows simulating runoff pollutant in single rainfall events. The CN method and Green-Ampt method allow the model to simulate both cumulative runoff and runoff rate in every small time step as well as the time to first runoff. The addition of sediment calculation code allows the model to simulate sediment concentration and sediment yield. The two additional parameters (*alpha* - the ratio of pesticide concentrations in mobile water and in static water; and *beta* - the ratio of pesticide concentrations in runoff water and in percolation water) allow the model to predict more accurately the pesticide concentrations in runoff water and in sediment.

The additional codes for statistical indexes were developed and integrated in the SPEC model support evaluating the model performance. This helps the users in a quick evaluation of the model performance without the need of any other software.

The codes for Monte Carlo simulation which were developed and integrated with the statistical indexes code in the SPEC model support the users in sensitivity analysis, in calibration and validation, as well as in uncertainty analysis.

The improved SPEC model was tested for three applications. The first case study applied to simulate the pollutant runoff for two types of pesticides (clothianidin and imidacloprid) under artificial rainfall event in Sakeacho upland bare soil (Tokyo, Japan) conducted on October 2nd, 2017. The second case study was conducted to simulate the fate and transport of imidacloprid and clothianidin in 4 layers of soils in Sakaecho upland bare soil (Tokyo, Japan) in 65 days from September 26th to November 29th, 2017. The third simulation was applied for the case study of Sakaecho upland bare soil (Tokyo, Japan) with two types of herbicides (atrazine and metolachlor) in 329 days from June 10th, 2013 to May 4th, 2014 under two options which were 2 and 3 soil layers simulations.

In the first application, the SPEC model simulated pollutant runoff using 4 layers of soils and 1-minute time steps for both input rainfall and output of the model. The artificial rainfall was 70mm/h in 70 minutes duration. The simulated results of runoff rate using CN method and Green-Ampt method matched with the observed data at a satisfactory level. The simulated results of cumulative runoff using both CN method and Green-Ampt method both performed a very good agreement with the observed data. The results of sediment yield also performed a very good agreement with the observed data. When evaluating based on *NSE*, the performance of sediment concentration results was not satisfied. However if *PBIAS* is used to evaluate the performance, the model performed a good prediction. The results of clothianidin concentrations in sediment and runoff water performed at a satisfactory level. The simulated imidacloprid concentration in runoff water was satisfied in calibration but was not satisfied in validation with the criteria based on *NSE*. However, it was good agreement if using *PBIAS* result. The results of imidacloprid concentration in sediment performed a very good agreement with the observed data. These results indicated the capability of the model to predict the pollutant runoff under single artificial rainfall events.

In the second application of the SPEC model, 4 layers of soils and 10-minute time step were chosen for rainfall input and model output to predict water content and concentrations in soil layers of imidacloprid and clothianidin in Sakaecho upland bare soil (Tokyo, Japan) in 65 days. The water content results had negative *NSE* (-10.95) indicated an unsatisfactory model performance; however, the *PBIAS* (-17.51%) indicated a satisfactory model performance. There were implications of errors in observed water content data. The performance of simulated pesticides in multiple soil layers was not good because of the imprecise observation data. However, the simulated pesticides in the first soil layer (0-1 cm) indicated the potential of the model to predict the pesticides concentrations in multiple soil layers. The simulated results of clothianidin in 0-1 cm for plot 1 indicated a satisfactory model performance (*NSE* = 0.63) and those for plot 2 indicated and a very good performance of the model (*NSE* = 0.77). The simulated results of imidacloprid in 0-1 cm for plot 1 indicated a satisfactory model performance (*NSE* = 0.56) and those for plot 2 indicated a good performance of the model (*NSE* = 0.71).

In the third application of the SPEC model, two scenarios for 2 layers (0-1 cm, 9-10 cm) and 3 layers (0-1 cm, 1-5 cm, 5-10 cm) of total 10 cm depth were simulated with hourly time step of rainfall and output for atrazine and metolachlor in the Sakaecho upland field (Tokyo, Japan) in 329 days. The simulated result of water content in 5 cm sampling depth was improved in which the *NSE* had positive value (0.29) and the *PBIAS* was only 3.2%. Comparing to the previous study (Boulange et al., 2016), the result of water content in 5 cm sampling depth was improved. For average atrazine concentrations in 5 cm, the *NSE* for 3 layers simulation was 0.74 indicated a good model performance; while *NSE* for 2 layers simulation was 0.47 indicated an acceptable model performance. For metolachlor, the *NSE* for 3 layers simulation were 0.87 indicated a very good model performance, while *NSE* for 2 layers simulation were 0.73 indicated a good model performance. It was found that the simulated results for 3 layers simulation performed better than those in 2 layers simulation indicated that using the a smaller depth or increasing numbers of soil layers in simulation would improve the model performance. The simulated results of 2 types of pesticides simulated by 3 layers scenario indicated a better model performance in the improved SPEC model as compared to those in the study calculated by the previous version of SPEC model (Boulange et al., 2016).

In summary, the development of the pollutant runoff module and the improvement of multiple layers simulation as well as the validations of pollutant runoff and two cases of continuous simulations in multiple layers of pesticides were conducted in this study. The improvement of the model and its applications indicated the potential capability of the model to predict pollutant runoff as well as the pesticide fate and transport in multiple soil layers.

Future research should be conducted to improve or test the consistency of the codes in the improved SPEC model as well as the consistency of the model capability. The consistency of the model capability should be conducted in (1) simulating pollutant runoff with other rainfall intensities in single events and (2) the continuous simulation of pesticide in multiple soil layers with qualified observed pesticide in multiple soil layers.

References

Abudi, I., Carmi, G., Berliner, P., 2012. Rainfall simulator for field runoff studies. Journal of Hydrology 454–455, 76–81. https://doi.org/10.1016/j.jhydrol.2012.05.056

Ahmad, I., Verma, V., Verma, M.K., 2015. Application of Curve Number Method for Estimation of Runoff Potential in GIS Environment, in: 4. Presented at the 2nd International Conference on Geological and Civil Engineering, IACSIT Press, Singapore. https://doi.org/10.7763/IPCBEE

Allen, R.G., Pereira, L.S., Raes, D., Smith, M., 1998. Chapter 2 - FAO Penman-Monteith equation, in: Crop Evapotranspiration - Guidelines for Computing Crop Water Requirements - FAO Irrigation and Drainage Paper 56. FAO - Food and Agriculture Organization of the United Nations, Rome.

Boesten, J., Helweg, A., Businelli, M., Bergstrom, L., Schaefer, H., Delmas, A., Kloskowski, R., Walker, A., Travis, K., Smeets, L., Jones, R., Vanderbroeck, V., van der Linden, A., Broerse, S., Klein, M., Layton, R., Jacobsen, O., Yon, D., 1997. Soil persistence models and EU registration.

Boulange, J., Thuyet, D.Q., Jaikaew, P., Ishihara, S., Watanabe, H., 2016. Development and validation of the SPEC model for simulating the fate and transport of pesticide applied to Japanese upland agricultural soil. J. Pest. Sci. 41, 152–162. https://doi.org/10.1584/jpestics.D16-027

Boulange, J., Watanabe, H., Inao, K., Iwafune, T., Zhang, M., Luo, Y., Arnold, J., 2014. Development and validation of a basin scale model PCPF-1@SWAT for simulating fate and transport of rice pesticides. J. Hydrol. 517, 146–156. https://doi.org/10.1016/j.jhydrol.2014.05.013

Bouwer, H., 1966. Rapid field measurement of air entry value and hydraulic conductivity of soil as significant parameters in flow system analysis. Water Resources Research 2, 729–738. https://doi.org/10.1029/WR002i004p00729

CDPR, 2016. Environmental Fate of Imidacloprid. California Department of Pesticide Regulation, California Environmental Protection Agency.

CDPR, 2001. Atrazine - Risk Characterization Document. California Department of Pesticide Regulation, California Environmental Protection Agency.

Chen, B., Li, Yifan, Huang, G.H., Huang, Y., Li, Yueren, 2004. PeLM: Modeling of Pesticide-Losses Through Runoff and Sediment Transport. Journal of Environmental Science and Health, Part B 39, 613–626. https://doi.org/10.1081/PFC-200026853

Chow, V.T., Maidment, D.R., Mays, L.W., 1988. Applied hydrology. McGraw-Hill, New York.

Damalas, C.A., Eleftherohorinos, I.G., 2011. Pesticide exposure, safety issues, and risk assessment indicators. International journal of environmental research and public health 8, 1402–1419. https://doi.org/10.3390/ijerph8051402

Dowd, B.M., Press, D., Huertos, M.L., 2008. Agricultural nonpoint source water pollution policy: The case of California's Central Coast. Agriculture, Ecosystems & Environment 128, 151–161. https://doi.org/10.1016/j.agee.2008.05.014

FAO, 2000. Assessing soil contamination A reference manual. FAO PESTICIDE DISPOSAL SERIES 8.

Franco, A.C.L., Bonuma, N.B., 2017. Multi-variable SWAT model calibration with remotely sensed evapotranspiration and observed flow. RBRH 22.

Green, W.H., Ampt, G.A., 1911. Studies on Soil Phyics. The Journal of Agricultural Science 4, 1–24.

Guo, J., Zhou, J., Lu, J., Zou, Q., Zhang, H., Bi, S., 2014. Multi-objective optimization of empirical hydrological model for streamflow prediction. J. Hydrol. 511, 242–253. https://doi.org/10.1016/j.jhydrol.2014.01.047

Gupta, H.V., Kling, H., Yilmaz, K.K., Martinez, G.F., 2009. Decomposition of the mean squared error and NSE performance criteria: Implications for improving hydrological modelling. J. Hydrol. 377, 80–91. https://doi.org/10.1016/j.jhydrol.2009.08.003

Hawkins, R.H., Ward, T.J., Woodward, E., Mullem, J.A.V., 2010. Continuing evolution of rainfall-runoff and the Curve Number precedent. Presented at the 2nd Joint Federal Interagency Conference, Las Vegas, NV, pp. 1–12.

Hayes, T.B., Khoury, V., Narayan, A., Nazir, M., Park, A., Brown, T., Adame, L., Chan, E., Buchholz, D., Stueve, T., Gallipeau, S., 2010. Atrazine induces complete feminization and chemical castration in male African clawed frogs (Xenopus laevis). Proc Natl Acad Sci U S A 107, 4612–4617. https://doi.org/10.1073/pnas.0909519107

Heydens, W.F., Lamb, I.C., Wilson, A.G.E., 2010. Chapter 82 - Chloracetanilides, in: Krieger, R. (Ed.), Hayes' Handbook of Pesticide Toxicology (Third Edition). Academic Press, New York, pp. 1753–1769. https://doi.org/10.1016/B978-0-12-374367-1.00082-3

Hoang Tu, L., Boulange, J., Iwafune, T., Yadav, I., Watanabe, H., 2018. Improvement and application of the PCPF-1@SWAT2012 model for predicting pesticide transport: A case study of the Sakura River watershed. Pest. Manage. Sci. 74, 2520–2529. https://doi.org/10.1002/ps.4934

Hodges, S.D., Moore, P.G., 1972. Data Uncertainties and Least Squares Regression. Journal of the Royal Statistical Society. Series C (Applied Statistics) 21, 185–195. https://doi.org/10.2307/2346491

Hudson, N.W., 1993. Chapter 6 Rainfall simulators, in: Field Measurement of Soil Erosion and Runoff. Food and Agriculture Organization of the United Nations, Rome.

Inao, K., Kitamura, Y., 1999. Pesticide paddy field model (PADDY) for predicting pesticide concentrations in water and soil in paddy fields. Pestic. Sci. 55, 38–46. https://doi.org/10.1002/(SICI)1096-9063(199901)55:1<38::AID-PS851>3.0.CO;2-P

Inao, K., Watanabe, H., Karpouzas, D.G., Capri, E., 2008. Simulation Models of Pesticide Fate and Transport in Paddy Environment for Ecological Risk Assessment and Management. JARQ 42, 13–21. https://doi.org/10.6090/jarq.42.13

Jacques, J., Lavergne, C., Devictor, N., 2006. Sensitivity analysis in presence of model uncertainty and correlated inputs. Reliability Engineering & System Safety 91, 1126–1134. https://doi.org/10.1016/j.ress.2005.11.047

Jaikaew, P., Boulange, J., Thuyet, D.Q., Malhat, F., Ishihara, S., Watanabe, H., 2015. Potential impacts of seasonal variation on atrazine and metolachlor persistence in andisol soil. Environ. Monit. Assess. https://doi.org/10.1007/s10661-015-4986-4

Japan Meteorological Agency, 2017. URL http://www.data.jma.go.jp/obd/stats/etrn/view/hourly_a1.php?prec_no=44&block_no=1133&year=2017&month=09&day=01&view=p1 (accessed 10.10.17).

Joutey, N.T., Bahafid, W., Sayel, H., Ghachtouli, N.E., 2013. Biodegradation: Involved Microorganisms and Genetically Engineered Microorganisms, in: Biodegradation - Life of Science. Rolando Chamy and Francisca Rosenkranz, IntechOpen.

Kannan, N., White, S.M., Worrall, F., Whelan, M.J., 2007. Sensitivity analysis and identification of the best evapotranspiration and runoff options for hydrological modelling in SWAT-2000. J. Hydrol. 332, 456–466. https://doi.org/10.1016/j.jhydrol.2006.08.001

Katagi, T., 2004. Photodegradation of pesticides on plant and soil surfaces. Reviews of environmental contamination and toxicology.

King, K.W., Arnold, J.G., Bingner, R.L., 1999. COMPARISON OF GREEN-AMPT AND CURVE NUMBER METHODS ON GOODWIN CREEK WATERSHED USING SWAT. Trans. ASAE 42, 919–926. https://doi.org/10.13031/2013.13272

Kirkham, M.B., 2014. Chapter 10 - Field Capacity, Wilting Point, Available Water, and the Nonlimiting Water Range, in: Kirkham, M.B. (Ed.), Principles of Soil and Plant Water Relations (Second Edition). Academic Press, Boston, pp. 153–170.

Kowalik, T., Walega, A., 2015. Estimation of CN Parameter for Small Agricultural Watersheds Using Asymptotic Functions. Water 7. https://doi.org/10.3390/w7030939

Krause, P., Boyle, D.P., Bäse, F., 2005. Comparison of different efficiency criteria for hydrological model assessment. ADGEO 5, 89–97. https://doi.org/10.5194/adgeo-5-89-2005

Lim, K.J., Engel, B.A., Muthukrishnan, S., Harbor, J., 2006. EFFECTS OF INITIAL ABSTRACTION AND URBANIZATION ON ESTIMATED RUNOFF USING CN TECHNOLOGY1. JAWRA 42, 629–643. https://doi.org/10.1111/j.1752-1688.2006.tb04481.x

Maeda, T., Soma, K., Warkentin, B.P., 1983. Physical and Engineering Characteristics of Volcanic Ash Soils in Japan Compared with Those in Other Countries. Journal of Irrigation Engineering and Rural Planning 1983, 16–31. https://doi.org/10.11408/jierp1982.1983.16

Menzel, R.G., 1980. Chapter 12. Enrichment ratios for water quality modelling, in: CREAMS A Field Scale Model for Chemicals, Runoff, and Erosion from Agricultural Management Systems. USDA-SEA-Conserv. Res. Report No. 26, pp. 486–492.

Moriasi, D.N., Arnold, J.G., Van Liew, M.W., Bingner, R.L., Harmel, R.D., Veith, T.L., 2007. Model Evaluation Guidelines for Systematic Quantification of Accuracy in Watershed Simulations. Trans. ASAE 50, 885–900. https://doi.org/10.13031/2013.23153

Moriasi, D.N., Gitau, M.W., Pai, N., Daggupati, P., 2015. Hydrologic and Water Quality Models: Performance Measures and Evaluation Criteria. Trans. ASAE 58, 1763–1785. https://doi.org/10.13031/trans.58.10715

Moussa, R., 2010. When monstrosity can be beautiful while normality can be ugly: assessing the performance of event-based flood models. HSJ 55, 1074–1084. https://doi.org/10.1080/02626667.2010.505893

Nash, J.E., Sutcliffe, J.V., 1970. River flow forecasting through conceptual models part I — A discussion of principles. Journal of Hydrology 10, 282–290. https://doi.org/10.1016/0022-1694(70)90255-6

National Research Council, 1993. Pesticides in the Diets of Infants and Children. National Academies Press, Washington, DC.

Nearing, M., Liu, B., Risse, M., Zhang, X.C., 1996. Curve numbers and Green-Ampt effective hydraulic conductivities. JAWRA 32, 125–136.

Neitsch, S.L., Arnold, J.G., Kiniry, J.R., Williams, J.R., 2011. Soil and Water Assessment Tool Theoretical Documentation Version 2009. Texas Water Resources Institute.

Numabe, A., Nagahora, S., 2006. Estimation of pesticide runoff from paddy fields to rural rivers. Water Sci. Technol. 53, 139–146. https://doi.org/10.2166/wst.2006.047

Okumura, Y., Kakehi, S., Yamashita, Y., 2013. Mass Balance of Dioxins Derived from Pesticides in Sendai Bay, Japan. Japan Agricultural Research Quarterly: JARQ 47, 115–126. https://doi.org/10.6090/jarq.47.115

Oliveira, P.T.S., Nearing, M.A., Hawkins, R.H., Stone, J.J., Rodrigues, D.B.B., Panachuki, E., Wendland, E., 2016. Curve number estimation from Brazilian Cerrado rainfall and runoff data. JSWC 71, 420–429. https://doi.org/10.2489/jswc.71.5.420

Parvizi, S., Eslamian, S., Ostad-Ali-Askari, K., Yazdani, A., Singh, V.P., 2018. Percolation, in: Bobrowsky, P., Marker, B. (Eds.), Encyclopedia of Engineering Geology. Springer International Publishing, Cham, pp. 1–3.

Rajbanshi, J., 2016. Estimation of Runoff Depth and Volume Using NRCS-CN Method in Konar Catchment (Jharkhand, India). J. Civil. Environ. Eng. 6, 1–6. https://doi.org/10.4172/2165-784X.1000236

Rawls, W.J., Brakensiek, D.L., 1986. Comparison Between Green-Ampt and Curve Number Runoff Predictions. Trans. ASAE 29, 1597–1599. https://doi.org/10.13031/2013.30359

Rawls, W.J., Brakensiek, D.L., 1985. Prediction of Soil Water Properties for Hydraulic Modeling.

Santhi, C., Arnold, J.G., Williams, J.R., Dugas, W.A., Srinivasan, R., Hauck, L.M., 2001. VALIDATION OF THE SWAT MODEL ON A LARGE RWER BASIN WITH POINT AND NONPOINT SOURCES1. JAWRA Journal of the American Water Resources Association 37, 1169–1188. https://doi.org/10.1111/j.1752-1688.2001.tb03630.x

Satheeshkumar, S., Venkateswaran, S., Kannan, R., 2017. Rainfall–runoff estimation using SCS–CN and GIS approach in the Pappiredipatti watershed of the Vaniyar sub basin, South India. Model. Earth Syst. Environ. 3, 24. https://doi.org/10.1007/s40808-017-0301-4

Sharpley, A.N., Williams, J.R., 1990. EPIC--Erosion/Productivity Impact Calculator: 1. Model Documentation. U.S. Department of Agriculture Technical Bulletin No. 1768.

Shi, Z.-H., Chen, L.-D., Fang, N.-F., Qin, D.-F., Cai, C.-F., 2009. Research on the SCS-CN initial abstraction ratio using rainfall-runoff event analysis in the Three Gorges Area, China. CATENA 77, 1–7. https://doi.org/10.1016/j.catena.2008.11.006

Smith, S.J., Williams, J.R., Menzel, R.G., Coleman, G.A., 1984. Prediction of sediment yield from southern plains grasslands with the Modified Universal Soil Loss Equation. J. Range Manag. 37, 295–297.

Soulis, K.X., Valiantzas, J.D., 2012. SCS-CN parameter determination using rainfall-runoff data in heterogeneous watersheds – the two-CN system approach. Hydrol. Earth Syst. 16, 1001–1015. https://doi.org/10.5194/hess-16-1001-2012

Statistics Bureau of Japan, 2019. Japan Statistical Yearbook [WWW Document]. URL http://www.stat.go.jp/english/data/nenkan/index.html (accessed 4.18.19).

Sterratt, D.C., 2013. Q10: The Effect of Temperature on Ion Channel Kinetics, in: Jaeger, D., Jung, R. (Eds.), Encyclopedia of Computational Neuroscience. Springer New York, New York, NY, pp. 1–3. https://doi.org/10.1007/978-1-4614-7320-6_236-1

Takahashi, Y., Odanaka, Y., Wada, Y., Minakawa, Y., Fukita, T., 1999. Analysis of agricultural runoff and balance of pesticides with commercially available immunoassay kits. Journal of Pesticide Science 24, 255–261. https://doi.org/10.1584/jpestics.24.255

Thinh, L.V., Yadav, I.C., Boulange, J., Thuyet, D.Q., Watanabe, H., 2019. Modeling of runoff water and runoff pesticide concentrations in upland bare soil using improved SPEC model. Journal of Pesticide Science advpub. https://doi.org/10.1584/jpestics.D19-007

Trucano, T.G., Swiler, L.P., Igusa, T., Oberkampf, W.L., Pilch, M., 2006. Calibration, validation, and sensitivity analysis: What's what. Reliability Engineering & System Safety 91, 1331–1357. https://doi.org/10.1016/j.ress.2005.11.031

U.S. EPA, 2010. Environmental Fate and Ecological Risk Assessmentfor the Registration of CLOTHIANIDIN for Use as a Seed Treatment on Mustard Seed (Oilseed and Condiment) and Cotton. U.S. Environmental Protection Agency, Washington, DC 20460.

U.S. EPA, 2008. Regulatory Determinations Support Document for CCL 2. U.S. Environmental Protection Agency, Washington, DC 20460.

U.S. EPA, 1996. Soil Screening Guidance: Technical Background Document. U.S. Environmental Protection Agency, Washington, DC 20460.

U.S. EPA, 1995. Reregistration Eligibility Decision (RED) - Metolachlor. U.S. Environmental Protection Agency, Washington, DC 20460.

U.S. EPA, n.d. Polluted Runoff: Nonpoint Source (NPS) Pollution [WWW Document]. Basic Information about Nonpoint Source (NPS) Pollution. URL https://www.epa.gov/nps/basic-information-about-nonpoint-source-nps-pollution (accessed 9.19.18).

USDA Natural Resources Conservation Service, 2015. Chapter 5: Streamflow Data.

USDA Natural Resources Conservation Service, 2004. Chapter 10: Estimation of Direct Runoff from Storm Rainfall.

USDA Natural Resources Conservation Service, 1999. Module 205. SCS Runoff Equation. National Employee Development Center.

USDA Natural Resources Conservation Service, 1986. Urban Hydrology for Small Watersheds - TR55.

Van Genuchten, M., J. Leij, F., R. Yates, S., R. Williams, J., 1991. The RETC Code for Quantifying Hydraulic Functions of Unsaturated Soils.

Varis, O., 1996. Water quality models: Typologies for environmental impact assessment. Water Sci. Technol. 34, 109–117. https://doi.org/10.1016/S0273-1223(96)00859-1

Vernon, R.S., van Herk, W.G., 2013. Chapter 5 - Wireworms as Pests of Potato, in: Alyokhin, A., Vincent, C., Giordanengo, P. (Eds.), Insect Pests of Potato. Academic Press, San Diego, pp. 103–164. https://doi.org/10.1016/B978-0-12-386895-4.00005-3

Vigiak, O., Malagó, A., Bouraoui, F., Vanmaercke, M., Poesen, J., 2015. Adapting SWAT hillslope erosion model to predict sediment concentrations and yields in large Basins. Sci. Total Environ. 538, 855–875. https://doi.org/10.1016/j.scitotenv.2015.08.095

Watanabe, H., Grismer, M.E., 2003. Numerical modeling of diazinon transport through inter-row vegetative filter strips. Journal of Environmental Management 69, 157–168. https://doi.org/10.1016/S0301-4797(03)00142-7

Watanabe, H., Grismer, M.E., 2001. Diazinon transport through inter-row vegetative filter strips: micro-ecosystem modeling. Journal of Hydrology 247, 183–199. https://doi.org/10.1016/S0022-1694(01)00385-7

Watanabe, H., Takagi, K., 2000. A Simulation Model for Predicting Pesticide Concentrations in Paddy Water and Surface Soil. I. Model Development. Environmental Technology 21, 1379–1391. https://doi.org/10.1080/09593332208618167

Watanabe, H., Takagi, K., Vu, S.H., 2006. Simulation of mefenacet concentrations in paddy fields by an improved PCPF-1 model. Pest. Manage. Sci. 62, 20–29. https://doi.org/10.1002/ps.1115

Watson, G.S., 1967. Linear Least Squares Regression. Ann. Math. Statist. 38, 1679–1699. https://doi.org/10.1214/aoms/1177698603

Williams, J.R., 1995. Chapter 25: The EPIC model, in: Singh, V.P. (Ed.), Computer Models of Watershed Hydrology. Water Resources Publications, pp. 909–1000.

Williams, J.R., 1975. Sediment-yield prediction with Universal Equation using runoff energy factor, in: Present and Prospective Technology for Predicting Sediment Yield and Sources. USDS. ARS-S40, pp. 244–252.

Williams, J.R., Kannan, N., Wang, X., Santhi, C., 2012. Evolution of the SCS Runoff Curve Number Method and Its Application to Continuous Runoff Simulation. J. Hydrol. Eng. 17, 1221–1229. https://doi.org/10.1061/(ASCE)HE.1943-5584.0000529

Wischmeier, W.H., Smith, D.D., 1978. Predicting rainfall erosion losses: A guide to conservation planning. U.S. Dep. Agric., Agric. Handb. No. 537.

Wischmeier, W.H., Smith, D.D., 1965. Predicting rainfall-erosion losses from cropland east of the Rocky Mountains: Guide for selection of practices for soil and water conservation. U.S. Dep. Agric., Agric. Handb. No. 282.

Woodward, D.E., Hawkins, R.H., Jiang, R., Allen T. Hjelmfelt, Jr., Mullem, J.A.V., Quan, Q.D., 2003. Runoff Curve Number Method: Examination of the Initial Abstraction Ratio, in: World Water & Environmental Resources Congress 2003.

World Health Organization, 2008. Pesticides [WWW Document]. URL http://www.who.int/ceh/capacity/Pesticides.pdf (accessed 9.10.18).

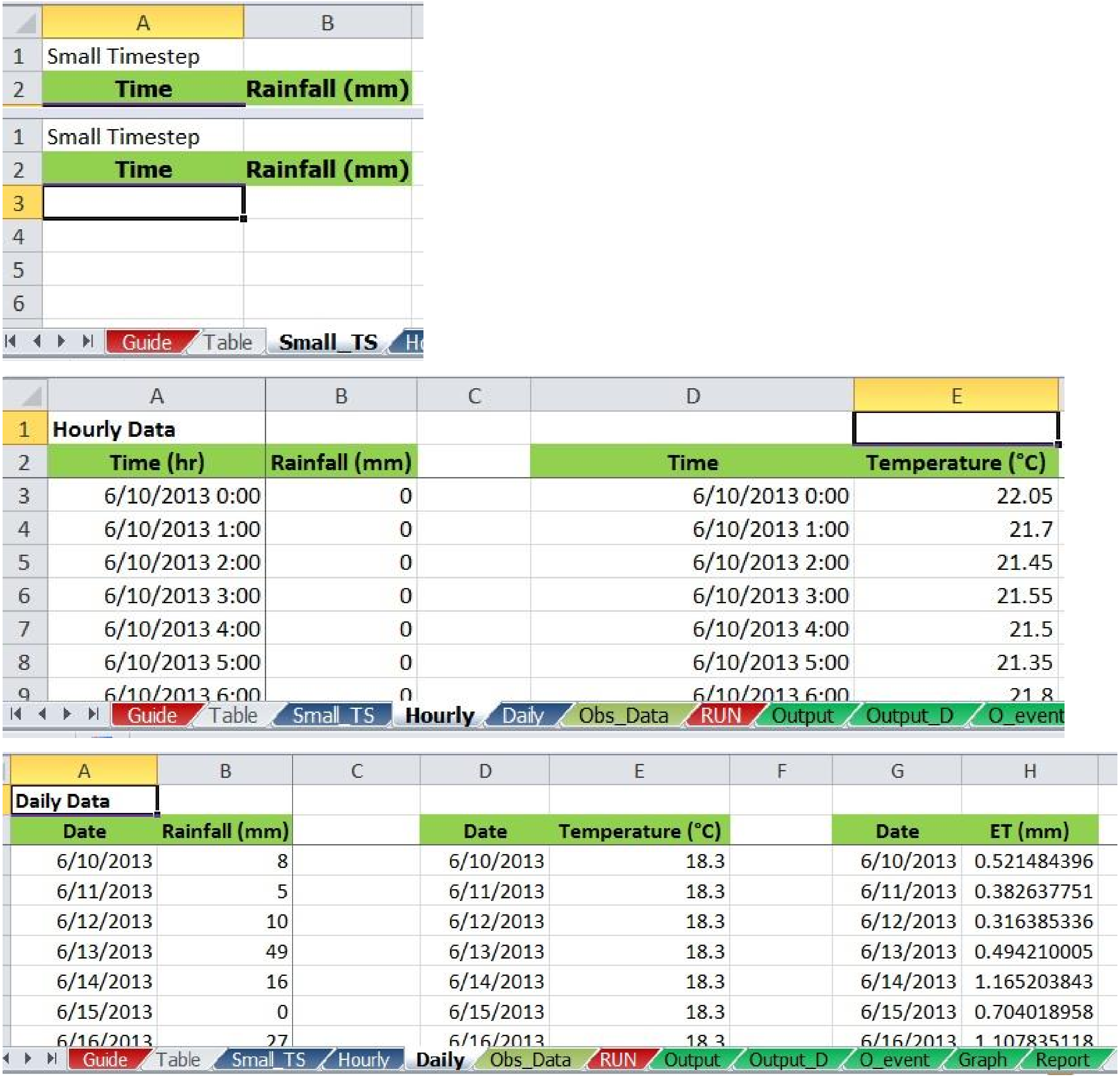
Yadav, I.C., Watanabe, H., 2018. Soil erosion and transport of Imidacloprid and Clothianidin in the upland field under simulated rainfall condition. 1 Sci. Total Environ. 640–641, 1354–1364. https://doi.org/10.1016/j.scitotenv.2018.06.008

Yuan, Y., Nie, W., McCutcheon, S.C., Taguas, E.V., 2012. Initial abstraction and curve numbers for semiarid watersheds in Southeastern Arizona. Hydrol. Process. 28, 774–783. https://doi.org/10.1002/hyp.9592

Zhang, R., Krzyszowska-Waitkus, A.J., Vance, G.F., Qi, J., 2000. Pesticide transport in field soils. Adv. Environ. Res. 4, 57–65. https://doi.org/10.1016/S1093-0191(00)00009-5

Appendices

Appendix 1. Input data in SPEC model



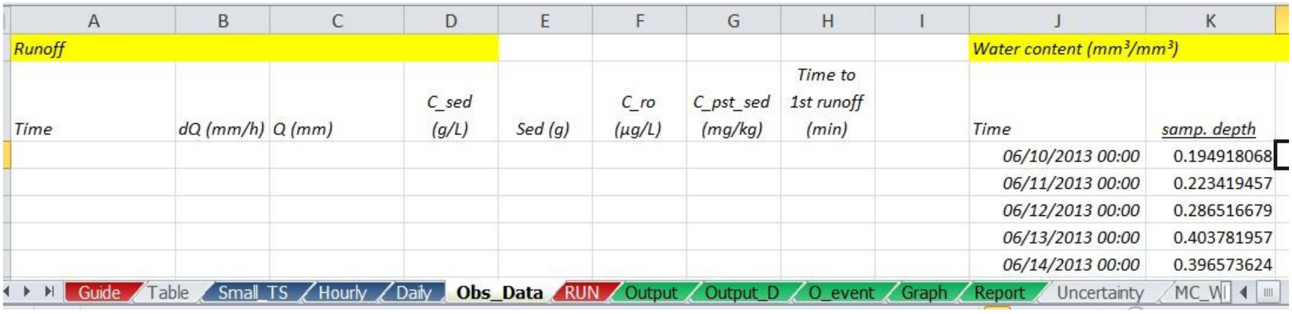
	A	B
1	Small Timestep	
2	**Time**	**Rainfall (mm)**

	A	B
1	Small Timestep	
2	**Time**	**Rainfall (mm)**
3		
4		
5		
6		

	A	B	C	D	E
1	**Hourly Data**				
2	**Time (hr)**	**Rainfall (mm)**		**Time**	**Temperature (°C)**
3	6/10/2013 0:00	0		6/10/2013 0:00	22.05
4	6/10/2013 1:00	0		6/10/2013 1:00	21.7
5	6/10/2013 2:00	0		6/10/2013 2:00	21.45
6	6/10/2013 3:00	0		6/10/2013 3:00	21.55
7	6/10/2013 4:00	0		6/10/2013 4:00	21.5
8	6/10/2013 5:00	0		6/10/2013 5:00	21.35
9	6/10/2013 6:00	0		6/10/2013 6:00	21.8

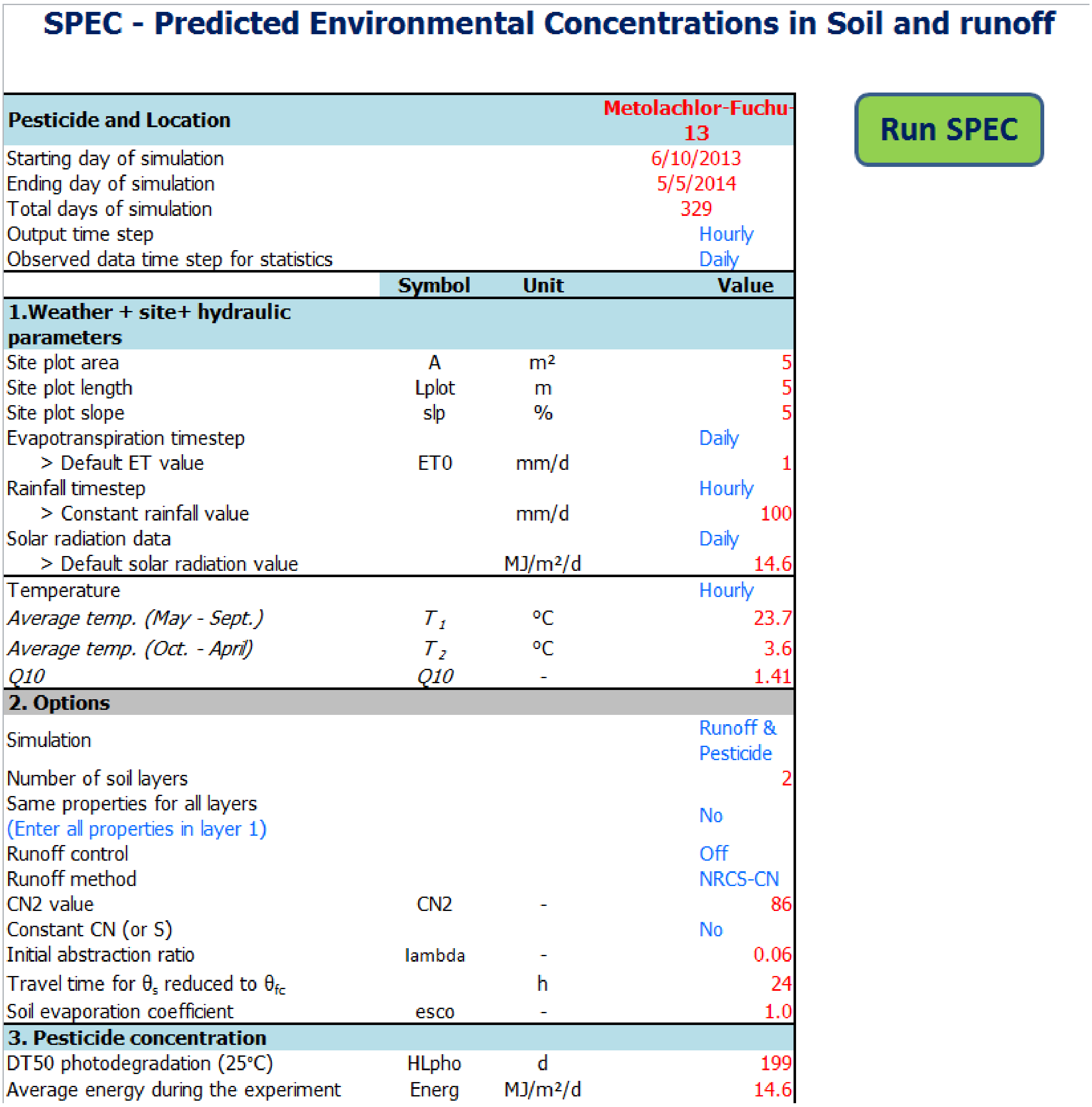
A	B	C	D	E	F	G	H
Daily Data							
Date	**Rainfall (mm)**		**Date**	**Temperature (°C)**		**Date**	**ET (mm)**
6/10/2013	8		6/10/2013	18.3		6/10/2013	0.521484396
6/11/2013	5		6/11/2013	18.3		6/11/2013	0.382637751
6/12/2013	10		6/12/2013	18.3		6/12/2013	0.316385336
6/13/2013	49		6/13/2013	18.3		6/13/2013	0.494210005
6/14/2013	16		6/14/2013	18.3		6/14/2013	1.165203843
6/15/2013	0		6/15/2013	18.3		6/15/2013	0.704018958
6/16/2013	27		6/16/2013	18.3		6/16/2013	1.107835118

Fig. A. 1. Fomats for 3 sheets of input variables (small, hourly and daily time step)



A	B	C	D	E	F	G	H	I	J	K
Runoff									*Water content (mm³/mm³)*	
Time	*dQ (mm/h)*	*Q (mm)*	*C_sed (g/L)*	*Sed (g)*	*C_ro (µg/L)*	*C_pst_sed (mg/kg)*	*Time to 1st runoff (min)*		*Time*	*samp. depth*
									06/10/2013 00:00	0.194918068
									06/11/2013 00:00	0.223419457
									06/12/2013 00:00	0.286516679
									06/13/2013 00:00	0.403781957
									06/14/2013 00:00	0.396573624

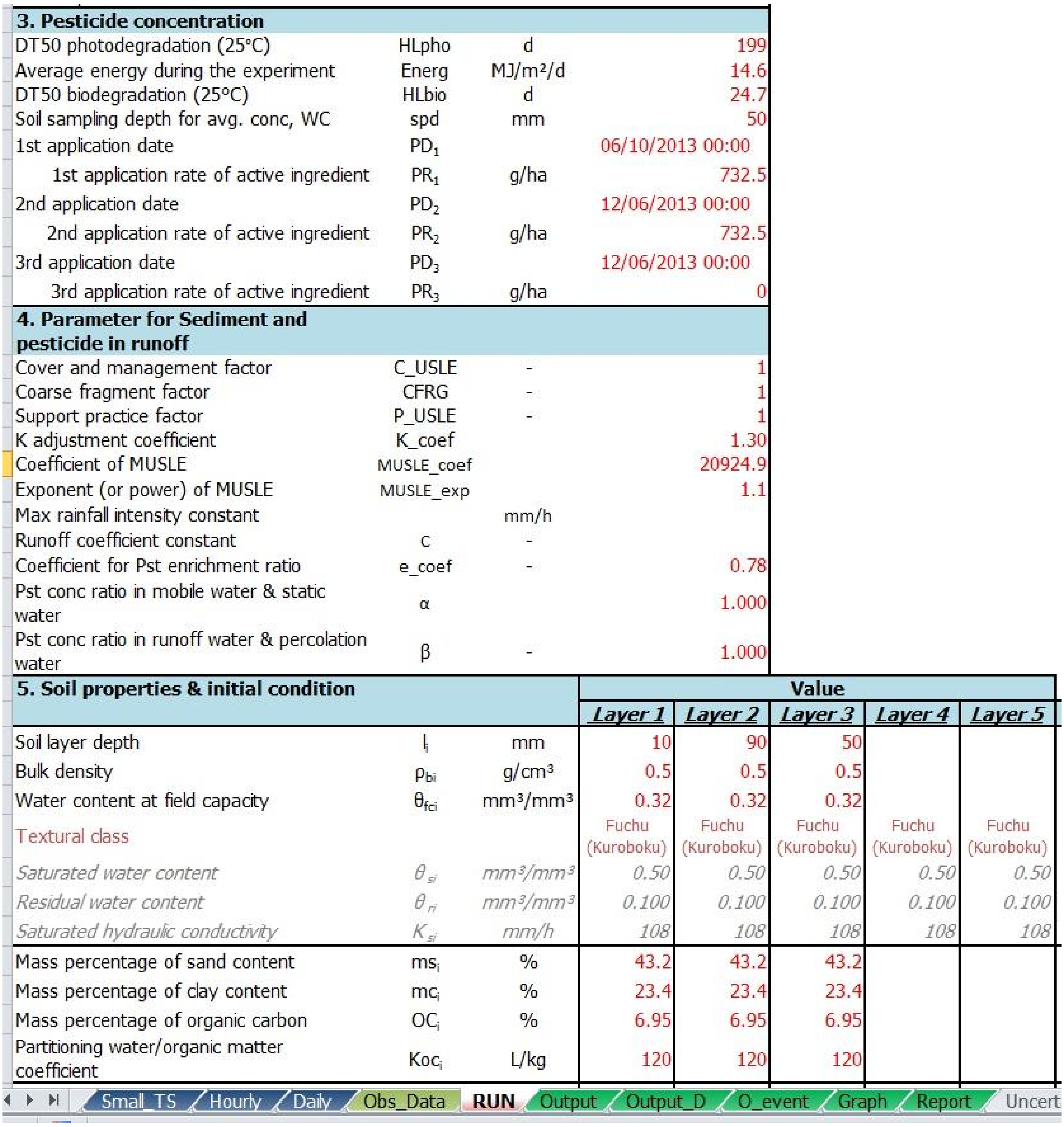
Fig. A. 2. Sheet for observed data



SPEC - Predicted Environmental Concentrations in Soil and runoff

Pesticide and Location			**Metolachlor-Fuchu-13**
Starting day of simulation			6/10/2013
Ending day of simulation			5/5/2014
Total days of simulation			329
Output time step			Hourly
Observed data time step for statistics			Daily
	Symbol	**Unit**	**Value**
1.Weather + site+ hydraulic parameters			
Site plot area	A	m²	5
Site plot length	Lplot	m	5
Site plot slope	slp	%	5
Evapotranspiration timestep			Daily
> Default ET value	ET0	mm/d	1
Rainfall timestep			Hourly
> Constant rainfall value		mm/d	100
Solar radiation data			Daily
> Default solar radiation value		MJ/m²/d	14.6
Temperature			Hourly
Average temp. (May - Sept.)	T_1	°C	23.7
Average temp. (Oct. - April)	T_2	°C	3.6
Q10	*Q10*	-	1.41
2. Options			
Simulation			Runoff & Pesticide
Number of soil layers			2
Same properties for all layers (Enter all properties in layer 1)			No
Runoff control			Off
Runoff method			NRCS-CN
CN2 value	CN2	-	86
Constant CN (or S)			No
Initial abstraction ratio	lambda	-	0.06
Travel time for θ_s reduced to θ_{fc}		h	24
Soil evaporation coefficient	esco	-	1.0
3. Pesticide concentration			
DT50 photodegradation (25°C)	HLpho	d	199
Average energy during the experiment	Energ	MJ/m²/d	14.6

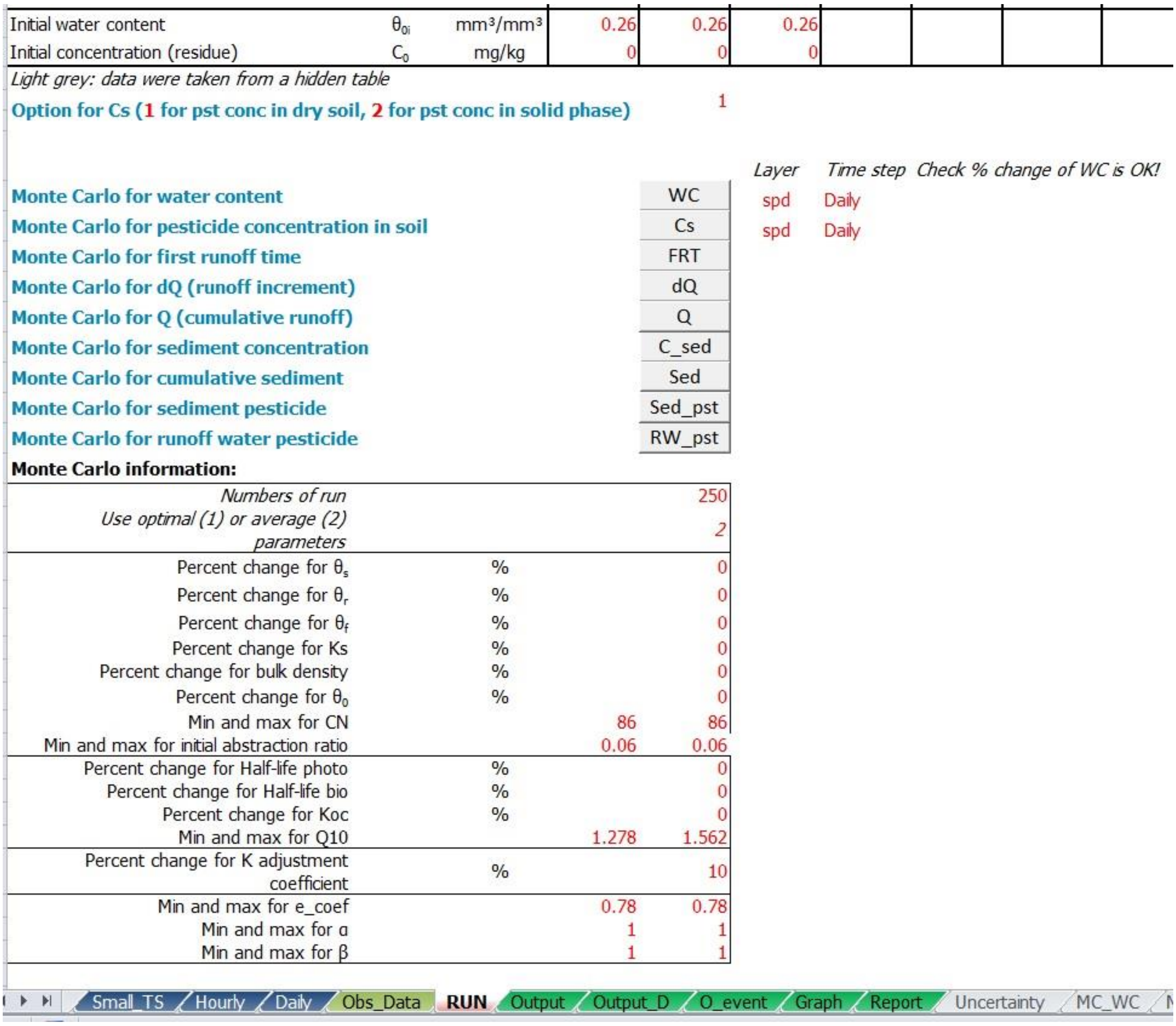
Fig. A. 3. RUN sheet for selecting model options



3. Pesticide concentration			
DT50 photodegradation (25°C)	HLpho	d	199
Average energy during the experiment	Energ	MJ/m²/d	14.6
DT50 biodegradation (25°C)	HLbio	d	24.7
Soil sampling depth for avg. conc, WC	spd	mm	50
1st application date	PD_1		06/10/2013 00:00
1st application rate of active ingredient	PR_1	g/ha	732.5
2nd application date	PD_2		12/06/2013 00:00
2nd application rate of active ingredient	PR_2	g/ha	732.5
3rd application date	PD_3		12/06/2013 00:00
3rd application rate of active ingredient	PR_3	g/ha	0
4. Parameter for Sediment and pesticide in runoff			
Cover and management factor	C_USLE	-	1
Coarse fragment factor	CFRG	-	1
Support practice factor	P_USLE	-	1
K adjustment coefficient	K_coef		1.30
Coefficient of MUSLE	MUSLE_coef		20924.9
Exponent (or power) of MUSLE	MUSLE_exp		1.1
Max rainfall intensity constant		mm/h	
Runoff coefficient constant	c	-	
Coefficient for Pst enrichment ratio	e_coef	-	0.78
Pst conc ratio in mobile water & static water	α		1.000
Pst conc ratio in runoff water & percolation water	β	-	1.000

5. Soil properties & initial condition			Value				
			Layer 1	***Layer 2***	***Layer 3***	***Layer 4***	***Layer 5***
Soil layer depth	l_i	mm	10	90	50		
Bulk density	ρ_{bi}	g/cm³	0.5	0.5	0.5		
Water content at field capacity	θ_{fci}	mm³/mm³	0.32	0.32	0.32		
Textural class			Fuchu (Kuroboku)	Fuchu (Kuroboku)	Fuchu (Kuroboku)	Fuchu (Kuroboku)	Fuchu (Kuroboku)
Saturated water content	θ_{si}	*mm³/mm³*	*0.50*	*0.50*	*0.50*	*0.50*	*0.50*
Residual water content	θ_{ri}	*mm³/mm³*	*0.100*	*0.100*	*0.100*	*0.100*	*0.100*
Saturated hydraulic conductivity	K_{si}	*mm/h*	*108*	*108*	*108*	*108*	*108*
Mass percentage of sand content	ms_i	%	43.2	43.2	43.2		
Mass percentage of clay content	mc_i	%	23.4	23.4	23.4		
Mass percentage of organic carbon	OC_i	%	6.95	6.95	6.95		
Partitioning water/organic matter coefficient	Koc_i	L/kg	120	120	120		

Fig. A. 3. RUN sheet for selecting model options (cont')



Initial water content	θ_{0i}	mm³/mm³	0.26	0.26	0.26
Initial concentration (residue)	C_0	mg/kg	0	0	0

Light grey: data were taken from a hidden table

Option for Cs (1 for pst conc in dry soil, 2 for pst conc in solid phase) 1

		Layer	*Time step*
Monte Carlo for water content	WC	spd	Daily
Monte Carlo for pesticide concentration in soil	Cs	spd	Daily
Monte Carlo for first runoff time	FRT		
Monte Carlo for dQ (runoff increment)	dQ		
Monte Carlo for Q (cumulative runoff)	Q		
Monte Carlo for sediment concentration	C_sed		
Monte Carlo for cumulative sediment	Sed		
Monte Carlo for sediment pesticide	Sed_pst		
Monte Carlo for runoff water pesticide	RW_pst		

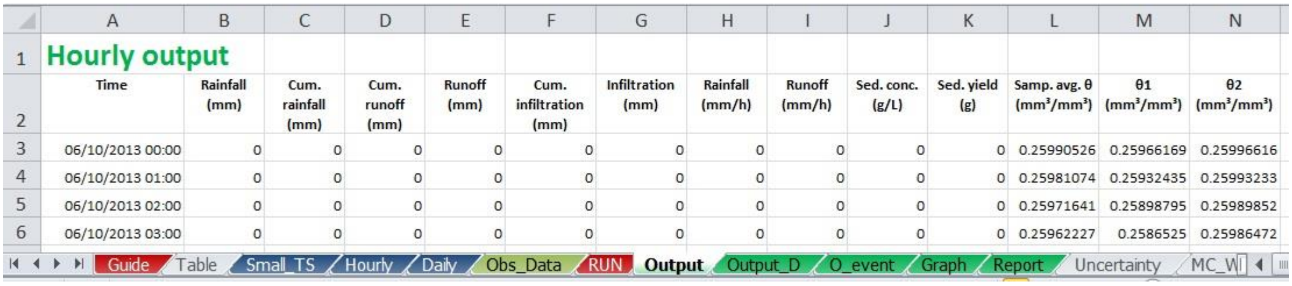
Check % change of WC is OK!

Monte Carlo information:

Numbers of run			250
Use optimal (1) or average (2) parameters			2
Percent change for θ_s	%		0
Percent change for θ_r	%		0
Percent change for θ_f	%		0
Percent change for Ks	%		0
Percent change for bulk density	%		0
Percent change for θ_0	%		0
Min and max for CN		86	86
Min and max for initial abstraction ratio		0.06	0.06
Percent change for Half-life photo	%		0
Percent change for Half-life bio	%		0
Percent change for Koc	%		0
Min and max for Q10		1.278	1.562
Percent change for K adjustment coefficient	%		10
Min and max for e_coef		0.78	0.78
Min and max for α		1	1
Min and max for β		1	1

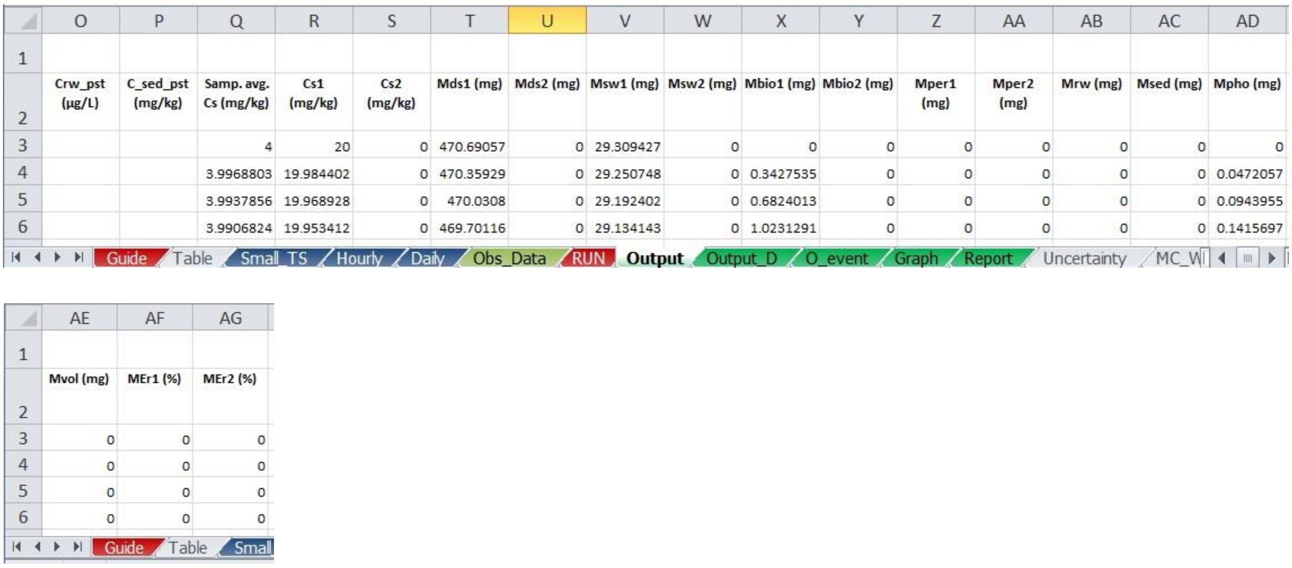
Fig. A. 3. RUN sheet for selecting model options (cont')

Appendix 2. Output in SPEC model



	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1	**Hourly output**													
2	**Time**	**Rainfall (mm)**	**Cum. rainfall (mm)**	**Cum. runoff (mm)**	**Runoff (mm)**	**Cum. infiltration (mm)**	**Infiltration (mm)**	**Rainfall (mm/h)**	**Runoff (mm/h)**	**Sed. conc. (g/L)**	**Sed. yield (g)**	**Samp. avg. θ (mm³/mm³)**	**θ1 (mm³/mm³)**	**θ2 (mm³/mm³)**
3	06/10/2013 00:00	0	0	0	0	0	0	0	0	0	0	0.25990526	0.25966169	0.25996616
4	06/10/2013 01:00	0	0	0	0	0	0	0	0	0	0	0.25981074	0.25932435	0.25993233
5	06/10/2013 02:00	0	0	0	0	0	0	0	0	0	0	0.25971641	0.25898795	0.25989852
6	06/10/2013 03:00	0	0	0	0	0	0	0	0	0	0	0.25962227	0.2586525	0.25986472

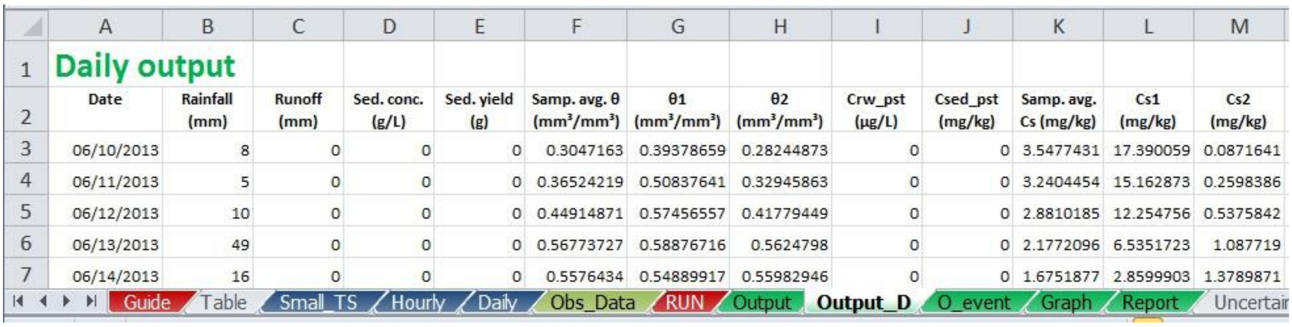
Fig. A. 4. Sheet "ouput" for small time step values of output



	O	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AB	AC	AD
1																
2	Crw_pst (µg/L)	C_sed_pst (mg/kg)	Samp. avg. Cs (mg/kg)	Cs1 (mg/kg)	Cs2 (mg/kg)	Mds1 (mg)	Mds2 (mg)	Msw1 (mg)	Msw2 (mg)	Mbio1 (mg)	Mbio2 (mg)	Mper1 (mg)	Mper2 (mg)	Mrw (mg)	Msed (mg)	Mpho (mg)
3			4	20	0	470.69057	0	29.309427	0	0	0	0	0	0	0	0
4			3.9968803	19.984402	0	470.35929	0	29.250748	0	0.3427535	0	0	0	0	0	0.0472057
5			3.9937856	19.968928	0	470.0308	0	29.192402	0	0.6824013	0	0	0	0	0	0.0943955
6			3.9906824	19.953412	0	469.70116	0	29.134143	0	1.0231291	0	0	0	0	0	0.1415697

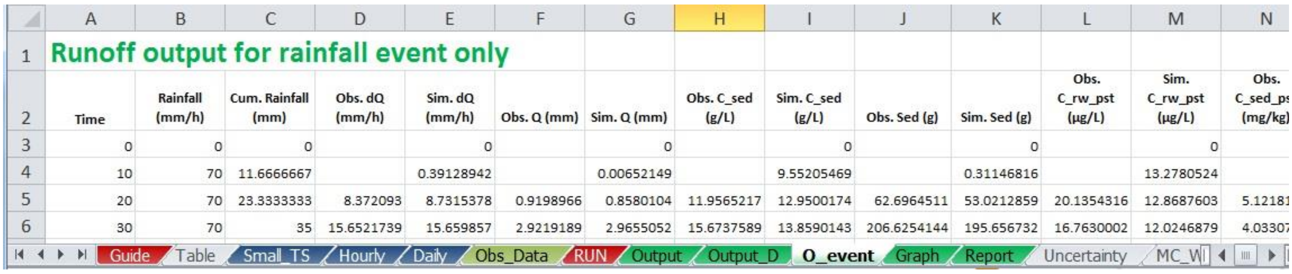
	AE	AF	AG
1			
2	Mvol (mg)	MEr1 (%)	MEr2 (%)
3	0	0	0
4	0	0	0
5	0	0	0
6	0	0	0

Fig. A. 4. Sheet “ouput” for small time step values of output (cont’)



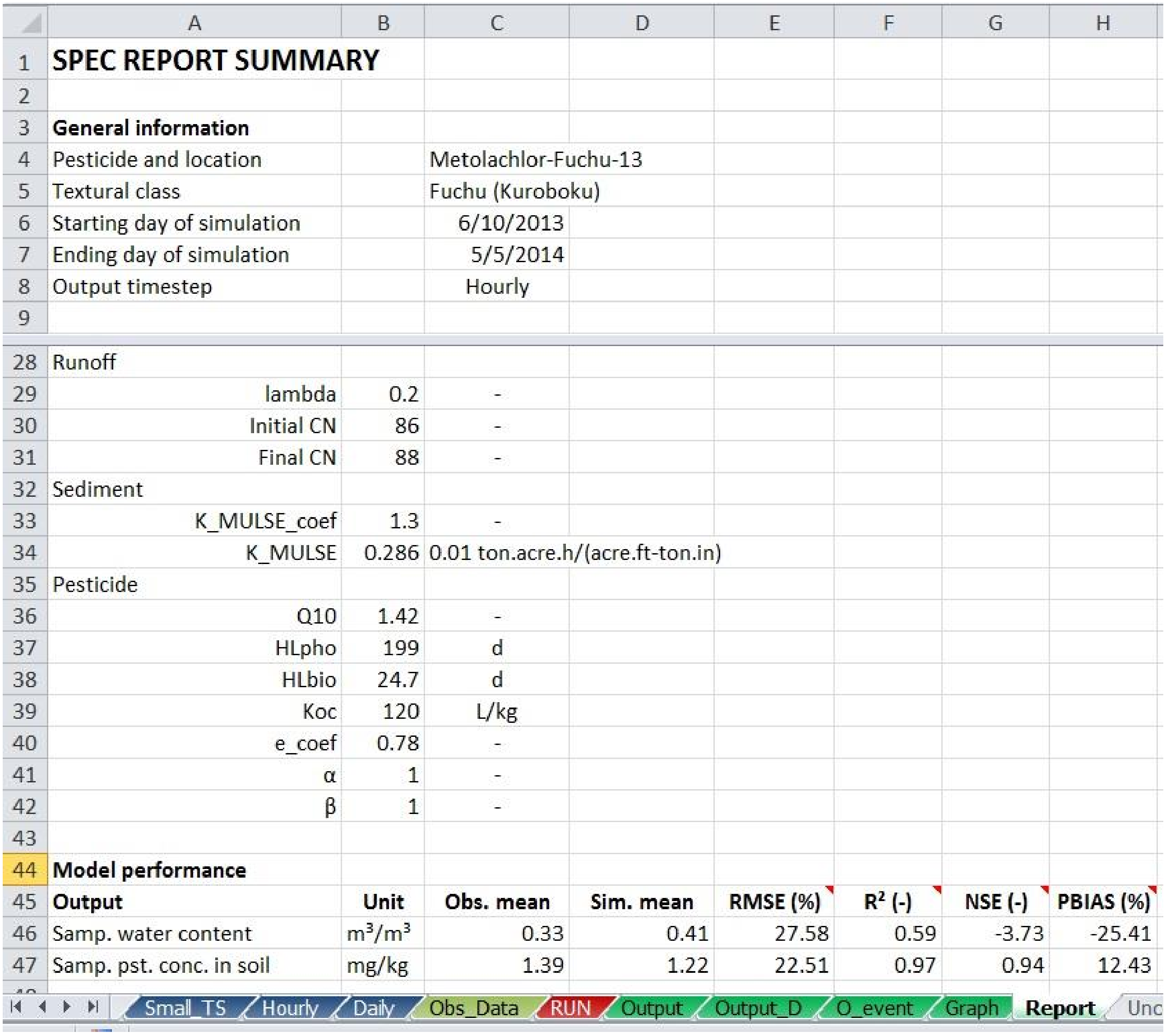
	A	B	C	D	E	F	G	H	I	J	K	L	M
1	Daily output												
2	Date	Rainfall (mm)	Runoff (mm)	Sed. conc. (g/L)	Sed. yield (g)	Samp. avg. θ (mm³/mm³)	θ1 (mm³/mm³)	θ2 (mm³/mm³)	Crw_pst (µg/L)	Csed_pst (mg/kg)	Samp. avg. Cs (mg/kg)	Cs1 (mg/kg)	Cs2 (mg/kg)
3	06/10/2013	8	0	0	0	0.3047163	0.39378659	0.28244873	0	0	3.5477431	17.390059	0.0871641
4	06/11/2013	5	0	0	0	0.36524219	0.50837641	0.32945863	0	0	3.2404454	15.162873	0.2598386
5	06/12/2013	10	0	0	0	0.44914871	0.57456557	0.41779449	0	0	2.8810185	12.254756	0.5375842
6	06/13/2013	49	0	0	0	0.56773727	0.58876716	0.5624798	0	0	2.1772096	6.5351723	1.087719
7	06/14/2013	16	0	0	0	0.5576434	0.54889917	0.55982946	0	0	1.6751877	2.8599903	1.3789871

Fig. A. 5. Sheet “ouput_D” for daily values of output



	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1	Runoff output for rainfall event only													
2	Time	Rainfall (mm/h)	Cum. Rainfall (mm)	Obs. dQ (mm/h)	Sim. dQ (mm/h)	Obs. Q (mm)	Sim. Q (mm)	Obs. C_sed (g/L)	Sim. C_sed (g/L)	Obs. Sed (g)	Sim. Sed (g)	Obs. C_rw_pst (µg/L)	Sim. C_rw_pst (µg/L)	Obs. C_sed_ps (mg/kg)
3	0	0	0		0		0		0		0		0	
4	10	70	11.6666667		0.39128942		0.00652149		9.55205469		0.31146816		13.2780524	
5	20	70	23.3333333	8.372093	8.7315378	0.9198966	0.8580104	11.9565217	12.9500174	62.6964511	53.0212859	20.1354316	12.8687603	5.12181
6	30	70	35	15.6521739	15.659857	2.9219189	2.9655052	15.6737589	13.8590143	206.6254144	195.656732	16.7630002	12.0246879	4.03307

Fig. A. 6. Sheet “O_event” for Output values in single rainfall event



	A	B	C	D	E	F	G	H
1	**SPEC REPORT SUMMARY**							
2								
3	**General information**							
4	Pesticide and location		Metolachlor-Fuchu-13					
5	Textural class		Fuchu (Kuroboku)					
6	Starting day of simulation		6/10/2013					
7	Ending day of simulation		5/5/2014					
8	Output timestep		Hourly					
9								
28	Runoff							
29	lambda	0.2	-					
30	Initial CN	86	-					
31	Final CN	88	-					
32	Sediment							
33	K_MULSE_coef	1.3	-					
34	K_MULSE	0.286	0.01 ton.acre.h/(acre.ft-ton.in)					
35	Pesticide							
36	Q10	1.42	-					
37	HLpho	199	d					
38	HLbio	24.7	d					
39	Koc	120	L/kg					
40	e_coef	0.78	-					
41	α	1	-					
42	β	1	-					
43								
44	**Model performance**							
45	**Output**	**Unit**	**Obs. mean**	**Sim. mean**	**RMSE (%)**	**R^2 (-)**	**NSE (-)**	**PBIAS (%)**
46	Samp. water content	m^3/m^3	0.33	0.41	27.58	0.59	-3.73	-25.41
47	Samp. pst. conc. in soil	mg/kg	1.39	1.22	22.51	0.97	0.94	12.43

Fig. A. 7. Sheet "Report" to report the summary of results

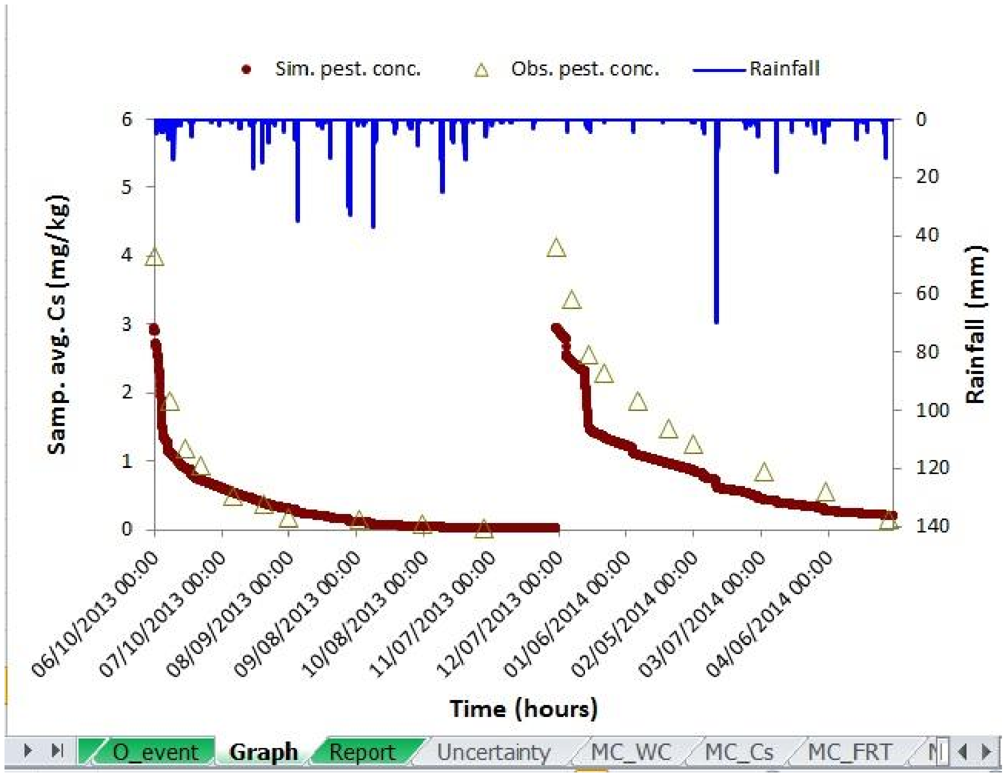


Fig. A. 8. Sheet “Graph” to display graphs of outputs

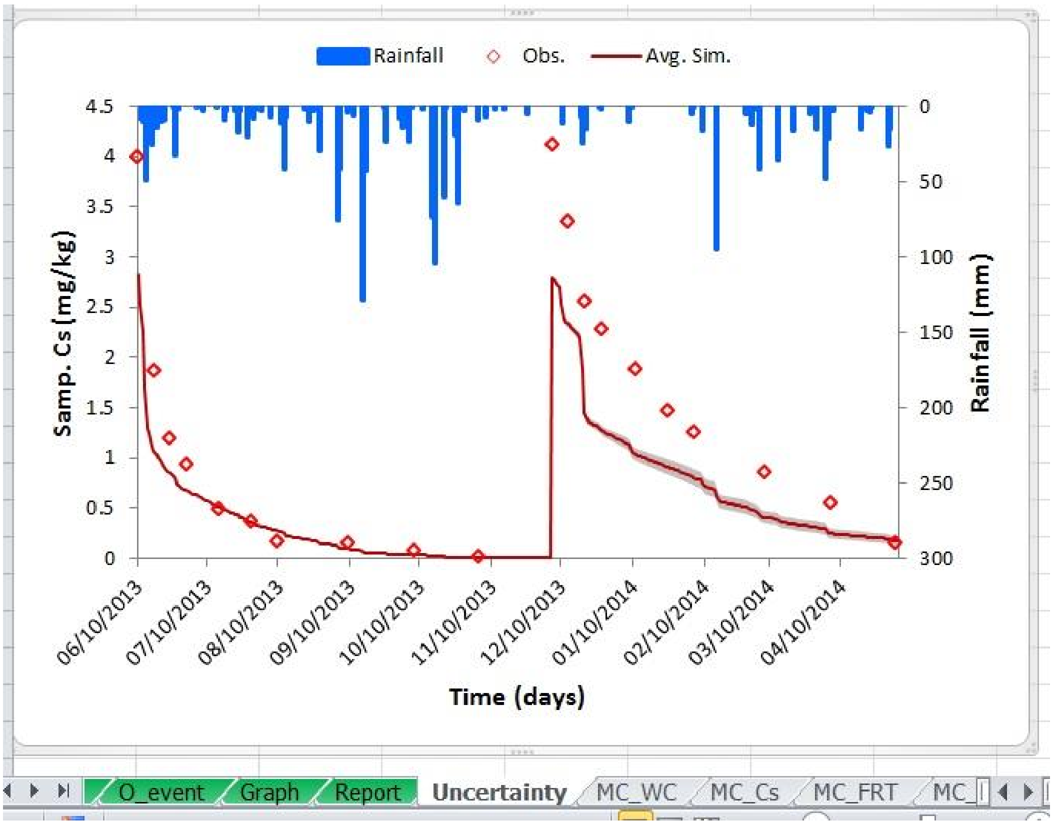
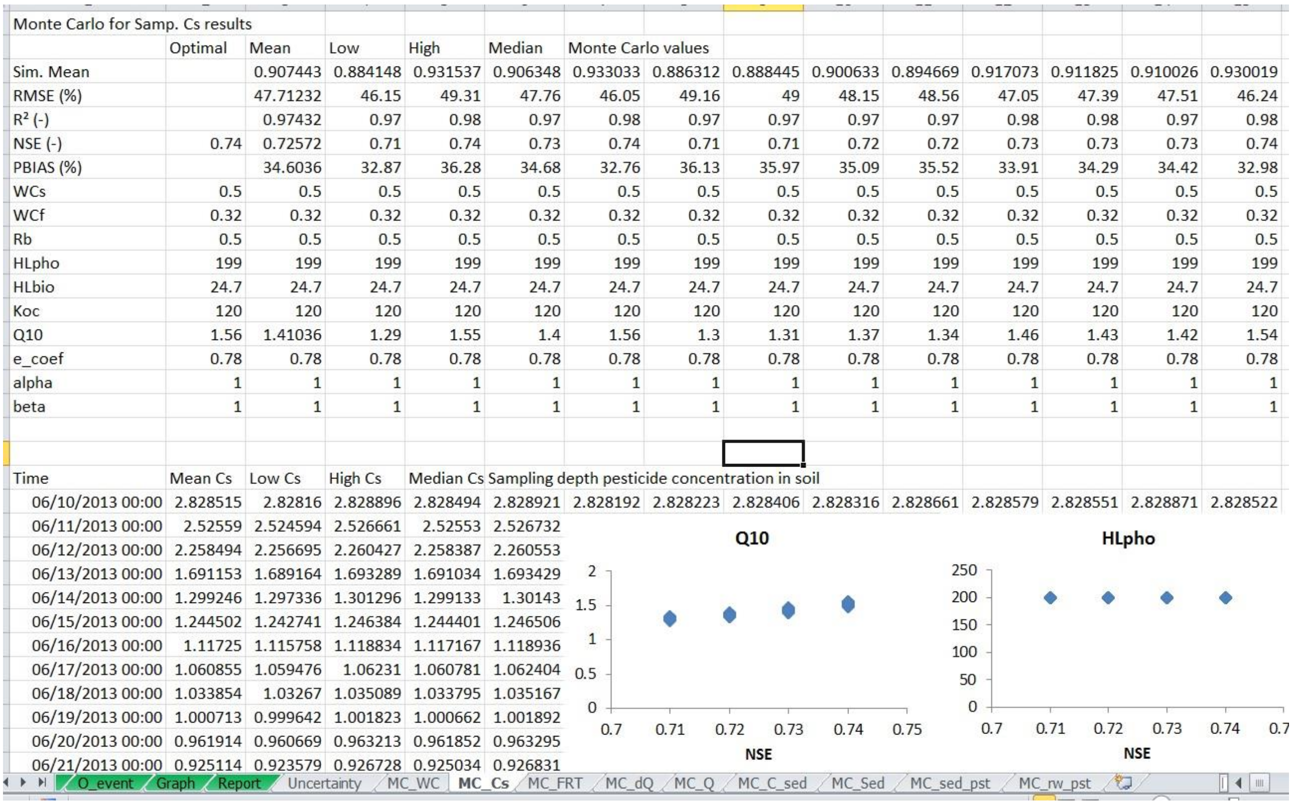


Fig. A. 9. Sheet “Uncertainty” to display uncertainty result



Monte Carlo for Samp. Cs results

	Optimal	Mean	Low	High	Median	Monte Carlo values								
Sim. Mean		0.907443	0.884148	0.931537	0.906348	0.933033	0.886312	0.888445	0.900633	0.894669	0.917073	0.911825	0.910026	0.930019
RMSE (%)		47.71232	46.15	49.31	47.76	46.05	49.16	49	48.15	48.56	47.05	47.39	47.51	46.24
R² (-)		0.97432	0.97	0.98	0.97	0.98	0.97	0.97	0.97	0.97	0.98	0.98	0.97	0.98
NSE (-)	0.74	0.72572	0.71	0.74	0.73	0.74	0.71	0.71	0.72	0.72	0.73	0.73	0.73	0.74
PBIAS (%)		34.6036	32.87	36.28	34.68	32.76	36.13	35.97	35.09	35.52	33.91	34.29	34.42	32.98
WCs	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
WCf	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32
Rb	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
HLpho	199	199	199	199	199	199	199	199	199	199	199	199	199	199
HLbio	24.7	24.7	24.7	24.7	24.7	24.7	24.7	24.7	24.7	24.7	24.7	24.7	24.7	24.7
Koc	120	120	120	120	120	120	120	120	120	120	120	120	120	120
Q10	1.56	1.41036	1.29	1.55	1.4	1.56	1.3	1.31	1.37	1.34	1.46	1.43	1.42	1.54
e_coef	0.78	0.78	0.78	0.78	0.78	0.78	0.78	0.78	0.78	0.78	0.78	0.78	0.78	0.78
alpha	1	1	1	1	1	1	1	1	1	1	1	1	1	1
beta	1	1	1	1	1	1	1	1	1	1	1	1	1	1

Time	Mean Cs	Low Cs	High Cs	Median Cs	Sampling depth pesticide concentration in soil									
06/10/2013 00:00	2.828515	2.82816	2.828896	2.828494	2.828921	2.828192	2.828223	2.828406	2.828316	2.828661	2.828579	2.828551	2.828871	2.828522
06/11/2013 00:00	2.52559	2.524594	2.526661	2.52553	2.526732									
06/12/2013 00:00	2.258494	2.256695	2.260427	2.258387	2.260553									
06/13/2013 00:00	1.691153	1.689164	1.693289	1.691034	1.693429									
06/14/2013 00:00	1.299246	1.297336	1.301296	1.299133	1.30143									
06/15/2013 00:00	1.244502	1.242741	1.246384	1.244401	1.246506									
06/16/2013 00:00	1.11725	1.115758	1.118834	1.117167	1.118936									
06/17/2013 00:00	1.060855	1.059476	1.06231	1.060781	1.062404									
06/18/2013 00:00	1.033854	1.03267	1.035089	1.033795	1.035167									
06/19/2013 00:00	1.000713	0.999642	1.001823	1.000662	1.001892									
06/20/2013 00:00	0.961914	0.960669	0.963213	0.961852	0.963295									
06/21/2013 00:00	0.925114	0.923579	0.926728	0.925034	0.926831									

Fig. A. 10. Sheet “MC_Cs” for Monte Carlo simulation of pesticide concentration in soil

Appendix 3. VBA codes for SPEC model

```
‘---------------------------------------------------------------------------------------------------------------------------
' ****************************************************************************************
' ***                    SPEC Program V.02                                                   ***
' ***                        - Predicted Environmental Concentrations in Soil and runoff -   ***
' ***                       Version 2.00 (multiple soil layers and runoff module)            ***
' ***                                                                                        ***
' ***                       Version 1.00 designed by Dang Quoc Thuyet 10, September 2014     ***
' ***                       Version 2.00 developed by Lam Van Thinh, April 2018              ***
' ***                                                                                        ***
' ***                                                                                        ***
' ****************************************************************************************
Option Explicit
Sub SPEC_Program()
   Application.Calculation = xlCalculationManual
   Dim duration As Double
   Dim Sta_ts, Sim_op, RC As String
   Dim ws_i As Worksheet
   Dim StartTime, SecondsElapsed As Double
'
StartTime = Timer
   Set ws_i = Sheets("RUN")
   duration = ws_i.Range("_duration")
   Sta_ts = ws_i.Range("_Sta_ts")
   Sim_op = ws_i.Range("_sim_op").Text
```

```
   RC = ws_i.Range("_RO_op")
      '
      Call Main_code
      Call Label

     Sheets("O_event").Cells.ClearContents
      '
      If duration = 1 And RC = "On" Then
         Call Event_Lookup
      End If
         Call SPEC_chart
         MsgBox "The SPEC code ran successfully module " & Sim_op & " in " & SecondsElapsed & "
seconds", vbInformation
      '
      If Sta_ts = "Daily" Then
         Call Statistics_D
      Else
         Call Statistics_sts
      End If
   '
   Application.Calculation = xlCalculationAutomatic
End Sub
‘-----------------------------------------------------------------------------------------------------------------------------
```

Appendix 4. Main code module

```
‘-----------------------------------------------------------------------------------------------------------------------------
' ****************************************************************************************
' ***                    SPEC V.02 - Main codes                                                ***
' ***                         - Predicted Environmental Concentrations in Soil and runoff -      ***
' ***                        Version 2.00 (multiple soil layers and runoff module)               ***
' ***                                                                                            ***
' ***                        Version 1.00 designed by Dang Quoc Thuyet 10, September 2014        ***
' ***                        Version 2.00 developed by Lam Van Thinh, April 2018                 ***
' ***                                                                                            ***
' ***                                                                                            ***
' ****************************************************************************************
Option Explicit
Sub Main_code()
'*** Modification Log ***
Application.ScreenUpdating = False
Application.DisplayAlerts = False
Application.EnableEvents = False
Application.Calculation = xlCalculationManual
'
' I. VARIABLES DECLARATION
'*** General input parameters and options ***
      Dim ws_sts, ws_h, ws_d, ws_i, ws_o, ws_od, ws_rp, ws_gr, ws_obs As Worksheet
      Dim s_date, e_date, PD1, PD2, PD3 As Date
      Dim Const_CN, Same_op As String
      Dim OPtsText, RFtsText, Tempts, Ets, SRts As String
      Dim ts, OPts, RFts, Es_op, n_GA As Integer
      Dim PestType, RC, RO_method As String
```

```
        Dim T_ts, T_ts_D, i, j, jj, duration, fr_rp As Double
        Dim StartTime, SecondsElapsed As Double
        Dim lastrow_o, lastrow_od, lastrow_sts, lastrow_h, lastrow_d  As Double
        Dim A, slp, CN1, CN3, Smax, S3, w1, w2 As Single
        Dim RF_const, ET_const, SR_const, T1, T2, esco As Single
        Dim CN2_0, S0, lambda, T_travel As Single
        Dim Q10, spd As Single
        Dim HLpho, Energ, HLbio, Kbio_ref, kv As Single
        Dim n As Double
        Dim Cs_op As Single
'
'*** Input Variables ***
        Dim PR1, PR2, PR3, PM1, PM2, PM3 As Double
        Dim Kpho As Double
        Dim L() As Double
        Dim Rb() As Double
        Dim WCf() As Double
        Dim WCs() As Double
        Dim WCr() As Double
        Dim Ks() As Double
        Dim WC0() As Double
        Dim ms() As Double
        Dim mc() As Double
        Dim Oc() As Double
        Dim Koc() As Double
        Dim Kd() As Double
        Dim z() As Double
        '
        Dim RF_t() As Double
        Dim RF_H() As Double
        Dim RF_D() As Double
        Dim RF() As Double
        Dim ET() As Double
        Dim ETj() As Double
        Dim SR() As Double
        Dim SRj() As Double
        Dim Kphoj() As Double
        Dim T() As Double
        Dim Time() As Date
        Dim TimeD() As Date
'
' II. INPUT DATA READING
'
StartTime = Timer
' II.1. Worksheets and lastrow assigned
'Call CreateSheets
        Set ws_sts = Worksheets("Small_TS")
        Set ws_h = Worksheets("Hourly")
        Set ws_d = Worksheets("Daily")
        Set ws_i = Worksheets("RUN")
        Set ws_o = Worksheets("Output")
        Set ws_od = Worksheets("Output_D")
        Set ws_rp = Worksheets("Report")
```

```
        Set ws_gr = Worksheets("Graph")
        Set ws_obs = Worksheets("Obs_Data")
        ' Last rows
        lastrow_sts = ws_sts.Cells(Rows.Count, 1).End(xlUp).Row
        lastrow_h = ws_h.Cells(Rows.Count, 1).End(xlUp).Row
        lastrow_d = ws_d.Cells(Rows.Count, 1).End(xlUp).Row
        lastrow_o = ws_o.Cells(Rows.Count, 1).End(xlUp).Row
        lastrow_od = ws_od.Cells(Rows.Count, 1).End(xlUp).Row
'
' II.2. Clear output sheets ***
        ws_o.Cells.Clear
        ws_o.Cells.Borders.LineStyle = xlLineStyleNone
        ws_od.Cells.Clear
        ws_od.Cells.Borders.LineStyle = xlLineStyleNone
'
' II.3. Read inputs
        ' Es selection, Enter 1 for Es1 and 2 for Es2
        Es_op = 1
        ' No of loops in Green-Ampt method
        n_GA = 30
        '
        'Soil evaporation coefficient varying with soil depth, default is equal to 1
        esco = ws_i.Range("_esco")
        PestType = ws_i.Range("_PestType")
        s_date = ws_i.Range("_s_date")
        e_date = ws_i.Range("_e_date")
        spd = ws_i.Range("_spd")
        duration = e_date - s_date
        OPtsText = ws_i.Range("_OPts")
        Same_op = ws_i.Range("_samepro")
        A = ws_i.Range("_A")
        slp = ws_i.Range("_slp")
        ' Constant values
        RF_const = ws_i.Range("_RFconst")
        ET_const = ws_i.Range("_Econst")
        SR_const = ws_i.Range("_SRconst")
        T1 = ws_i.Range("_T1")
        T2 = ws_i.Range("_T2")
        Q10 = ws_i.Range("_Q10")
        HLpho = ws_i.Range("_HLpho")
        Energ = ws_i.Range("_energ")
        HLbio = ws_i.Range("_HLbio")
        CN2_0 = ws_i.Range("_CN2")
        lambda = ws_i.Range("_lambda")
        T_travel = ws_i.Range("_T_travel")
        Ets = ws_i.Range("_Ets")
        RFtsText = ws_i.Range("_RFts")
        SRts = ws_i.Range("_SRts")
        Tempts = ws_i.Range("_Tempts")
        RC = ws_i.Range("_RO_op")
        RO_method = ws_i.Range("_RO_method")
        Const_CN = ws_i.Range("_CN_op")
        PD1 = ws_i.Range("_PD1")
```

```
    PD2 = ws_i.Range("_PD2")
    PD3 = ws_i.Range("_PD3")
    PR1 = ws_i.Range("_PR1")
    PR2 = ws_i.Range("_PR2")
    PR3 = ws_i.Range("_PR3")
    Cs_op = ws_i.Range("_Cs_op")    ' option for output of pst conc in soil
'
' II.4. Selection of simulation time step based on output time step
    If OPtsText = "1-minute" Then              '1
        OPts = 1
        ts = 1
      ElseIf OPtsText = "2-minute" Then
        OPts = 2
        ts = 2
      ElseIf OPtsText = "5-minute" Then
        OPts = 5
        ts = 5
      ElseIf OPtsText = "10-minute" Then
        OPts = 10
        ts = 10
      ElseIf OPtsText = "30-minute" Then
        OPts = 30
        ts = 30
      ElseIf OPtsText = "Hourly" Then
        OPts = 60
        ts = 60
      ElseIf OPtsText = "Daily" Then
        OPts = 60
        ts = 60
    End If        '1
' Assigned value for rainfall time step when it is smaller than 60 minutes
    If RFtsText = "1-minute" Then              '1
        RFts = 1
      ElseIf RFtsText = "2-minute" Then
        RFts = 2
      ElseIf RFtsText = "5-minute" Then
        RFts = 5
      ElseIf RFtsText = "10-minute" Then
        RFts = 10
      ElseIf RFtsText = "30-minute" Then
        RFts = 30
      ElseIf RFtsText = "Hourly" Then
        RFts = 60
      ElseIf RFtsText = "Daily" Then
        RFts = 24 * 60
      ElseIf RFtsText = "Not available" Then
        RFts = 24 * 60 + 1
    End If        '1
'
' III. INPUTS PROCESSING
' III.1 Process parameter inputs
'
  ' Number of soil layers
```

```
    n = ws_i.Range("_n")
'
    ReDim L(1 To n) As Double
    ReDim Rb(1 To n) As Double
    ReDim WCf(1 To n) As Double
    ReDim WCs(1 To n) As Double
    ReDim WCr(1 To n) As Double
    ReDim Ks(1 To n) As Double
    ReDim WC0(1 To n) As Double
    ReDim ms(1 To n) As Double
    ReDim mc(1 To n) As Double
    ReDim Oc(1 To n) As Double
    ReDim Koc(1 To n) As Double
    ReDim z(1 To n) As Double

    Dim rgn_l As Range
    Dim rgn_Rb As Range
    Dim rgn_WCf As Range
    Dim rgn_WCs As Range
    Dim rgn_WCr As Range
    Dim rgn_Ks As Range
    Dim rgn_WC0 As Range
    Dim rgn_ms As Range
    Dim rgn_mc As Range
    Dim rgn_Oc As Range
    Dim rgn_Koc As Range

    Set rgn_l = ws_i.Range("_rgn_l")
    Set rgn_Rb = ws_i.Range("_rgn_Rb")
    Set rgn_WCf = ws_i.Range("_rgn_WCf")
    Set rgn_WCs = ws_i.Range("_rgn_WCs")
    Set rgn_WCr = ws_i.Range("_rgn_WCr")
    Set rgn_Ks = ws_i.Range("_rgn_Ks")
    Set rgn_ms = ws_i.Range("_rgn_ms")
    Set rgn_mc = ws_i.Range("_rgn_mc")
    Set rgn_Oc = ws_i.Range("_rgn_Oc")
    Set rgn_Koc = ws_i.Range("_rgn_Koc")
    Set rgn_WC0 = ws_i.Range("_rgn_WC0")
    '
    For i = 1 To n
       If Same_op = "Yes" Then
          L(i) = rgn_l.Offset(0, 1)       ' depth of all layers is 10 mm
          Rb(i) = rgn_Rb.Offset(0, 1)
          WCf(i) = rgn_WCf.Offset(0, 1)
          WCs(i) = rgn_WCs.Offset(0, 1)
          WCr(i) = rgn_WCr.Offset(0, 1)
          Ks(i) = rgn_Ks.Offset(0, 1)
          WC0(i) = rgn_WC0.Offset(0, 1)
          ms(i) = rgn_ms.Offset(0, 1)
          mc(i) = rgn_mc.Offset(0, 1)
          Oc(i) = rgn_Oc.Offset(0, 1)
          Koc(i) = rgn_Koc.Offset(0, 1)
```

```
            Else
                L(i) = rgn_l.Offset(0, i)
                Rb(i) = rgn_Rb.Offset(0, i)
                WCf(i) = rgn_WCf.Offset(0, i)
                WCs(i) = rgn_WCs.Offset(0, i)
                WCr(i) = rgn_WCr.Offset(0, i)
                Ks(i) = rgn_Ks.Offset(0, i)
                WC0(i) = rgn_WC0.Offset(0, i)
                ms(i) = rgn_ms.Offset(0, i)
                mc(i) = rgn_mc.Offset(0, i)
                Oc(i) = rgn_Oc.Offset(0, i)
                Koc(i) = rgn_Koc.Offset(0, i)
            End If
        Next i
'
' III.2 Process variable inputs
'
    ' Total simulation time steps in whole duration
        T_ts = duration * 24 * (60 / ts)
    '
    ' Number of simulation time steps in a day
        T_ts_D = 24 * 60 / ts
'
' III.2.1 Process 2 types of Times
        ' Daily Time
            ReDim TimeD(1 To duration, 1 To 1) As Date
        For j = 1 To duration
            TimeD(j, 1) = s_date + (j - 1)
        Next j

        ' Small time step Time
            ReDim Time(1 To T_ts, 1 To 1) As Date
        For j = 1 To T_ts
            Time(j, 1) = s_date + (j - 1) / T_ts_D
        Next j

        ' Month of Time
            Dim Mon() As Double
            ReDim Mon(1 To T_ts, 1 To 1) As Double
        For j = 1 To T_ts
            Mon(j, 1) = Month(Time(j, 1))
        Next j
'
' III.2.2 Process 3 types of rainfall time step
        Dim rgn_RF_sts As Range
        Dim rgn_RF_H As Range
        Dim rgn_RF_D As Range

        Set rgn_RF_sts = ws_sts.Range("B2")
        Set rgn_RF_H = ws_h.Range("B2")
        Set rgn_RF_D = ws_d.Range("B2")

        ReDim dRF(1 To T_ts, 1 To 1) As Double
```

```
    Dim ratio1, ratio2 As Double

    If RFts < 60 Then
       ' Small time step rainfall input
       If RFts = OPts Then
          For j = 1 To T_ts
             dRF(j, 1) = rgn_RF_sts.Offset(j, 0)
          Next j

       ElseIf RFts < OPts Then
          ratio1 = OPts / RFts
             If ratio1 <> Int(ratio1) Then  ' Check if OP-RF time step ratio is integer or not
                MsgBox "Ratio between Output and RF time steps is not integer! Please enter another Output
time step!"
                Exit Sub

             Else
                For j = 1 To T_ts
                   ReDim RF_t(1 To T_ts, 1 To ratio1) As Double

                   For jj = 1 To ratio1
                      RF_t(j, jj) = rgn_RF_sts.Offset((j - 1) * (ratio1) + jj, 0)
                   Next jj

                      Dim RF_t_cum() As Double
                      ReDim RF_t_cum(1 To T_ts, 1 To ratio1) As Double
                         RF_t_cum(j, 1) = RF_t(j, 1)
                   For jj = 2 To ratio1
                      RF_t_cum(j, jj) = RF_t_cum(j, jj - 1) + RF_t(j, jj)
                   Next jj
                      dRF(j, 1) = RF_t_cum(j, ratio1)
                Next j
             End If  ' check ratio1

       Else    ' RFTs > Opts
          ratio2 = RFts / OPts
             If ratio2 <> Int(ratio2) Then  ' Check if OP-RF time step ratio is integer or not
                MsgBox "Ratio between RF and Output time steps is not integer! Please enter another Output
time step!"
                Exit Sub

             Else
                   ReDim RF_t(1 To T_ts / ratio2, 1 To 1) As Double
                For j = 1 To T_ts / ratio2
                   RF_t(j, 1) = rgn_RF_sts.Offset(j, 0)

                   For jj = 1 To ratio2
                      dRF((j - 1) * (ratio2) + jj, 1) = RF_t(j, 1) / ratio2
                   Next jj
                Next j
             End If  ' check ratio2
       End If  ' End of small time step RF input
```

```
        ElseIf RFts = 60 Then   ' Hourly RF Input
          ' Hourly rainfall input
                ReDim RF_H(1 To duration * 24, 1 To 1) As Double
            For j = 1 To duration * 24
                RF_H(j, 1) = rgn_RF_H.Offset(j, 0)  ' Read hourly Rainfall

                    For jj = 1 To 60 / ts
                        ' Process time step RF
                        dRF((j - 1) * 60 / ts + jj, 1) = RF_H(j, 1) * ts / 60
                    Next jj
            Next j

        ElseIf RFts = 24 * 60 Then  ' Daily RF Input
                ReDim RF_D(1 To duration, 1 To 1) As Double

            For j = 1 To duration
                RF_D(j, 1) = rgn_RF_D.Offset(j, 0)  ' Read daily Rainfall

                    For jj = 1 To T_ts_D
                        ' Process time step RF
                        dRF((j - 1) * T_ts_D + jj, 1) = RF_D(j, 1) / T_ts_D
                    Next jj
            Next j

        Else ' Constant RF Input
            For j = 1 To T_ts
                dRF(j, 1) = RF_const / T_ts_D
            Next j
        End If
'
' III.2.3 Process evaporation
'
        '
        ' Lower depth of every layer, in mm
          z(1) = L(1)
        For i = 2 To n
          z(i) = z(i - 1) + L(i)
        Next i
          Dim rgn_ET_D As Range
          Set rgn_ET_D = ws_d.Range("H2")
          ReDim ET(1 To duration, 1 To 1) As Double
          ReDim ETj(1 To T_ts, 1 To 1) As Double
        For j = 1 To duration
          If Ets = "Daily" Then
                ET(j, 1) = rgn_ET_D.Offset(j, 0).Value
            If IsError(ET) = True Then
                MsgBox "Daily Evaporation dataset is not available!"
                Exit Sub
            End If

          Else
            ET(j, 1) = ET_const
          End If
```

```
         For jj = 1 To T_ts_D
            ETj((j - 1) * T_ts_D + jj, 1) = ET(j, 1) / T_ts_D
         Next jj
      Next j
      '
      ' Ez
         Dim Ez() As Double
         ReDim Ez(1 To T_ts, 1 To n) As Double
      For j = 1 To T_ts
         For i = 1 To n
            Ez(j, i) = Max2(ETj(j, 1) * z(i) / (z(i) + Exp(2.374 - 0.00713 * z(i))), 0)
         Next i
      Next j
      '
      ' Es
         Dim Es() As Double
         ReDim Es(1 To T_ts, 1 To n) As Double
      For j = 1 To T_ts
            Es(j, 1) = Max2(Ez(j, 1), 0)
         For i = 2 To n
            Es(j, i) = Max2(Ez(j, i) - Ez(j, i - 1) * esco, 0)
         Next i
      Next j
'
' III.2.4 Process event 30-minute rainfall intensity (mm/h) and runoff coefficient (same values for same day)
'

         Dim rgn_I30, rgn_C As Range
         Set rgn_I30 = ws_d.Cells(2, 14)
         Set rgn_C = ws_d.Cells(2, 15)

         ' Daily 30-minute rainfall intensity and runoff coefficient
            Dim I30() As Double
            ReDim I30(1 To duration, 1 To 1) As Double
            Dim C() As Double
            ReDim C(1 To duration, 1 To 1) As Double

         ' time step 30-minute rainfall intensity and runoff coefficient
            Dim I30j() As Double
            ReDim I30j(1 To T_ts, 1 To 1) As Double
            Dim Cj() As Double
            ReDim Cj(1 To T_ts, 1 To 1) As Double
            Dim I30_const, C_const As Single
               I30_const = ws_i.Range("_I30_const")
               C_const = ws_i.Range("_C_const")
         '
         ' 30-minute rainfall intensity
         For j = 1 To duration
            If IsEmpty(I30_const) Or I30_const = 0 Then
                  I30(j, 1) = rgn_I30.Offset(j, 0).Value
               If IsError(I30) = True Then
                  MsgBox "Daily 30-minute rainfall intensity dataset is not available!"
                  Exit Sub
```

```
                    End If

                Else
                        I30(j, 1) = I30_const
                End If

                For jj = 1 To T_ts_D
                    I30j((j - 1) * T_ts_D + jj, 1) = I30(j, 1)
                Next jj
            Next j
            '
            ' Runoff coefficient
            For j = 1 To duration
                If IsEmpty(C_const) Or C_const = 0 Then
                        C(j, 1) = rgn_C.Offset(j, 0).Value
                    If IsError(C) = True Then
                        MsgBox "Daily 30-minute runoff coefficient dataset is not available!"
                        Exit Sub
                    End If

                Else
                    C(j, 1) = C_const
                End If

                For jj = 1 To T_ts_D
                    Cj((j - 1) * T_ts_D + jj, 1) = C(j, 1)
                Next jj
            Next j
'
' III.2.5 Parameters of Modified Universial Sediment Loss Equation (MUSLE) (William, 1995)
'
        ' Max discharge rate, q_peak (m3/s)
                Dim q_peakj() As Double
                ReDim q_peakj(1 To T_ts, 1 To 1) As Double
            For j = 1 To T_ts
                q_peakj(j, 1) = Cj(j, 1) * I30j(j, 1) * A * 10 ^ -5 / 36
            Next j
        '
        ' Calculate Soil erodibility factor. K_USLE ((Metric ton.m2.hr)/(m3.Metric ton.cm))
                ' Percent silk, msilk
                Dim ms1, mc1, m_si, OC1 As Single
                ms1 = rgn_ms.Offset(0, 1)
                mc1 = rgn_mc.Offset(0, 1)
                OC1 = rgn_Oc.Offset(0, 1)

                m_si = 100 - ms1 - mc1
                '
                Dim f_csand, f_cl_si, f_orgC, f_hisand, K_USLE As Double

                f_csand = 0.2 + 0.3 * Exp(-0.0256 * ms1 * (1 - m_si / 100))
                f_cl_si = (m_si / (mc1 + m_si)) ^ 0.3
                f_orgC = 1 - (0.25 * OC1 / (OC1 + Exp(3.72 - 2.95 * OC1)))
                f_hisand = 1 - (0.7 * (1 - ms1 / 100) / ((1 - ms1 / 100) + Exp(-5.51 + 22.9 * (1 - ms1 / 100))))
```

```
        '
        ' K formula (Sharpley & Williams, 1990) (used in EPIC model)
          Dim SN1, K_coef As Single
              K_coef = Range("_K_coef")   ' Adjust value of K, used to calibrate K

        ' K_USLE
          K_USLE = K_coef * f_csand * f_cl_si * f_orgC * f_hisand
        '
        ' Calculate Topographic factor, LS_USLE
        Dim Lplot As Single
        Dim Theta, Lslp, m_USLE, LS_USLE As Double

          Lplot = ws_i.Range("_Lplot")
          Theta = Atn(slp / 100)
          Lslp = Lplot / Cos(Theta)
          m_USLE = 0.6 * (1 - Exp(-35.835 * slp / 100))

        LS_USLE = (Lslp / 22.1) ^ m_USLE * (65.41 * Sin(Theta) ^ 2 + 4.56 * Sin(Theta) + 0.065)

        ' Cover and management factor
        Dim C_USLE As Double
          C_USLE = ws_i.Range("_C_USLE")
        ' Coarse fragment factor
        Dim CFRG As Double
          CFRG = ws_i.Range("_CFRG")
        ' Support practice factor
        Dim P_USLE As Double
          P_USLE = ws_i.Range("_P_USLE")
        Dim MUSLE_coef, MUSLE_exp As Double
        '
        ' Coefficient and Exponent of MUSLE
        ' Original values for MUSLE (William, 1995) were 11.8 and 0.56 respectively
        ' Coefficient of MUSLE
          MUSLE_coef = ws_i.Range("_MUSLE_coef")
        ' Exponent of MUSLE
          MUSLE_exp = ws_i.Range("_MUSLE_exp")
        ' Overall coefficient of MUSLE
        Dim SLE_coef As Double
          SLE_coef = MUSLE_coef * K_USLE * C_USLE * P_USLE * LS_USLE * CFRG
'
    Dim Sim_op As String
        Sim_op = ws_i.Range("_sim_op").Text

If Sim_op = "Runoff & Pesticide" Then
'
' III.2.6 Process temperature and biodegradation
'
          Dim rgn_T3_H As Range
          Dim rgn_T3_D As Range
          Set rgn_T3_H = ws_h.Range("E2")
          Set rgn_T3_D = ws_d.Range("E2")
          ' Time step value
```

```
        Kbio_ref = Log(2) / HLbio / T_ts_D
          ReDim Kbioj(1 To T_ts, 1 To 1) As Double

        If Tempts = "Not available" Then
              For j = 1 To T_ts
                Kbioj(j, 1) = Kbio_ref
              Next j

          ElseIf Tempts = "Two temp." Then
              For j = 1 To T_ts
                If Month(Time(j, 1)) >= 5 And Month(Time(j, 1)) <= 9 Then
                  Kbioj(j, 1) = Kbio_ref * Q10 ^ ((T1 - 25) / 10)
                Else
                  Kbioj(j, 1) = Kbio_ref * Q10 ^ ((T2 - 25) / 10)
                End If
              Next j

          ElseIf Tempts = "Hourly" Then
                ReDim T(1 To duration * 24, 1 To 1) As Double
              For j = 1 To duration * 24
                  T(j, 1) = rgn_T3_H.Offset(j, 0)
                  For jj = 1 To 60 / ts
                    Kbioj((j - 1) * 60 / ts + jj, 1) = Kbio_ref * Q10 ^ ((T(j, 1) - 25) / 10) * ts / 60
                  Next jj
              Next j

          ElseIf Tempts = "Daily (air)" Then
                ReDim T(1 To duration, 1 To 1) As Double
              For j = 1 To duration
                  T(j, 1) = 0.996 * rgn_T3_D.Offset(j, 0)
                  For jj = 1 To T_ts_D
                    Kbioj((j - 1) * T_ts_D + jj, 1) = Kbio_ref * Q10 ^ ((T(j, 1) - 25) / 10) / T_ts_D
                  Next jj
              Next j

          ElseIf Tempts = "Daily" Then
                ReDim T(1 To duration, 1 To 1) As Double
              For j = 1 To duration
                  T(j, 1) = rgn_T3_D.Offset(j, 0)
                  For jj = 1 To T_ts_D
                    Kbioj((j - 1) * T_ts_D + jj, 1) = Kbio_ref * Q10 ^ ((T(j, 1) - 25) / 10) / T_ts_D
                  Next jj
              Next j
        End If
'
' III.2.7 Process Kd, in L/kg
'
          ReDim Kd(1 To n) As Double
        For i = 1 To n
          Kd(i) = Koc(i) * Oc(i) / 100
        Next i
'
' III.2.8 Process solar radiation and photodegradation
```

```
'
            Dim rgn_SR_D As Range
            Set rgn_SR_D = ws_d.Range("K2")
            ' Daily solar radiation
               ReDim SR(1 To duration, 1 To 1) As Double
            ' time step solar radiation
               ReDim SRj(1 To T_ts, 1 To 1) As Double
            For j = 1 To duration
               If SRts = "Daily" Then
                     SR(j, 1) = rgn_SR_D.Offset(j, 0).Value
                     If IsError(SR) = True Then
                        MsgBox "Daily solar radiation dataset is not available!"
                        Exit Sub
                     End If

               Else
                     SR(j, 1) = SR_const
               End If

               For jj = 1 To T_ts_D
                  SRj((j - 1) * T_ts_D + jj, 1) = SR(j, 1) / (T_ts_D)
               Next jj
            Next j

            If HLpho = 0 Then
                  Kpho = 0
            Else
               ' The first-order rate coefficient of photodegradation (in m2/kJ)
                  Kpho = Log(2) / (HLpho * 0.001232 * (Energ * 1000)) ' fUS = 0.001232
               ' The coefficient of photodegradation in every time step (1/ts)
                  ReDim Kphoj(1 To T_ts, 1 To 1) As Double
               For j = 1 To T_ts
                  Kphoj(j, 1) = Kpho * 0.001232 * 1000 * SRj(j, 1)
               Next j
            End If
End If  ' of simulation option
'
' IV. SIMULATION OF WATER
'
      ' Initial CN2_0
         CN1 = CN2_0 - (20 * (100 - CN2_0)) / (100 - CN2_0 + Exp(2.533 - 0.0636 * (100 - CN2_0)))
         CN3 = CN2_0 * Exp(0.00673 * (100 - CN2_0))

         If slp <> 5 Then
            CN2_0 = (CN3 - CN2_0) / 3 * (1 - 2 * Exp(-13.86 * slp / 100)) + CN2_0
            CN1 = CN2_0 - (20 * (100 - CN2_0)) / (100 - CN2_0 + Exp(2.533 - 0.0636 * (100 - CN2_0)))
            CN3 = CN2_0 * Exp(0.00673 * (100 - CN2_0))
         End If
            Smax = 25.4 * (1000 / CN1 - 10)
            S3 = 25.4 * (1000 / CN3 - 10)

         Dim l_acc() As Double
         ReDim l_acc(1 To n) As Double
```

```
Dim WC0_mm() As Double
Dim WC0_acc_mm() As Double

ReDim WC0_mm(1 To n) As Double
ReDim WC0_acc_mm(1 To n) As Double

ReDim WCs_mm(1 To n) As Double
ReDim WCs_acc_mm(1 To n) As Double

ReDim WCf_mm(1 To n) As Double
ReDim WCf_acc_mm(1 To n) As Double

ReDim WCr_mm(1 To n) As Double
ReDim WCr_acc_mm(1 To n) As Double

Dim msl() As Double
ReDim msl(1 To n) As Double

Dim mcl() As Double
ReDim mcl(1 To n) As Double

Dim msl_acc() As Double
ReDim msl_acc(1 To n) As Double

Dim mcl_acc() As Double
ReDim mcl_acc(1 To n) As Double

Dim Ksl() As Double
ReDim Ksl(1 To n) As Double

Dim Ksl_acc() As Double
ReDim Ksl_acc(1 To n) As Double
'
' Calculate average values for soil properties
For i = 1 To n
   WC0_mm(i) = WC0(i) * L(i)
   WCs_mm(i) = WCs(i) * L(i)
   WCf_mm(i) = WCf(i) * L(i)
   WCr_mm(i) = WCr(i) * L(i)
   msl(i) = ms(i) * L(i)
   mcl(i) = mc(i) * L(i)
   Ksl(i) = Ks(i) * L(i)

Next i

   l_acc(1) = L(1)
   WC0_acc_mm(1) = WC0_mm(1)
   WCs_acc_mm(1) = WCs_mm(1)
   WCf_acc_mm(1) = WCf_mm(1)
   WCr_acc_mm(1) = WCr_mm(1)
   msl_acc(1) = msl(1)
   mcl_acc(1) = mcl(1)
```

```
           Ksl_acc(1) = Ksl(1)

        For i = 2 To n
           l_acc(i) = l_acc(i - 1) + L(i)
           WC0_acc_mm(i) = WC0_acc_mm(i - 1) + WC0_mm(i)
           WCs_acc_mm(i) = WCs_acc_mm(i - 1) + WCs_mm(i)
           WCf_acc_mm(i) = WCf_acc_mm(i - 1) + WCf_mm(i)
           WCr_acc_mm(i) = WCr_acc_mm(i - 1) + WCr_mm(i)
           msl_acc(i) = msl_acc(i - 1) + msl(i)
           mcl_acc(i) = mcl_acc(i - 1) + mcl(i)
           Ksl_acc(i) = Ksl_acc(i - 1) + Ksl(i)

        Next i
        '
        ' Average mass percents of sand and clay
           Dim ms_a, mc_a, por, WCf_a, WCr_a, Ks_a  As Double
           ms_a = msl_acc(n) / l_acc(n)    ' in %
           mc_a = mcl_acc(n) / l_acc(n)    ' in %
        '
        ' Average porosity (staurated WC), field capacity and residual water contents, saturated hydraulic
conductivity
           WCf_a = WCf_acc_mm(n) / l_acc(n)     ' mm3/mm3
           WCr_a = WCr_acc_mm(n) / l_acc(n)   ' mm3/mm3
           Ks_a = Ksl_acc(n) / l_acc(n)    ' in mm/ts
           por = WCs_acc_mm(n) / l_acc(n)     ' mm3/mm3 ' porosity = saturated WC
        '
        ' First time step avergaed water content
           Dim WC_a() As Double
           ReDim WC_a(1 To T_ts, 1 To 1) As Double
              WC_a(1, 1) = WC0_acc_mm(n) / l_acc(n)
        '
        ' Matric Potential, MP, across the wetting front (in mm) (Rawls and Brakensiek, 1985) for Green-
Ampt method
           Dim MP As Double
              MP = 10 * Exp((6.5309 - 7.32561 * por + 0.001583 * mc_a ^ 2 + 3.809479 * por ^ 2 _
              + 0.000344 * ms_a * mc_a - 0.049837 * ms_a * por + 0.001608 * ms_a ^ 2 * por ^ 2 _
              + 0.001602 * mc_a ^ 2 * por ^ 2 - 0.0000136 * ms_a ^ 2 * mc_a - 0.003479 * mc_a ^ 2 * por -
0.000799 * ms_a ^ 2 * por))
       '
       ' Initial retention S0
           w2 = (Log((WCf_acc_mm(n)) / (1 - S3 / Smax) - WCf_acc_mm(n)) - (Log((WCs_acc_mm(n)) / _
           (1 - 2.54 / Smax) - WCs_acc_mm(n)))) / (WCs_acc_mm(n) - WCf_acc_mm(n))

           w1 = (Log(WCf_acc_mm(n) / (1 - S3 / Smax) - WCf_acc_mm(n))) + w2 * WCf_acc_mm(n)
           S0 = 254 * (100 / CN2_0 - 1)
     '
     ' Accumulated runoff
        ReDim RF(1 To T_ts, 1 To 1) As Double
        Dim WC() As Double
        Dim WC_acc_mm() As Double
        Dim WCc() As Double
        Dim S() As Double
        Dim Ia() As Double
```

```
    Dim CN2() As Double
    Dim xx() As Double
    Dim Q() As Double
    Dim dQ() As Double
    Dim Inf() As Double
    Dim dInf() As Double

    ReDim WC(1 To T_ts + 1, 1 To n) As Double
    ReDim WC_acc_mm(1 To T_ts, 1 To n) As Double
    ReDim WCc(1 To T_ts, 1 To n) As Double
    ReDim S(1 To T_ts, 1 To 1) As Double
    ReDim Ia(1 To T_ts, 1 To 1) As Double
    ReDim CN2(1 To T_ts, 1 To 1) As Double
    ReDim xx(1 To T_ts, 1 To 1) As Double
    ReDim Q(1 To T_ts, 1 To 1) As Double
    ReDim dQ(1 To T_ts, 1 To 1) As Double
    ReDim Inf(1 To T_ts, 1 To 1) As Double
    ReDim dInf(1 To T_ts, 1 To 1) As Double
'
' Initial conditions
    RF(1, 1) = dRF(1, 1)
    S(1, 1) = S0
    Ia(1, 1) = lambda * S0
    CN2(1, 1) = CN2_0
'
' Initial runoff, infiltration in mm
If RC = "On" Then
        If RO_method = "NRCS-CN" Then
            If RF(1, 1) > Ia(1, 1) Then
                Q(1, 1) = (RF(1, 1) - Ia(1, 1)) ^ 2 / (RF(1, 1) - Ia(1, 1) + S(1, 1))
                dQ(1, 1) = Q(1, 1)
                Inf(1, 1) = RF(1, 1) - Q(1, 1)
                dInf(1, 1) = Inf(1, 1)
            Else
                Q(1, 1) = 0
                dQ(1, 1) = 0
                Inf(1, 1) = RF(1, 1)
                dInf(1, 1) = dRF(1, 1)
            End If

        Else    ' Green-Ampt method
            Dim DelWC() As Double
            ReDim DelWC(1 To T_ts, 1 To 1) As Double
            Dim Ke() As Double
            ReDim Ke(1 To T_ts, 1 To 1) As Double
            Dim Facc() As Double
            ReDim Facc(1 To T_ts, 1 To 50) As Double
            Dim dInfC() As Double
            ReDim dInfC(1 To T_ts, 1 To 1) As Double
            Dim InfC() As Double
            ReDim InfC(1 To T_ts, 1 To 1) As Double
            '
            'DelWC (Ven Te Chow, 1988)
```

```
            DelWC(1, 1) = (por - WC_a(1, 1))
         '
         ' Effective hydraulic conductivity, Ke (Ven Te Chow, 1988)
            Ke(1, 1) = 0.5 * Ks_a * ts / 60
         '
         ' Fist trial value of cumulative infiltration capacity
               Facc(1, 1) = 0
         '
         ' Next loop (to find final loop cumulative infiltration capacity)
            For jj = 2 To n_GA
               If dRF(1, 1) <> 0 Then
                  ' Neitsch et al., 2011
                  Facc(1, jj) = Ke(1, 1) + MP * DelWC(1, 1) * Log((Facc(1, jj - 1) + _
                           MP * DelWC(1, 1)) / (MP * DelWC(1, 1)))
               Else
                  Facc(1, jj) = 0
               End If
            Next jj
         '
         ' Write final trial value of cumulative infiltration capacity (in mm)
               InfC(1, 1) = Facc(1, n_GA)
         ' Infiltration rate capacity for 1st timnestep
         'dInfC(1, 1) = InfC(1, 1)
            If InfC(1, 1) = 0 Then
               dInfC(1, 1) = 0
            Else
               dInfC(1, 1) = Ke(1, 1) * (1 + (MP * DelWC(1, 1)) / InfC(1, 1))
            End If
            '
            If dInfC(1, 1) > dRF(1, 1) Then
               dInf(1, 1) = dRF(1, 1)
               dQ(1, 1) = 0
            Else
               dInf(1, 1) = dInfC(1, 1)
               dQ(1, 1) = dRF(1, 1) - dInf(1, 1)
            End If
               Inf(1, 1) = dInf(1, 1)
               Q(1, 1) = dQ(1, 1)
      End If

Else
   Q(1, 1) = 0
   dQ(1, 1) = 0
   Inf(1, 1) = RF(1, 1)
   dInf(1, 1) = dRF(1, 1)
End If
'
' First time step Es1 & Es2
   Dim WCu() As Double
   ReDim WCu(1 To T_ts, 1 To n) As Double
   Dim Es1() As Double
   ReDim Es1(1 To T_ts, 1 To n) As Double
   Dim Es2() As Double
```

```
    ReDim Es2(1 To T_ts, 1 To n) As Double
    Dim WCX() As Double
    Dim Per() As Double
    ReDim WCX(1 To T_ts, 1 To n) As Double
    ReDim Per(1 To T_ts, 1 To n) As Double
'
' Initial water content and Es
    WC(1, 1) = WC0(1)
        If WC(1, 1) < WCf(1) Then
            Es1(1, 1) = Max2(Es(1, 1) * Exp(2.5 * (WC(1, 1) - WCf(1)) / (WCf(1) - WCr(1))), 0)
        Else
            Es1(1, 1) = Max2(Es(1, 1), 0)
        End If

    Es2(1, 1) = Max2(Min2(Es1(1, 1), 0.8 * (WC(1, 1) - WCr(1)) * L(1)), 0)
'
' First time step updated WC
' in Layer 1
    If Es_op = 1 Then
        WCc(1, 1) = WC(1, 1) + (dInf(1, 1) - Es1(1, 1)) / L(1)
    Else
        WCc(1, 1) = WC(1, 1) + (dInf(1, 1) - Es2(1, 1)) / L(1)
    End If
    '
    If WCc(1, 1) <= WCr(1) Then
        WCu(1, 1) = WCr(1)
        Es1(1, 1) = 0
        Es2(1, 1) = 0
        Per(1, 1) = 0

    ElseIf WCc(1, 1) <= WCf(1) Then
        WCu(1, 1) = WCc(1, 1)
        Per(1, 1) = 0

    ElseIf WCc(1, 1) <= WCs(1) Then
        WCu(1, 1) = WCc(1, 1) - (1 / (T_travel * 60 / ts)) * (WCc(1, 1) - WCf(1))
        WCX(1, 1) = (WCc(1, 1) - WCu(1, 1)) * L(1)
        Per(1, 1) = WCX(1, 1) * (1 - Exp(-(ts / 60) * Ks(1) / ((WCs(1) - WCf(1)) * L(1))))

    Else
        WCu(1, 1) = WCs(1) - (1 / (T_travel * 60 / ts)) * (WCs(1) - WCf(1))
        WCX(1, 1) = (WCc(1, 1) - WCu(1, 1)) * L(1)
        Per(1, 1) = WCX(1, 1) * (1 - Exp(-(ts / 60) * Ks(1) / ((WCs(1) - WCf(1)) * L(1))))

    End If
        WC(2, 1) = WCu(1, 1)
        WC_acc_mm(1, 1) = WCu(1, 1) * L(1)
'
' in layers 2 to n
    For i = 2 To n
            WC(1, i) = WC0(i)
        If WC(1, i) < WCf(i) Then
            Es1(1, i) = Max2(Es(1, i) * Exp(2.5 * (WC(1, i) - WCf(i)) / (WCf(i) - WCr(i))), 0)
```

```
            Else
               Es1(1, i) = Max2(Es(1, i), 0)
            End If
                  Es2(1, i) = Max2(Min2(Es1(1, i), 0.8 * (WC(1, i) - WCf(i)) * L(i)), 0)
            '
            If Es_op = 1 Then
               WCc(1, i) = WC(1, i) + (Per(1, i - 1) - Es1(1, i)) / L(i)
            Else
               WCc(1, i) = WC(1, i) + (Per(1, i - 1) - Es2(1, i)) / L(i)
            End If
            '
            If WCc(1, i) <= WCr(i) Then
               WCu(1, i) = WCr(i)
               Es1(1, i) = 0
               Es2(1, i) = 0
               Per(1, i) = 0

            ElseIf WCc(1, i) <= WCf(i) Then
               WCu(1, i) = WCc(1, i)
               Per(1, i) = 0

            ElseIf WCc(1, i) <= WCs(i) Then
               WCu(1, i) = WCc(1, i) - (1 / (T_travel * 60 / ts)) * (WCc(1, i) - WCf(i))
               WCX(1, i) = (WCc(1, i) - WCu(1, i)) * L(i)
               Per(1, i) = WCX(1, i) * (1 - Exp(-(ts / 60) * Ks(i) / ((WCs(i) - WCf(i)) * L(i))))

            Else
               WCu(1, i) = WCs(i) - (1 / (T_travel * 60 / ts)) * (WCs(i) - WCf(i))
               WCX(1, i) = (WCc(1, i) - WCu(1, i)) * L(i)
               Per(1, i) = WCX(1, i) * (1 - Exp(-(ts / 60) * Ks(i) / ((WCs(i) - WCf(i)) * L(i))))

            End If
               WC(2, i) = WCu(1, i)
               WC_acc_mm(1, i) = WC_acc_mm(1, i - 1) + WCu(1, i) * L(i)
         Next i
               WC_a(1, 1) = WC_acc_mm(1, n) / l_acc(n)
      '
      ' Next time steps
         '
         Dim d_eff As Integer
         d_eff = l_acc(n)   ' effective depth (in mm) for retention S calculation
         ' Initial cumulative rainfall
            RF(1, 1) = dRF(1, 1)
      For j = 2 To T_ts
         '
         ' Cumulative rainfalls
         If dRF(j - 1, 1) > 0 And dRF(j, 1) > 0 Then 'And XLMod(j, T_ts_D) <> 1      'reset at the fist time of
the day
            RF(j, 1) = RF(j - 1, 1) + dRF(j, 1)
         Else
            RF(j, 1) = dRF(j, 1)
         End If
         '
```

```
        ' Check CN constant
          If Const_CN = "Yes" Then
            S(j, 1) = S0
          Else
            xx(j - 1, 1) = w1 - w2 * (WC_a(j - 1, 1) - WCr_a) * d_eff
            S(j, 1) = Smax * (1 - ((WC_a(j - 1, 1) - WCr_a) * d_eff) / (((WC_a(j - 1, 1) - WCr_a) * d_eff) +
Exp(xx(j - 1, 1))))
              If S(j, 1) < S3 Then
                S(j, 1) = S3
              ElseIf S(j, 1) > Smax Then
                S(j, 1) = Smax
              End If

          End If
            Ia(j, 1) = lambda * S(j, 1)
        '
        ' Calculate CN2
            CN2(j, 1) = 25400 / (S(j, 1) + 254)
        '
        If RC = "On" Then
          If RO_method = "NRCS-CN" Then
            '
            If RF(j, 1) > Ia(j, 1) Then
                Q(j, 1) = (RF(j, 1) - Ia(j, 1)) ^ 2 / (RF(j, 1) - Ia(j, 1) + S(j, 1))
              '
              If Q(j, 1) < Q(j - 1, 1) Then 'If XLMod(j, T_ts_D) = 1 Then
                dQ(j, 1) = 0
              Else
                dQ(j, 1) = Q(j, 1) - Q(j - 1, 1)
              End If
                Inf(j, 1) = RF(j, 1) - Q(j, 1)
                  '
                  If Inf(j, 1) > Inf(j - 1, 1) Then
                              dInf(j, 1) = Inf(j, 1) - Inf(j - 1, 1)
                  Else
                              dInf(j, 1) = Inf(j, 1)
                  End If
                  '
            Else
                    Q(j, 1) = 0
                    dQ(j, 1) = 0
                    Inf(j, 1) = RF(j, 1)
                    dInf(j, 1) = dRF(j, 1)
            End If
            '
          Else    ' Green-Ampt method,
            DelWC(j, 1) = (por - WC_a(j - 1, 1))
            '
            ' Effective hydraulic conductivity, Ke (mm/ts) (Ven Te Chow, 1988)
              Ke(j, 1) = 0.5 * Ks_a * ts / 60
            '
            ' First loop 2nd time step
            ' Intermediate capacity of cumulative infiltration
```

```
            Facc(j, 1) = Facc(j - 1, n_GA)    ' in mm
        ' Capacity of cumulative infiltration
            InfC(1, 1) = Facc(1, n_GA)   ' in mm
        ' Capacity of infiltration
            dInfC(1, 1) = Facc(1, n_GA)      ' in mm
            ' Next loop
                For jj = 2 To n_GA
                    If dRF(j, 1) <> 0 And RF(j, 1) > RF(j - 1, 1) Then
                        Facc(j, jj) = Facc(j - 1, n_GA) + Ke(j, 1) + MP * DelWC(j, 1) * Log((Facc(j, jj - 1) + _
                                    MP * DelWC(j, 1)) / (Facc(j - 1, n_GA) + MP * DelWC(j, 1)))
                    Else
                        Facc(j, jj) = 0
                    End If
                Next jj
            '
            ' Write final cumulative infiltration (in mm) from above loop
                For jj = 2 To j
                    InfC(j, 1) = Facc(jj, n_GA)
                    '
                        If InfC(j, 1) = 0 Then
                            dInfC(j, 1) = 0
                        Else
                            dInfC(j, 1) = Ke(j, 1) * (1 + (MP * DelWC(j, 1)) / InfC(j, 1))
                        End If
                Next jj
                '
                If dInfC(j, 1) > dRF(j, 1) Then
                    dInf(j, 1) = dRF(j, 1)
                    dQ(j, 1) = 0
                Else
                    dInf(j, 1) = dInfC(j, 1)
                    dQ(j, 1) = dRF(j, 1) - dInf(j, 1)
                End If
                '
                If dInf(j, 1) > 0 Then
                    Inf(j, 1) = Inf(j - 1, 1) + dInf(j, 1)
                    Q(j, 1) = Q(j - 1, 1) + dQ(j, 1)
                Else
                    Inf(j, 1) = 0
                    Q(j, 1) = 0
                End If
    End If  ' Runoff method ends
    '
Else    ' In case no runoff
    Q(j, 1) = 0
    dQ(j, 1) = 0
    Inf(j, 1) = RF(j, 1)
    dInf(j, 1) = dRF(j, 1)
End If
'
' Updated WC for time step j > 1
' Layer 1
    If WC(j, 1) < WCf(1) Then
```

```
        Es1(j, 1) = Max2(Es(j, 1) * Exp(2.5 * (WC(j, 1) - WCf(1)) / (WCf(1) - WCr(1))), 0)
    Else
        Es1(j, 1) = Max2(Es(j, 1), 0)
    End If
            Es2(j, 1) = Max2(Min2(Es1(j, 1), 0.8 * (WC(j, 1) - WCr(1)) * L(1)), 0)

    If Es_op = 1 Then
        WCc(j, 1) = WC(j, 1) + (dInf(j, 1) - Es1(j, 1)) / L(1)
    Else
        WCc(j, 1) = WC(j, 1) + (dInf(j, 1) - Es2(j, 1)) / L(1)
    End If
    ' Calculate water content for layer 1
        If WCc(j, 1) <= WCr(1) Then
            WCu(j, 1) = WCr(1)
            Es1(j, 1) = 0
            Es2(j, 1) = 0
            Per(j, 1) = 0

        ElseIf WCc(j, 1) <= WCf(1) Then
            WCu(j, 1) = WCc(j, 1)
            Per(j, 1) = 0

        ElseIf WCc(j, 1) <= WCs(1) Then
            WCu(j, 1) = WCc(j, 1) - (1 / (T_travel * 60 / ts)) * (WCc(j, 1) - WCf(1))
            WCX(j, 1) = (WCc(j, 1) - WCu(j, 1)) * L(1)
            Per(j, 1) = WCX(j, 1) * (1 - Exp(-(ts / 60) * Ks(1) / ((WCs(1) - WCf(1)) * L(1))))

        ElseIf WCc(j, 1) > WCs(1) Then
            WCu(j, 1) = WCs(1) - (1 / (T_travel * 60 / ts)) * (WCs(1) - WCf(1))
            WCX(j, 1) = (WCc(j, 1) - WCu(j, 1)) * L(1)
            Per(j, 1) = WCX(j, 1) * (1 - Exp(-(ts / 60) * Ks(1) / ((WCs(1) - WCf(1)) * L(1))))
        End If
            WC(j + 1, 1) = WCu(j, 1)
            WC_acc_mm(j, 1) = WCu(j, 1) * L(1)
'
' Layer 2 to n (time step j > 1)
    For i = 2 To n
        If WC(j, i) < WCf(i) Then
            Es1(j, i) = Max2(Es(j, i) * Exp(2.5 * (WC(j, i) - WCf(i)) / (WCf(i) - WCr(i))), 0)
        Else
            Es1(j, i) = Max2(Es(j, i), 0)
        End If
            Es2(j, i) = Max2(Min2(Es1(j, i), 0.8 * (WC(j, i) - WCf(i)) * L(i)), 0)
        '
        ' Option for Es1 or Es2
            If Es_op = 1 Then
                WCc(j, i) = WC(j, i) + (Per(j, i - 1) - Es1(j, i)) / L(i)
            Else
                WCc(j, i) = WC(j, i) + (Per(j, i - 1) - Es2(j, i)) / L(i)
            End If
        ' Calculate water contents
            If WCc(j, i) <= WCr(i) Then
                WCu(j, i) = WCr(i)
```

```
                Es1(j, i) = 0
                Es2(j, i) = 0
                Per(j, i) = 0

            ElseIf WCc(j, i) <= WCf(i) Then
                WCu(j, i) = WCc(j, i)
                Per(j, i) = 0

            ElseIf WCc(j, i) <= WCs(i) Then
                WCu(j, i) = WCc(j, i) - (1 / (T_travel * 60 / ts)) * (WCc(j, i) - WCf(i))
                WCX(j, i) = (WCc(j, i) - WCu(j, i)) * L(i)
                Per(j, i) = WCX(j, i) * (1 - Exp(-(ts / 60) * Ks(i) / ((WCs(i) - WCf(i)) * L(i))))

            ElseIf WCc(j, i) > WCs(i) Then
                WCu(j, i) = WCs(i) - (1 / (T_travel * 60 / ts)) * (WCs(i) - WCf(i))
                WCX(j, i) = (WCc(j, i) - WCu(j, i)) * L(i)
                Per(j, i) = WCX(j, i) * (1 - Exp(-(ts / 60) * Ks(i) / ((WCs(i) - WCf(i)) * L(i))))

            End If
                WC(j + 1, i) = WCu(j, i)
                WC_acc_mm(j, i) = WC_acc_mm(j, i - 1) + WCu(j, i) * L(i)
        Next i
            WC_a(j, 1) = WC_acc_mm(j, n) / l_acc(n)
    Next j  ' Next time step
    '
    '
    ' Hourly rainfall and runoff
    Dim dRF_hr() As Double
    Dim dQ_hr() As Double

    ReDim dRF_hr(1 To T_ts, 1 To 1) As Double
    ReDim dQ_hr(1 To T_ts, 1 To 1) As Double

    For j = 1 To T_ts
        dRF_hr(j, 1) = dRF(j, 1) * 60 / ts
        dQ_hr(j, 1) = dQ(j, 1) * 60 / ts
    Next j
'
' V. SIMULATION OF SEDIMENT
'
        Dim Sed() As Double
        Dim dSed() As Double
        Dim C_sed() As Double
        ReDim Sed(1 To T_ts, 1 To 1) As Double
        ReDim dSed(1 To T_ts, 1 To 1) As Double
        ReDim C_sed(1 To T_ts, 1 To 1) As Double
        Dim epsilon() As Double
        ReDim epsilon(1 To T_ts, 1 To 1) As Double
        Dim e_coef As Double
            e_coef = Range("_e_coef")
        '
        ' Initial conditions
        Sed(1, 1) = 0
```

```
            dSed(1, 1) = 0
            C_sed(1, 1) = 0
        '
        'Sediment mass (in g), sediment concentration (in g/L)
        If RC = "On" Then
            For j = 2 To T_ts
                If dQ(j, 1) = 0 Then
                    Sed(j, 1) = 0
                    dSed(j, 1) = 0
                    C_sed(j, 1) = 0
                Else
                    Sed(j, 1) = 10 ^ 6 * SLE_coef * (Q(j, 1) / 1000 * A * q_peakj(j, 1)) ^ MUSLE_exp
                    dSed(j, 1) = Max2(0, Sed(j, 1) - Sed(j - 1, 1))
                    C_sed(j, 1) = dSed(j, 1) / (A * dQ(j, 1))
                    ' Pesticide enrichment ratio, epsilon (Menzel (1980))
                    If C_sed(j, 1) = 0 Then
                        epsilon(j, 1) = 0
                    Else
                        epsilon(j, 1) = e_coef * (C_sed(j, 1) / 1000) ^ -0.2468
                    End If
                End If
            Next j
        Else
            For j = 2 To T_ts
                Sed(j, 1) = 0
                dSed(j, 1) = 0
                C_sed(j, 1) = 0
            Next j
        End If
'
' VI. SIMULATION OF PESTICIDE/ HERBICIDE
'
If Sim_op = "Runoff & Pesticide" Then
'
' VI.1 Process applied mass of pesticide
            ' Initial pesticide concentration (residue)
                Dim C0() As Double
                ReDim C0(1 To n) As Double
                Dim rgn_C0 As Range
                Set rgn_C0 = ws_i.Range("_rgn_C0")
                '
                For i = 1 To n
                    If Same_op = "Yes" Then
                            C0(i) = rgn_C0.Offset(0, 1)
                    Else
                            C0(i) = rgn_C0.Offset(0, i)
                    End If
                Next i
                '
            ' Applied pesticide masses, in mg
                    PM1 = 0.1 * PR1 * A
                    PM2 = 0.1 * PR2 * A
                    PM3 = 0.1 * PR3 * A
```

```
'
' Calculate applied time (date and hour) of pesticide masses
    Dim dt1, dt2, dt3 As Date
    '
    Dim MEr() As Double
    Dim M0() As Double
    Dim Mpst() As Double
    Dim Mbio() As Double
    Dim Mper() As Double
    Dim Mrw_pst() As Double
    Dim Msed_pst() As Double
    Dim Mpho() As Double
    Dim Mvol() As Double
    Dim Mds() As Double
    Dim Msw() As Double
    Dim Mds0() As Double
    Dim Msw0() As Double
    '
    Dim dMbio() As Double
    Dim dMper() As Double
    Dim dMper_f() As Double
    Dim dMrw_pst() As Double
    Dim dMsed_pst() As Double
    Dim dMpho() As Double
    Dim dMvol() As Double
    '
    Dim Cs() As Double
    Dim Cs_0W() As Double
    Dim Cds() As Double
    Dim Cw() As Double
    Dim Csw() As Double
    Dim Cper_pst() As Double
    Dim Crw_pst() As Double
    Dim Csed_pst() As Double
    '
    ReDim MEr(1 To T_ts, 1 To n) As Double
    ReDim M0(1 To T_ts, 1 To 1) As Double
    ReDim Mpst(1 To T_ts, 1 To n) As Double
    ReDim Mbio(1 To T_ts, 1 To n) As Double
    ReDim Mper(1 To T_ts, 1 To n) As Double
    ReDim Mper_f(1 To T_ts, 1 To n) As Double
    ReDim Mrw_pst(1 To T_ts, 1 To 1) As Double
    ReDim Msed_pst(1 To T_ts, 1 To 1) As Double
    ReDim Mpho(1 To T_ts, 1 To 1) As Double
    ReDim Mvol(1 To T_ts, 1 To 1) As Double
    ReDim Mds(1 To T_ts, 1 To n) As Double
    ReDim Msw(1 To T_ts, 1 To n) As Double
    ReDim Mds0(1 To n) As Double
    ReDim Msw0(1 To n) As Double
    '
    ReDim dMbio(1 To T_ts, 1 To n) As Double
    ReDim dMper(1 To T_ts, 1 To n) As Double
    ReDim dMrw_pst(1 To T_ts, 1 To 1) As Double
```

```
ReDim dMsed_pst(1 To T_ts, 1 To 1) As Double
ReDim dMpho(1 To T_ts, 1 To 1) As Double
ReDim dMvol(1 To T_ts, 1 To 1) As Double
'
ReDim Cs(1 To T_ts, 1 To n) As Double
ReDim Cs_0W(1 To T_ts, 1 To n) As Double
ReDim Cds(1 To T_ts, 1 To n) As Double
ReDim Cw(1 To T_ts, 1 To n) As Double
ReDim Csw(1 To T_ts, 1 To n) As Double
ReDim Cper_pst(1 To T_ts, 1 To n) As Double
ReDim Crw_pst(1 To T_ts, 1 To n) As Double
ReDim Csed_pst(1 To T_ts, 1 To 1) As Double

Dim alpha, beta As Single
alpha = ws_i.Range("_alpha")
beta = ws_i.Range("_beta")
'
' Initial masses in dry soil and soil water for all layers
For i = 1 To n
    Mds0(i) = C0(i) * A * L(i) * Rb(i)
    Msw0(i) = (C0(i) / Kd(i)) * A * WCu(1, i) * L(i)
Next i
'
' Initial condition in layer 1
Mbio(1, 1) = 0
Mper(1, 1) = 0
Mrw_pst(1, 1) = 0
Msed_pst(1, 1) = 0
Mpho(1, 1) = 0
Mvol(1, 1) = 0
Mrw_pst(1, 1) = 0
'
dMbio(1, 1) = 0
dMper(1, 1) = 0
dMrw_pst(1, 1) = 0
dMsed_pst(1, 1) = 0
dMpho(1, 1) = 0
dMvol(1, 1) = 0
'
Cper_pst(1, 1) = 0
Crw_pst(1, 1) = 0
Csed_pst(1, 1) = 0
'
' Time difference between application time and start time of simulation (in minute)
    dt1 = DateDiff("n", s_date, PD1)
    dt2 = DateDiff("n", s_date, PD2)
    dt3 = DateDiff("n", s_date, PD3)
'
' Application pst mass
For j = 1 To T_ts
    If j * ts > dt3 Then
            M0(j, 1) = Mds0(1) + Msw0(1) + PM1 + PM2 + PM3
        ElseIf j * ts > dt2 Then
```

```
                M0(j, 1) = Mds0(1) + Msw0(1) + PM1 + PM2
            ElseIf j * ts > dt1 Then
                M0(j, 1) = Mds0(1) + Msw0(1) + PM1
            Else
                M0(j, 1) = Mds0(1) + Msw0(1)
          End If
        Next j
'
' VI.2 Pesticide concentration in layer 1
'
        ' First time step values in layer 1
          Mpst(1, 1) = M0(1, 1) - (Mvol(1, 1) + Mpho(1, 1) + Mrw_pst(1, 1) + Msed_pst(1, 1) +
Mbio(1, 1) + Mper(1, 1))
          ' Pest conc in dry soil
          Cs(1, 1) = Mpst(1, 1) / (A * L(1) * (Rb(1) + WCu(1, 1)))
          Cs_0W(1, 1) = Mpst(1, 1) / (A * L(1) * Rb(1))  ' Cs for dry soil
          Cds(1, 1) = Mpst(1, 1) * Kd(1) / (A * L(1) * (Rb(1) * Kd(1) + WCu(1, 1) * _
                (WCu(1, 1) * L(1) + Per(1, 1) + dQ(1, 1)) / (WCu(1, 1) * L(1) + alpha * (Per(1, 1) +
dQ(1, 1)))))
          ' Pest mass in dry soil
          Mds(1, 1) = Cds(1, 1) * A * L(1) * Rb(1)
            ' Pest conc in liquid phase
            Cw(1, 1) = Cds(1, 1) / Kd(1)
            ' Pest conc in soil water
            Csw(1, 1) = Cw(1, 1) * (dQ(1, 1) + Per(1, 1) + WCu(1, 1) * L(1)) / _
              (alpha * (dQ(1, 1) + Per(1, 1)) + WCu(1, 1) * L(1))
          ' Pest mass in soil water
          Msw(1, 1) = Csw(1, 1) * A * L(1) * WCu(1, 1)
          ' Mass error
          If M0(1, 1) = 0 Then
              MEr(1, 1) = 0
            Else
              MEr(1, 1) = Round((M0(1, 1) - Mds(1, 1) - Msw(1, 1) - Mbio(1, 1) - Mper(1, 1) - _
                    Mrw_pst(1, 1) - Msed_pst(1, 1) - Mpho(1, 1) - Mvol(1, 1)) * 100 / M0(1, 1), 2)
          End If
        '
        ' Next time steps
        For j = 2 To T_ts
          If HLpho = 0 Then
              Mpho(j, 1) = 0
          Else
                dMpho(j, 1) = Kphoj(j, 1) * Cs(j - 1, 1) * A * L(1) * Rb(1)
              Mpho(j, 1) = Mpho(j - 1, 1) + dMpho(j, 1)
          End If

            dMvol(j, 1) = kv * Cs(j - 1, 1) * A * L(1) * Rb(1)
          Mvol(j, 1) = Mvol(j - 1, 1) + dMvol(j, 1)

            dMbio(j, 1) = Kbioj(j, 1) * Cs(j - 1, 1) * A * L(1) * Rb(1)
          Mbio(j, 1) = Mbio(j - 1, 1) + dMbio(j, 1)

            dMper(j, 1) = Cper_pst(j - 1, 1) * A * Per(j, 1)
          Mper(j, 1) = Mper(j - 1, 1) + dMper(j, 1)
```

```
              dMrw_pst(j, 1) = beta * Cper_pst(j - 1, 1) * A * dQ(j, 1)
            Mrw_pst(j, 1) = Mrw_pst(j - 1, 1) + dMrw_pst(j, 1)

              dMsed_pst(j, 1) = epsilon(j, 1) * Cds(j - 1, 1) * dSed(j, 1) / 1000
            Msed_pst(j, 1) = Msed_pst(j - 1, 1) + dMsed_pst(j, 1)
            '
            ' Pst mass in soil layer 1 at time j
            Mpst(j, 1) = M0(j, 1) - (Mvol(j, 1) + Mpho(j, 1) + Mrw_pst(j, 1) + Msed_pst(j, 1) + Mbio(j, 1)
+ Mper(j, 1))
            Cs(j, 1) = Max2(0, Mpst(j, 1) / (A * L(1) * (Rb(1) + WCu(j, 1)))) ' pst conc in wet soil
            Cs_0W(j, 1) = Max2(0, Mpst(j, 1) / (A * L(1) * Rb(1)))  ' pst conc in dry soil
            Cds(j, 1) = Max2(0, Mpst(j, 1) * Kd(1) / (A * L(1) * (Rb(1) * Kd(1) + WCu(j, 1) * _
                  (WCu(j, 1) * L(1) + Per(j, 1) + dQ(j, 1)) / (WCu(j, 1) * L(1) + alpha * (Per(j, 1) +
dQ(j, 1))))))
            Cw(j, 1) = Cds(j, 1) / Kd(1)
            Csw(j, 1) = Cw(j, 1) * (dQ(j, 1) + Per(j, 1) + L(1) * WCu(j, 1)) / (alpha * (dQ(j, 1) + Per(j, 1))
+ L(1) * WCu(j, 1))
            '
            Mds(j, 1) = Cds(j, 1) * A * L(1) * Rb(1)
            Msw(j, 1) = Csw(j, 1) * A * WCu(j, 1) * L(1)
            '
            If dQ(j, 1) = 0 And Per(j, 1) = 0 Then
              Cper_pst(j, 1) = 0
            Else
              Cper_pst(j, 1) = alpha * Csw(j, 1) * (dQ(j, 1) + Per(j, 1)) / (beta * dQ(j, 1) + Per(j, 1))
            End If
            '
            ' Pesticide concentration in sediment (mg/kg)
              Csed_pst(j, 1) = epsilon(j, 1) * Cds(j, 1)
            '
            ' Mass error
            If M0(j, 1) = 0 Then
                MEr(j, 1) = 0
              Else
                MEr(j, 1) = Round((M0(j, 1) - Mds(j, 1) - Msw(j, 1) - Mbio(j, 1) - Mper(j, 1) - _
                      Mrw_pst(j, 1) - Msed_pst(j, 1) - Mpho(j, 1) - Mvol(j, 1)) * 100 / M0(j, 1), 2)
            End If

          Next j
          '
          ' Pesticide concentration in runoff water (micro g/L)
          For j = 2 To T_ts
            '
            If dQ(j, 1) = 0 Or dMrw_pst(j, 1) = 0 Then
                Crw_pst(j, 1) = 0
              Else
                Crw_pst(j, 1) = 1000 * dMrw_pst(j, 1) / (A * dQ(j, 1))
            End If
            '
          Next j
'
' VI.3 Pesticide concentration in layer i > 1
```

```
'
        ' Initial compartment masses in Layer i > 1
        For i = 2 To n
          Mds(1, i) = Mds0(i)
          Msw(1, i) = Msw0(i)
          Mbio(1, i) = 0
          Mper(1, i) = 0
          dMbio(1, i) = 0
          dMper(1, i) = 0
        Next i
        '
        ' First time step compartment masses and concentrations in Layer i > 1
        '
        For i = 2 To n
          ' First time step Input from upper layer and residual concentration in current layer
          Mper_f(1, i - 1) = Mper(1, i - 1) + Mds0(i) + Msw0(i)

          Mpst(1, i) = Mper_f(1, i - 1) - (Mbio(1, i) + Mper(1, i))
          Cs(1, i) = Max2(0, Mpst(1, i) / (A * L(i) * (Rb(i) + WCu(1, i))))
          Cds(1, i) = Max2(0, Mpst(1, i) * Kd(i) / (A * L(i) * (Rb(i) * Kd(i) + WCu(1, i) * _
                (WCu(1, i) * L(i) + Per(1, i)) / (WCu(1, i) * L(i) + alpha * Per(1, i))))) ' in solid
compartment
          Cs_0W(1, i) = Max2(0, Mpst(1, i) / (A * L(i) * Rb(i)))  ' in dry soil
          Cw(1, i) = Cds(1, i) / Kd(i)
          Csw(1, i) = Cw(1, i) * (Per(1, i) + WCu(1, i) * L(i)) / (alpha * Per(1, i) + WCu(1, i) * L(i))
          '
          Mds(1, i) = Cds(1, i) * A * L(i) * Rb(i)
          Msw(1, i) = Csw(1, i) * A * WCu(1, i) * L(i)
          ' Calculate mass error
          '
          If Mper_f(1, i - 1) = 0 Then
              MEr(1, i) = 0
            Else
              MEr(1, i) = Round((Mper_f(1, i - 1) - Mds(1, i) - Msw(1, i) - Mbio(1, i) - Mper(1, i)) * _
                    100 / (Mper_f(1, i - 1)), 2)
          End If
          '
        Next i
        '
        ' Next time steps
        For j = 2 To T_ts
          For i = 2 To n
            '
            dMbio(j, i) = Kbioj(j, 1) * Cs(j - 1, i) * A * L(i) * Rb(i)
            dMper(j, i) = Cper_pst(j - 1, i) * A * Per(j, i)
            '
            ' Input pesticide from upper layer including residual pst mass
            Mper_f(j, i - 1) = Mper_f(j - 1, i - 1) + dMper(j, i - 1)
            '
            ' Output of current layer or input to lower layer
            Mper(j, i) = Mper(j - 1, i) + dMper(j, i)
            Mbio(j, i) = Mbio(j - 1, i) + dMbio(j, i)
            Mpst(j, i) = Mper_f(j, i - 1) - (Mbio(j, i) + Mper(j, i))
```

```
              '
              Cs(j, i) = Max2(0, Mpst(j, i) / (A * L(i) * (Rb(i) + WCu(j, i))))
              Cds(j, i) = Max2(0, Mpst(j, i) * Kd(i) / (A * L(i) * (Rb(i) * Kd(i) + WCu(j, i) * _
                    (WCu(j, i) * L(i) + Per(j, i)) / (WCu(j, i) * L(i) + alpha * Per(j, i))))) ' in solid
compartment
              Cs_0W(j, i) = Max2(0, Mpst(j, i) / (A * L(i) * Rb(i)))  ' in dry soil
              Cw(j, i) = Cds(j, i) / Kd(i)
              Csw(j, i) = Cw(j, i) * (Per(j, i) + WCu(j, i) * L(i)) / (alpha * Per(j, i) + WCu(j, i) * L(i))
              '
              Mds(j, i) = Cds(j, i) * A * L(i) * Rb(i)
              Msw(j, i) = Csw(j, i) * A * WCu(j, i) * L(i)
              '
              If Per(j, i) = 0 Then
                Cper_pst(j, i) = 0
              Else
                Cper_pst(j, i) = alpha * Csw(j, i)
              End If
              '
              ' Calculate mass error
              If Mper_f(j, i - 1) = 0 Then
                  MEr(j, i) = 0
                Else
                  MEr(j, i) = Round((Mper_f(j, i - 1) - Mds(j, i) - Msw(j, i) - Mbio(j, i) - Mper(j, i)) * _
                        100 / (Mper_f(j, i - 1)), 2)
              End If
            Next i
          Next j
End If  ' of Pesticide option
'
' VII. SIMULATION OF DAILY OUTPUT
'
        Dim RainD_cum() As Double
        ReDim RainD_cum(1 To T_ts, 1 To 1)
        Dim RainD() As Double
        ReDim RainD(1 To duration, 1 To 1)
        Dim RunoffD_cum() As Double
        ReDim RunoffD_cum(1 To T_ts, 1 To 1)
        Dim RunoffD() As Double
        ReDim RunoffD(1 To duration, 1 To 1)
        Dim InfilD_cum() As Double
        ReDim InfilD_cum(1 To T_ts, 1 To 1)
        Dim InfilD() As Double
        ReDim InfilD(1 To duration, 1 To 1)
        Dim SedD_cum() As Double
        ReDim SedD_cum(1 To T_ts, 1 To 1)
        Dim SedD() As Double
        ReDim SedD(1 To duration, 1 To 1)
        Dim CN2D_cum() As Double
        ReDim CN2D_cum(1 To T_ts, 1 To 1)
        Dim CN2D() As Double
        ReDim CN2D(1 To duration, 1 To 1)
'
```

```
' VII.1 Calulate daily rainfall, runoff, infiltration, and percolation from layer 1, sediment mass (accumulated values)
'
            RainD_cum(1, 1) = dRF(1, 1)
            RunoffD_cum(1, 1) = dQ(1, 1)
            InfilD_cum(1, 1) = dInf(1, 1)
            SedD_cum(1, 1) = dSed(1, 1)
            CN2D_cum(1, 1) = CN2(1, 1)

      For j = 1 To duration
         '
         For jj = 2 To T_ts_D
            RainD_cum((j - 1) * T_ts_D + jj, 1) = RainD_cum((j - 1) * T_ts_D + jj - 1, 1) + dRF((j - 1) * T_ts_D + jj, 1)
            RunoffD_cum((j - 1) * T_ts_D + jj, 1) = RunoffD_cum((j - 1) * T_ts_D + jj - 1, 1) + dQ((j - 1) * T_ts_D + jj, 1)
            InfilD_cum((j - 1) * T_ts_D + jj, 1) = InfilD_cum((j - 1) * T_ts_D + jj - 1, 1) + dInf((j - 1) * T_ts_D + jj, 1)
            SedD_cum((j - 1) * T_ts_D + jj, 1) = SedD_cum((j - 1) * T_ts_D + jj - 1, 1) + dSed((j - 1) * T_ts_D + jj, 1)
            CN2D_cum((j - 1) * T_ts_D + jj, 1) = CN2D_cum((j - 1) * T_ts_D + jj - 1, 1) + CN2((j - 1) * T_ts_D + jj, 1)
         Next jj
         '
            RainD(j, 1) = RainD_cum((j - 1) * T_ts_D + T_ts_D, 1)
            RunoffD(j, 1) = RunoffD_cum((j - 1) * T_ts_D + T_ts_D, 1)
            InfilD(j, 1) = InfilD_cum((j - 1) * T_ts_D + T_ts_D, 1)
            SedD(j, 1) = SedD_cum((j - 1) * T_ts_D + T_ts_D, 1)
            CN2D(j, 1) = Round(CN2D_cum((j - 1) * T_ts_D + T_ts_D, 1) / T_ts_D, 0)
      Next j
'
' VII.2 Calculate daily average water content
'
         Dim WCD_cum() As Double       ' Cumulative from small ts
         ReDim WCD_cum(1 To T_ts, 1 To n)
         Dim WCD() As Double        ' daily WC for all layers
         ReDim WCD(1 To duration, 1 To n)
      '
      For j = 1 To duration
         '
         ' For Layer 1
            WCD_cum(1, 1) = WCu(1, 1)
            '
            For jj = 2 To T_ts_D
               WCD_cum((j - 1) * T_ts_D + jj, 1) = WCD_cum((j - 1) * T_ts_D + jj - 1, 1) + WCu((j - 1) * T_ts_D + jj, 1)

            Next jj
            '
               WCD(j, 1) = (WCD_cum((j - 1) * T_ts_D + T_ts_D, 1)) / T_ts_D
         ' For Layer i
         '
         For i = 2 To n
```

```
            WCD_cum(1, i) = WCu(1, i)
              '
              For jj = 2 To T_ts_D
                 WCD_cum((j - 1) * T_ts_D + jj, i) = WCD_cum((j - 1) * T_ts_D + jj - 1, i) + WCu((j - 1) *
T_ts_D + jj, i)
              Next jj
              '
                 WCD(j, i) = (WCD_cum((j - 1) * T_ts_D + T_ts_D, i)) / T_ts_D
         Next i
      Next j
'
' VII.3 Calulate daily sediment concentration(average value)
'
         Dim C_SedD_cum() As Double
         ReDim C_SedD_cum(1 To T_ts, 1 To 1)
         Dim C_SedD() As Double
         ReDim C_SedD(1 To duration, 1 To 1)

         C_SedD_cum(1, 1) = C_sed(1, 1)
      For j = 1 To duration
         For jj = 2 To T_ts_D
            C_SedD_cum((j - 1) * T_ts_D + jj, 1) = C_SedD_cum((j - 1) * T_ts_D + jj - 1, 1) + C_sed((j - 1) *
T_ts_D + jj, 1)
         Next jj
            C_SedD(j, 1) = (C_SedD_cum((j - 1) * T_ts_D + T_ts_D, 1)) / T_ts_D
      Next j
'
If Sim_op = "Runoff & Pesticide" Then
'
' VII.4 Calulate daily pesticide concentration in sediment (average value)
'
         Dim Csed_pstD_cum() As Double     ' Cumulative ts values
         ReDim Csed_pstD_cum(1 To T_ts, 1 To 1)
         Dim Csed_pstD() As Double      ' daily value
         ReDim Csed_pstD(1 To duration, 1 To 1)

         Csed_pstD_cum(1, 1) = Csed_pst(1, 1)
      For j = 1 To duration
         For jj = 2 To T_ts_D
            Csed_pstD_cum((j - 1) * T_ts_D + jj, 1) = Csed_pstD_cum((j - 1) * T_ts_D + jj - 1, 1) +
Csed_pst((j - 1) * T_ts_D + jj, 1)
         Next jj
            Csed_pstD(j, 1) = (Csed_pstD_cum((j - 1) * T_ts_D + T_ts_D, 1)) / T_ts_D
      Next j
'
' VII.5 Calulate daily pesticide concentration in runoff (average value)
'
         Dim Crw_pstD_cum() As Double
         ReDim Crw_pstD_cum(1 To T_ts, 1 To 1)
         Dim Crw_pstD() As Double
         ReDim Crw_pstD(1 To duration, 1 To 1)

         Crw_pstD_cum(1, 1) = Crw_pst(1, 1)
```

```
      For j = 1 To duration
         For jj = 2 To T_ts_D
            Crw_pstD_cum((j - 1) * T_ts_D + jj, 1) = Crw_pstD_cum((j - 1) * T_ts_D + jj - 1, 1) + Crw_pst((j
- 1) * T_ts_D + jj, 1)
         Next jj
            Crw_pstD(j, 1) = (Crw_pstD_cum((j - 1) * T_ts_D + T_ts_D, 1)) / T_ts_D
      Next j
'
' VII.6 Calulate daily pesticide mass in sediment and in runoff
'
         Dim Msed_pstD() As Double
         ReDim Msed_pstD(1 To duration, 1 To 1)
         Dim Mrw_pstD() As Double
         ReDim Mrw_pstD(1 To duration, 1 To 1)

         Dim Msed_pstD_cum() As Double
         ReDim Msed_pstD_cum(1 To T_ts, 1 To 1)
         Dim Mrw_pstD_cum() As Double
         ReDim Mrw_pstD_cum(1 To T_ts, 1 To 1)

         Msed_pstD_cum(1, 1) = dMsed_pst(1, 1)
         Mrw_pstD_cum(1, 1) = dMrw_pst(1, 1)
      For j = 1 To duration
         '
         For jj = 2 To T_ts_D
            Msed_pstD_cum((j - 1) * T_ts_D + jj, 1) = Msed_pstD_cum((j - 1) * T_ts_D + jj - 1, 1) +
dMsed_pst((j - 1) * T_ts_D + jj, 1)
            Mrw_pstD_cum((j - 1) * T_ts_D + jj, 1) = Mrw_pstD_cum((j - 1) * T_ts_D + jj - 1, 1) +
dMrw_pst((j - 1) * T_ts_D + jj, 1)
         Next jj
            Msed_pstD(j, 1) = Msed_pstD_cum((j - 1) * T_ts_D + T_ts_D, 1)
            Mrw_pstD(j, 1) = Mrw_pstD_cum((j - 1) * T_ts_D + T_ts_D, 1)
      Next j
'
' VII.7 Calculate daily pesticde concentration in soil layers
'
         Dim CdsD_cum() As Double    ' Cumulative ts value
         ReDim CdsD_cum(1 To T_ts, 1 To n)
         Dim CdsD() As Double      ' Daily Cs (average value from ts values)
         ReDim CdsD(1 To duration, 1 To n)
         Dim CsD_0W_cum() As Double    ' Cumulative ts value in dry soil
         ReDim CsD_0W_cum(1 To T_ts, 1 To n)
         Dim CsD_0W() As Double      ' Daily Cs_0W
         ReDim CsD_0W(1 To duration, 1 To n)

         CdsD_cum(1, 1) = Cds(1, 1)
         CsD_0W_cum(1, 1) = Cs_0W(1, 1)
      For j = 1 To duration
         '
         ' For Layer 1
         For jj = 2 To T_ts_D
            CdsD_cum((j - 1) * T_ts_D + jj, 1) = CdsD_cum((j - 1) * T_ts_D + jj - 1, 1) + Cds((j - 1) * T_ts_D
+ jj, 1)
```

```
            CsD_0W_cum((j - 1) * T_ts_D + jj, 1) = CsD_0W_cum((j - 1) * T_ts_D + jj - 1, 1) + Cs_0W((j - 1) * T_ts_D + jj, 1)
         Next jj
            CdsD(j, 1) = (CdsD_cum((j - 1) * T_ts_D + T_ts_D, 1)) / T_ts_D
            CsD_0W(j, 1) = (CsD_0W_cum((j - 1) * T_ts_D + T_ts_D, 1)) / T_ts_D
         '
         ' For Layer i
         For i = 2 To n
               CdsD_cum(1, i) = Cds(1, i)
               CsD_0W_cum(1, i) = Cs_0W(1, i)
            For jj = 2 To T_ts_D
               CdsD_cum((j - 1) * T_ts_D + jj, i) = CdsD_cum((j - 1) * T_ts_D + jj - 1, i) + Cds((j - 1) * T_ts_D + jj, i)
               CsD_0W_cum((j - 1) * T_ts_D + jj, i) = CsD_0W_cum((j - 1) * T_ts_D + jj - 1, i) + Cs_0W((j - 1) * T_ts_D + jj, i)
            Next jj
               CdsD(j, i) = (CdsD_cum((j - 1) * T_ts_D + T_ts_D, i)) / T_ts_D
               CsD_0W(j, i) = (CsD_0W_cum((j - 1) * T_ts_D + T_ts_D, i)) / T_ts_D
         Next i
      Next j

End If  ' End of Pesticide option
   '
   'Check soil properties option and sampling depth
   If IsEmpty(spd) = False Then
      If Same_op = "Yes" Then
         If n * L(1) < spd Then
            MsgBox "Sampling depth must be smaller or equal to total soil depth!"
            Exit Sub
         End If

      ElseIf spd > l_acc(n) Then
         MsgBox "Sampling depth must be smaller or equal to total soil depth!"
         Exit Sub
      End If
   End If
'
' VIII. Calculate water content and pesticide concentration corresponding to sampling depth (ts values)
'
   If IsEmpty(spd) Or spd = 0 Then
      GoTo 999
   Else
      '
      ' VIII.1 Calculate sampling depth WC
      '
         Dim WC_spd() As Double
         ReDim WC_spd(1 To T_ts, 1 To 1) As Double
      If IsEmpty(spd) = False Then
            Dim order_s, order As Integer
            ' Find layer's correspoding to sampling depth
               order = Application.Match(spd, z, 1)
            Dim WC_spd_cum() As Double
            ReDim WC_spd_cum(1 To T_ts, 1 To order) As Double
```

```
            ' For same option use only, order_s: layer's order correspoding to sampling depth
            order_s = spd / L(1)

        If Same_op = "Yes" Then
            For j = 1 To T_ts
                    WC_spd_cum(j, 1) = WC_acc_mm(j, 1)
                For i = 2 To order_s
                    WC_spd_cum(j, i) = WC_spd_cum(j, i - 1) + WCu(j, i) * L(i)
                Next i
                    WC_spd(j, 1) = WC_spd_cum(j, order_s) / spd
            Next j

        Else
            For j = 1 To T_ts
                    WC_spd_cum(j, 1) = WC_acc_mm(j, 1)
                For i = 2 To order
                    WC_spd_cum(j, i) = WC_spd_cum(j, i - 1) + WCu(j, i) * L(i)
                Next i
                '
                If order = n Then
                    WC_spd(j, 1) = WC_spd_cum(j, order) / spd
                Else
                    WC_spd(j, 1) = (WC_spd_cum(j, order) + Max2(0, WCu(j, order + 1) * (spd - z(order)))) /
spd

                End If
            Next j
        End If

    Else
        For j = 1 To T_ts
            WC_spd(j, 1) = 0
        Next j
    End If
    '
    ' VIII.2 Calculate sampling depth Cs
    '
        Dim Cds_spd() As Double      ' for Cs_avg in wet soil
        ReDim Cds_spd(1 To T_ts, 1 To 1) As Double
        Dim Cs_spd_0W() As Double       ' for Cs_avg in dry soil
        ReDim Cs_spd_0W(1 To T_ts, 1 To 1) As Double
    If IsEmpty(spd) = False Then
            Dim Cds_spd_cum() As Double
            ReDim Cds_spd_cum(1 To T_ts, 1 To order) As Double
            Dim Cs_spd_0W_cum() As Double   ' multiplied with depth
            ReDim Cs_spd_0W_cum(1 To T_ts, 1 To order) As Double
        If Sim_op = "Runoff & Pesticide" Then
            If Same_op = "Yes" Then
                For j = 1 To T_ts
                        Cds_spd_cum(j, 1) = Cds(j, 1) * L(1)
                        Cs_spd_0W_cum(j, 1) = Cs_0W(j, 1) * L(1)
                    For i = 2 To order_s
                        Cds_spd_cum(j, i) = Cds_spd_cum(j, i - 1) + Cds(j, i) * L(i)
```

```
              Cs_spd_0W_cum(j, i) = Cs_spd_0W_cum(j, i - 1) + Cs_0W(j, i) * L(i)
            Next i
              Cds_spd(j, 1) = Cds_spd_cum(j, order_s) / spd
              Cs_spd_0W(j, 1) = Cs_spd_0W_cum(j, order_s) / spd
          Next j
        Else
          For j = 1 To T_ts
              Cds_spd_cum(j, 1) = Cds(j, 1) * L(1)
              Cs_spd_0W_cum(j, 1) = Cs_0W(j, 1) * L(1)
            For i = 2 To order
              Cds_spd_cum(j, i) = Cds_spd_cum(j, i - 1) + Cds(j, i) * L(i)
              Cs_spd_0W_cum(j, i) = Cs_spd_0W_cum(j, i - 1) + Cs_0W(j, i) * L(i)
            Next i
            '
            If order = n Then
              Cds_spd(j, 1) = Cds_spd_cum(j, order) / spd
              Cs_spd_0W(j, 1) = Cs_spd_0W_cum(j, order) / spd
            Else
              Cds_spd(j, 1) = (Cds_spd_cum(j, order) + Max2(0, Cds(j, order + 1) * (spd - z(order)))) /
spd
              Cs_spd_0W(j, 1) = (Cs_spd_0W_cum(j, order) + Max2(0, Cs_0W(j, order + 1) * (spd -
z(order)))) / spd
            End If
          Next j
         End If
      End If

    Else
      For j = 1 To T_ts
        Cds_spd(j, 1) = 0
        Cs_spd_0W(j, 1) = 0
      Next j
    End If
    '
    ' VIII.3 Calculate daily sampling depth water content
    '
      Dim WCD_spd() As Double         ' sampling depth daily WC
      ReDim WCD_spd(1 To duration, 1 To 1) As Double
    If IsEmpty(spd) = False Then
        Dim WCD_spd_cum() As Double
        ReDim WCD_spd_cum(1 To duration, 1 To order) As Double

      If Same_op = "Yes" Then
        For j = 1 To duration
            WCD_spd_cum(j, 1) = WCD(j, 1) * L(1)
          For i = 2 To order_s
            WCD_spd_cum(j, i) = WCD_spd_cum(j, i - 1) + WCD(j, i) * L(i)
          Next i
            WCD_spd(j, 1) = WCD_spd_cum(j, order_s) / spd
        Next j

      Else
        For j = 1 To duration
```

```
                WCD_spd_cum(j, 1) = WCD(j, 1) * L(1)
             For i = 2 To order
                WCD_spd_cum(j, i) = WCD_spd_cum(j, i - 1) + WCD(j, i) * L(i)
             Next i
             '
             If order = n Then
                WCD_spd(j, 1) = WCD_spd_cum(j, order) / spd
             Else
                WCD_spd(j, 1) = (WCD_spd_cum(j, order) + Max2(0, WCD(j, order + 1) * (spd - z(order))))
/ spd
             End If
          Next j
       End If

    Else
       For j = 1 To duration
          WCD_spd(j, 1) = 0
       Next j

    End If
    '
    ' VIII.4 Calculate daily sampling depth pesticide concentration in soil
    '
          Dim CdsD_spd() As Double
          ReDim CdsD_spd(1 To duration, 1 To 1) As Double
          ' For dry soil
          Dim CsD_0W_spd() As Double
          ReDim CsD_0W_spd(1 To duration, 1 To n)
       If IsEmpty(spd) = False Then
          If Sim_op = "Runoff & Pesticide" Then
                Dim CdsD_spd_cum() As Double
                ReDim CdsD_spd_cum(1 To duration, 1 To order) As Double
                ' For dry soil
                Dim CsD_0W_spd_cum() As Double
                ReDim CsD_0W_spd_cum(1 To duration, 1 To order) As Double
             If Same_op = "Yes" Then
                For j = 1 To duration
                      CdsD_spd_cum(j, 1) = CdsD(j, 1) * L(1)
                      CsD_0W_spd_cum(j, 1) = CsD_0W(j, 1) * L(1)
                   For i = 2 To order_s
                      CdsD_spd_cum(j, i) = CdsD_spd_cum(j, i - 1) + CdsD(j, i) * L(i)
                      CsD_0W_spd_cum(j, i) = CsD_0W_spd_cum(j, i - 1) + CsD_0W(j, i) * L(i)
                   Next i
                      CdsD_spd(j, 1) = CdsD_spd_cum(j, order_s) / spd
                      CsD_0W_spd(j, 1) = CsD_0W_spd_cum(j, order_s) / spd
                Next j
             Else
                For j = 1 To duration
                      CdsD_spd_cum(j, 1) = CdsD(j, 1) * L(1)
                      CsD_0W_spd_cum(j, 1) = CsD_0W(j, 1) * L(1)
                   For i = 2 To order
                      CdsD_spd_cum(j, i) = CdsD_spd_cum(j, i - 1) + CdsD(j, i) * L(i)
                      CsD_0W_spd_cum(j, i) = CsD_0W_spd_cum(j, i - 1) + CsD_0W(j, i) * L(i)
```

```
                            Next i
                            '
                            If order = n Then
                                CdsD_spd(j, 1) = CdsD_spd_cum(j, order) / spd
                                CsD_0W_spd(j, 1) = CsD_0W_spd_cum(j, order) / spd
                            Else
                                CdsD_spd(j, 1) = (CdsD_spd_cum(j, order) + Max2(0, CdsD(j, order + 1) * (spd -
z(order)))) / spd
                                CsD_0W_spd(j, 1) = (CsD_0W_spd_cum(j, order) + Max2(0, CsD_0W(j, order + 1) *
(spd - z(order)))) / spd
                            End If
                        Next j
                    End If ' check same option
                Else
                        For j = 1 To duration
                            CdsD_spd(j, 1) = 0
                            CsD_0W_spd(j, 1) = 0
                        Next j
                End If  ' check Runoff & Pesticide
            End If ' check empty
    End If
999
'
' IX. OUTPUTS
'
' IX.1 Write outputs in Ouput sheet
'
        ws_o.Visible = xlSheetVisible
        ws_o.Activate
        ws_o.Cells.Clear
        '
        If Sim_op = "Runoff & Pesticide" Then
            ws_o.Range(Cells(3, 17), Cells(T_ts + 2, 17)).Value = Crw_pst
            ws_o.Range(Cells(3, 18), Cells(T_ts + 2, 18)).Value = Csed_pst
            ws_o.Range(Cells(3, 16 + 2 * n), Cells(T_ts + 2, 15 + 3 * n)).Value = Mds
            ws_o.Range(Cells(3, 16 + 3 * n), Cells(T_ts + 2, 15 + 4 * n)).Value = Msw
            ws_o.Range(Cells(3, 16 + 4 * n), Cells(T_ts + 2, 15 + 5 * n)).Value = Mbio
            ws_o.Range(Cells(3, 16 + 5 * n), Cells(T_ts + 2, 15 + 6 * n)).Value = Mper
            ws_o.Range(Cells(3, 16 + 6 * n), Cells(T_ts + 2, 16 + 6 * n)).Value = Mrw_pst
            ws_o.Range(Cells(3, 17 + 6 * n), Cells(T_ts + 2, 17 + 6 * n)).Value = Msed_pst
            ws_o.Range(Cells(3, 18 + 6 * n), Cells(T_ts + 2, 18 + 6 * n)).Value = Mpho
            ws_o.Range(Cells(3, 19 + 6 * n), Cells(T_ts + 2, 19 + 6 * n)).Value = Mvol
            ws_o.Range(Cells(3, 20 + 6 * n), Cells(T_ts + 2, 19 + 7 * n)).Value = MEr
            '
            If Cs_op = 1 Then   ' Pst conc in dry soil condition
                    ws_o.Range(Cells(3, 16 + 1 * n), Cells(T_ts + 2, 15 + 2 * n)).Value = Cs_0W
                If IsEmpty(spd) Or spd = 0 Then
                Else
                    ws_o.Range(Cells(3, 15 + n), Cells(T_ts + 2, 15 + n)).Value = Cs_spd_0W
                End If
            Else                ' Enter 2, pst conc in soil solid compartment
                    ws_o.Range(Cells(3, 16 + 1 * n), Cells(T_ts + 2, 15 + 2 * n)).Value = Cds
                If IsEmpty(spd) Or spd = 0 Then
```

```
            Else
               ws_o.Range(Cells(3, 15 + n), Cells(T_ts + 2, 15 + n)).Value = Cds_spd
            End If
         End If

      End If
         ws_o.Range(Cells(3, 1), Cells(T_ts + 2, 1)) = Time
         ws_o.Range(Cells(3, 1), Cells(T_ts + 2, 1)).NumberFormat = "mm/dd/yyyy hh:mm"
         ws_o.Range(Cells(3, 2), Cells(T_ts + 2, 2)).Value = dRF
         ws_o.Range(Cells(3, 3), Cells(T_ts + 2, 3)).Value = RF
         ws_o.Range(Cells(3, 4), Cells(T_ts + 2, 4)).Value = Q
         ws_o.Range(Cells(3, 5), Cells(T_ts + 2, 5)).Value = dQ
         ws_o.Range(Cells(3, 6), Cells(T_ts + 2, 6)).Value = Inf
         ws_o.Range(Cells(3, 7), Cells(T_ts + 2, 7)).Value = dInf
         ws_o.Range(Cells(3, 8), Cells(T_ts + 2, 8)).Value = dRF_hr
         ws_o.Range(Cells(3, 9), Cells(T_ts + 2, 9)).Value = dQ_hr
         ws_o.Range(Cells(3, 10), Cells(T_ts + 2, 10)).Value = C_sed
         ws_o.Range(Cells(3, 11), Cells(T_ts + 2, 11)).Value = Sed
         ws_o.Range(Cells(3, 13), Cells(T_ts + 2, 12 + n)).Value = WCu
         '
         If IsEmpty(spd) Or spd = 0 Then
         Else
            ws_o.Range(Cells(3, 12), Cells(T_ts + 2, 12)).Value = WC_spd
         End If
         'CN2
         ws_o.Cells(2, 20 + 7 * n) = "CN2"
         ws_o.Range(Cells(3, 20 + 7 * n), Cells(T_ts + 2, 20 + 7 * n)).Value = CN2
'
' IX.2 Write outputs in OuputD sheet
'
   ws_od.Activate
   ws_od.Cells.Clear
      ws_od.Range(Cells(3, 1), Cells(duration + 2, 1)).Value = TimeD
      ws_od.Range(Cells(3, 1), Cells(duration + 2, 1)).NumberFormat = "mm/dd/yyyy"
      ws_od.Range(Cells(3, 2), Cells(duration + 2, 2)).Value = RainD
      ws_od.Range(Cells(3, 3), Cells(duration + 2, 3)).Value = RunoffD
      ws_od.Range(Cells(3, 4), Cells(duration + 2, 4)).Value = C_SedD
      ws_od.Range(Cells(3, 5), Cells(duration + 2, 5)).Value = SedD
      ws_od.Range(Cells(3, 7), Cells(duration + 2, 6 + n)).Value = WCD
      '
      If IsEmpty(spd) Or spd = 0 Then
      Else
         ws_od.Range(Cells(3, 6), Cells(duration + 2, 6)).Value = WCD_spd
      End If
   If Sim_op = "Runoff & Pesticide" Then
      ws_od.Range(Cells(3, 7 + n), Cells(duration + 2, 7 + n)).Value = Crw_pstD
      ws_od.Range(Cells(3, 8 + n), Cells(duration + 2, 8 + n)).Value = Csed_pstD
      If Cs_op = 1 Then   ' Pst conc in dry soil condition
         ws_od.Range(Cells(3, 10 + n), Cells(duration + 2, 9 + 2 * n)).Value = CsD_0W
         '
         If IsEmpty(spd) Or spd = 0 Then
         Else
            ws_od.Range(Cells(3, 9 + n), Cells(duration + 2, 9 + n)).Value = CsD_0W_spd
```

```
         End If

      Else               ' Enter 2, pst conc in soil solid compartment
         ws_od.Range(Cells(3, 10 + n), Cells(duration + 2, 9 + 2 * n)).Value = CdsD
         '
         If IsEmpty(spd) Or spd = 0 Then
         Else
            ws_od.Range(Cells(3, 9 + n), Cells(duration + 2, 9 + n)).Value = CdsD_spd
         End If
      End If

         ws_od.Range(Cells(3, 10 + 2 * n), Cells(duration + 2, 10 + 2 * n)).Value = Mrw_pstD
         ws_od.Range(Cells(3, 11 + 2 * n), Cells(duration + 2, 11 + 2 * n)).Value = Msed_pstD

   End If
'
' IX.3 Report general information on "Report" sheet
'
   'First row's positions for report sheet
      fr_rp = 5
      Dim n1 As Integer
      n1 = Min2(5, n)
   ws_rp.Activate
   ws_rp.Cells.Clear
   '
   If Sim_op = "Runoff & Pesticide" Then
      ws_rp.Cells(fr_rp + n + 29, 2).Value = Format(Q10, "#.00")
      ws_rp.Cells(fr_rp + n + 30, 2).Value = HLpho
      ws_rp.Cells(fr_rp + n + 31, 2).Value = HLbio
      ws_rp.Cells(fr_rp + n + 32, 2).Value = Koc(1)
   End If
      ws_rp.Cells(fr_rp - 1, 3).Value = PestType
      ws_rp.Cells(fr_rp + 0, 3).Value = ws_i.Range("_Texture")
      ws_rp.Cells(fr_rp + 1, 3).Value = s_date
      ws_rp.Cells(fr_rp + 2, 3).Value = e_date
      ws_rp.Cells(fr_rp + 3, 3).Value = OPtsText
      ws_rp.Cells(fr_rp + 6, 3).Value = RFtsText
      ws_rp.Cells(fr_rp + 7, 3).Value = Tempts
      ws_rp.Cells(fr_rp + 8, 3).Value = Ets
      ws_rp.Cells(fr_rp + 9, 3).Value = SRts
      ws_rp.Cells(fr_rp + 17, 2).Value = n
      ws_rp.Cells(fr_rp + 18, 2).Value = l_acc(n)
      ws_rp.Cells(fr_rp + n + 24, 2).Value = Format(CN2(T_ts, 1), "0")
      ws_rp.Cells(fr_rp + n + 27, 2).Value = Format(K_USLE, "#.0000")
   '
   For i = 1 To n
      ws_rp.Cells(fr_rp + 18 + i, 2).Value = L(i)
   Next i
      Application.Calculation = xlCalculationAutomatic
End Sub
‘---------------------------------------------------------------------------------------------------------------------
```

Appendix 5. Charts module

The three typical sub programs for (1) calling all charts, (2) deleting all charts and (3) creating daily runoff rate chart are shown as below,

```
‘------------------------------------------------------------------------------------------------------------------------------
Option Explicit
Sub SPEC_chart()
   Dim ws_i, ws_obs As Worksheet
   Dim n, n1, duration As Single
   Dim Sim_op, OPts, RC As String
   '
   Set ws_i = Sheets("RUN")
   Set ws_obs = Sheets("Obs_Data")
   Sim_op = ws_i.Range("_Sim_op").Text
   RC = ws_i.Range("_RO_op")
   OPts = ws_i.Range("_OPts")
   '
   n = ws_i.Range("_n").Value
   n1 = Min2(5, n)
   duration = ws_i.Range("_duration")
   '
   Call DeleteallCharts
   '
      If OPts = "Daily" Then
         Call Chart1a_D_RF_RO
         Call Chart1b_D_RF_WC
         Call Chart1c_D_Sed_yield
         Call Chart1d_D_Sed_conc

      Else
         '
         If duration > 1 Then
            Call Chart1a_D_RF_RO
            Call Chart1b_D_RF_WC
            Call Chart2a_RF_RO
            Call Chart2b_Cum_RF_Cum_RO
            Call Chart2c_Sed_cum
            Call Chart2d_Sed_conc

            Call Chart2g_RF_WC
            Call Chart2h_5LA_WC
            Call Chart2i_L1_WC
            Call Chart2i_L2_WC


         ElseIf RC = "On" And IsEmpty(ws_obs.Cells(3, 1)) = False Then
               Call Chart2a1_RO_rate_event
               Call Chart2b1_Cum_RO_event
               Call Chart2c1_Sed_cum_event
               Call Chart2d1_Sed_conc_event
         End If

         '
```

```
      '
      If n = 3 Then
          Call Chart2i_L3_WC

      ElseIf n = 4 Then
          Call Chart2i_L3_WC
          Call Chart2i_L4_WC

      ElseIf n = 5 Then
          Call Chart2i_L3_WC
          Call Chart2i_L4_WC
          Call Chart2i_L5_WC
      End If
End If
'
If Sim_op = "Runoff & Pesticide" Then
    '
    If OPts = "Daily" Then
      Call Chart1e_D_RF_Crw_pst
      Call Chart1f_D_RF_Csed_pst
      Call Chart1g_D_RF_Csa

    Else
      If duration > 1 Then
          Call Chart2e_Pst_conc_in_Sed
          Call Chart2f_Pst_conc_in_RW
      Else
          If IsEmpty(ws_obs.Cells(3, 1)) = False Then
            Call Chart2e1_Pst_conc_in_Sed_event
            Call Chart2f1_Pst_conc_in_RW_event
          End If
      End If
      '
          Call Chart2j_Soil_Conc
          Call Chart2k_5LA_Soil_Conc
          Call Chart2l_L1_Soil_Conc
          Call Chart2l_L2_Soil_Conc
        '
        If n = 3 Then
            Call Chart2l_L3_Soil_Conc

        ElseIf n = 4 Then
            Call Chart2l_L3_Soil_Conc
            Call Chart2l_L4_Soil_Conc

        ElseIf n = 5 Then
            Call Chart2l_L3_Soil_Conc
            Call Chart2l_L4_Soil_Conc
            Call Chart2l_L5_Soil_Conc

        End If
        '
    End If
```

```
          '
        End If
        '
    End Sub
‘-------------------------------------------------------------------------------------------------------------------------------
' Delete All charts in "Graph" sheet
Private Sub DeleteallCharts()
Dim chtObj As ChartObject
Sheets("Graph").Activate
    For Each chtObj In Sheets("Graph").ChartObjects
        chtObj.Delete
    Next
End Sub
‘-------------------------------------------------------------------------------------------------------------------------------
' Chart for runoff rate (daily)
Private Sub Chart1a_D_RF_RO()
    Dim Chart1a As Chart
    Dim lastrow, lastrow2 As Single
    Dim small_TS As String
    Dim basedcell As Range
    '
    Set basedcell = Sheets("Graph").Range("A2")
    Dim ws_od, ws_i, ws_obs As Worksheet
    Set ws_i = Sheets("RUN")
    Set ws_od = Sheets("Output_D")
    Set ws_obs = Sheets("Obs_Data")
    Dim n As Single
    n = ws_i.Range("_n")
    '
    Dim duration As Single
    duration = ws_i.Range("_duration")
    '
        small_TS = ws_i.Range("_OPts")
        lastrow = ws_od.Cells(Rows.Count, 1).End(xlUp).Row
        lastrow2 = ws_obs.Cells(Rows.Count, 1).End(xlUp).Row
    '
    Set Chart1a = Sheets("Graph").Shapes.AddChart(xlXYScatterLinesNoMarkers, _
        Left:=0, Width:=238, Top:=basedcell.Top + 0 * 170, Height:=170).Chart
    '
    With Chart1a
        .SetSourceData Source:=ws_od.Range(Cells(3, 1).Address, Cells(lastrow, 1).Address)
        .SeriesCollection(1).xValues = ws_od.Range(Cells(3, 1).Address, Cells(lastrow, 1).Address)
        .SeriesCollection(1).Values = ws_od.Range(Cells(3, 3).Address, Cells(lastrow, 3).Address)
        '
        .SeriesCollection(1).Name = "Runoff"
        .SeriesCollection(1).Border.ColorIndex = 21
        .SeriesCollection(1).Format.Line.Weight = 2
        '
        ' Add series for observed runoff
        .SeriesCollection.NewSeries
        .SeriesCollection(2).ChartType = xlXYScatter
        .SeriesCollection(2).xValues = ws_obs.Range(Cells(3, 1).Address, Cells(lastrow2, 1).Address)
        .SeriesCollection(2).Values = ws_obs.Range(Cells(3, 2).Address, Cells(lastrow2, 2).Address)
```

```
'
.SeriesCollection(2).Name = "Obs. Runoff"
.SeriesCollection(2).MarkerStyle = xlMarkerStyleX
.SeriesCollection(2).MarkerSize = 3
.SeriesCollection(2).MarkerBackgroundColorIndex = 0
.SeriesCollection(2).MarkerForegroundColorIndex = 9
'
' Set minimum and maximum values for X axis
.Axes(xlCategory).MinimumScale = ws_od.Cells(3, "A")
.Axes(xlCategory).MaximumScale = ws_od.Range("A" & lastrow)
'
' Set major and minor units
If duration < 15 Then
        .Axes(xlCategory).MajorUnit = 1

    ElseIf duration < 30 Then
        .Axes(xlCategory).MajorUnit = 2

    ElseIf duration < 60 Then
        .Axes(xlCategory).MajorUnit = 5

    Else
        .Axes(xlCategory).MajorUnit = 30
End If
'
' Add rainfall data
.SeriesCollection.NewSeries
.SeriesCollection(3).ChartType = xlXYScatterLinesNoMarkers
.SeriesCollection(3).xValues = ws_od.Range(Cells(3, 1).Address, Cells(lastrow, 1).Address)
.SeriesCollection(3).Values = ws_od.Range(Cells(3, 2).Address, Cells(lastrow, 2).Address)
'
.SeriesCollection(3).Name = "Rainfall"
.SeriesCollection(3).Border.ColorIndex = 5
.SeriesCollection(3).Format.Line.Weight = 2
'
' Change rainfall data to secondary axis
.SeriesCollection(3).AxisGroup = 2
'
' Reverse values for Y secondary
.Axes(xlValue, xlSecondary).ReversePlotOrder = True
.Axes(xlValue, xlSecondary).HasTitle = True
.Axes(xlValue, xlSecondary).AxisTitle.Font.Size = 11
.Axes(xlValue, xlSecondary).TickLabels.Font.Size = 9
.Axes(xlValue, xlSecondary).AxisTitle.Characters.Text = "Rainfall (mm/d)"
'
' Name the X axis
.Axes(xlCategory, xlPrimary).HasTitle = True
.Axes(xlCategory, xlPrimary).AxisTitle.Characters.Text = "Time (days)"
'
' Rotate tick mark text on X axis by 45 degrees
.Axes(xlCategory).TickLabels.Orientation = 45
'
' Name the Y axis
```

```
        .Axes(xlValue, xlPrimary).HasTitle = True
        .Axes(xlValue, xlPrimary).AxisTitle.Characters.Text = "Runoff rate (mm/d)"
        '
        ' Set text sizes for axis title in 2 axes
        .Axes(xlCategory).AxisTitle.Font.Size = 11
        .Axes(xlValue).AxisTitle.Font.Size = 11
        '
        ' Set text sizes for data label in 2 axes
        .Axes(xlCategory).TickLabels.Font.Size = 9
        .Axes(xlValue).TickLabels.Font.Size = 9
        '
        ' Set text sizes for legend
        .Legend.Font.Size = 9
        .Legend.Position = xlLegendPositionTop
        '
        ' Set no borders for chart and plot area
        .ChartArea.Border.LineStyle = xlNone
        .PlotArea.Border.LineStyle = xlNone
        '
        ' Set no gridlines
        .Axes(xlValue).HasMajorGridlines = False
        '
        ' Set the minimum and maximum value for Y axes
        .Axes(xlValue, xlPrimary).MinimumScale = 0
        .Axes(xlValue, xlPrimary).MaximumScale = Round(2 * Application.Max(ws_od.Range(Cells(3,
2).Address, Cells(lastrow, 2).Address)) + 0.5, 0)
        '
        .Axes(xlValue, xlSecondary).MinimumScale = 0
        .Axes(xlValue, xlSecondary).MaximumScale = Round(2 * Application.Max(ws_od.Range(Cells(3,
2).Address, Cells(lastrow, 2).Address)) + 0.5, 0)
        '
    End With
End Sub
‘-----------------------------------------------------------------------------------------------------------------------
```

Appendix 6. Statistical indexes module

The small time step statistical code is shown here as a typical code. It is used when the outputs are small time steps that generated in “output” sheet of the SPEC.

```
‘-----------------------------------------------------------------------------------------------------------------------
Option Explicit
Sub Statistics_sts()
    Application.ScreenUpdating = False
    Dim StartTime, SecondsElapsed As Double
    Dim ws_i, ws_obs, ws_o, ws_M As Worksheet
    Dim n As Double ' number of soil layers
    Dim i, k, spd As Double
    Dim Sim_op, RC As String
    '
    Set ws_i = Sheets("RUN")
    Set ws_obs = Sheets("Obs_Data")
    Set ws_o = Sheets("Output")
    '
```

```
   Sim_op = ws_i.Range("_sim_op").Text
   RC = ws_i.Range("_RO_op")
   n = ws_i.Range("_n")
   Dim n_col1, n_col2, n_col3 As Integer ' No of cols in obs runoff; WC and pst in soil data
   ' Check obs water contents exist
   If IsEmpty(ws_obs.Cells(3, 10)) = False Then
      n_col2 = Application.Count(ws_obs.Range(ws_obs.Cells(3, 10), ws_obs.Cells(3, 16)))
      Else
      n_col2 = 1
   End If
   ' Check obs Cs exist
   If ws_i.Cells(26, 5) = "Runoff & Pesticide" Then
      If IsEmpty(ws_obs.Cells(3, 18)) = False Then
         n_col3 = Application.Count(ws_obs.Range(ws_obs.Cells(3, 18), ws_obs.Cells(3, 24)))
      End If
   Else
      n_col3 = 1
   End If
   '
   spd = ws_i.Range("_spd")
'
StartTime = Timer
'
   Dim M_lk1() As Double   ' Matrix for all runoff outputs
   Dim M_lk2() As Double   ' Matrix for all water content outputs
   Dim M_lk3() As Double   ' Matrix for all soil Pst. conc. outputs
   Dim lastrow_o As Double
   ' Find lastrow of output data
   lastrow_o = ws_o.Cells(Rows.Count, 1).End(xlUp).Row - 2
   Dim M1() As Double  ' Matrix for observed runoff data
   Dim M2() As Double  ' Matrix for observed water content in soil layers
   Dim M3() As Double  ' Matrix for observed pesticide concentration in soil layers
   Dim lastrow1 As Double
   Dim lastrow2 As Double
   Dim lastrow3 As Double
   Dim M1o() As Double
   Dim M2o() As Double
   Dim M3o() As Double
   Dim X1avg() As Double
   Dim X2avg() As Double
   Dim X3avg() As Double
   Dim Y1avg() As Double
   Dim Y2avg() As Double
   Dim XY1() As Double
   Dim S_XY1() As Double
   Dim S_XX1() As Double
   Dim S_YY1() As Double
   Dim RMSE1() As Double
   Dim r1() As Double
   Dim NSE1() As Double
   Dim Bias1() As Double
   Dim XY2() As Double
   Dim S_XY2() As Double
```

```
    Dim S_XX2() As Double
    Dim S_YY2() As Double
    Dim RMSE2() As Double
    Dim r2() As Double
    Dim NSE2() As Double
    Dim Bias2() As Double
    Dim XY3() As Double
    Dim S_XY3() As Double
    Dim S_XX3() As Double
    Dim S_YY3() As Double
    Dim RMSE3() As Double
    Dim r3() As Double
    Dim NSE3() As Double
    Dim Bias3() As Double
'
' 1. Write all required for lookup tables
'

        ' Write lookup table for runoff
        If RC = "On" Then   ' If runoff simulation is allowed
            If IsEmpty(ws_obs.Cells(3, 1)) = False Then
                If Sim_op = "Runoff" Then
                    n_col1 = Application.Count(ws_obs.Range(ws_obs.Cells(3, 1), ws_obs.Cells(3, 5)))
                Else
                    n_col1 = Application.Count(ws_obs.Range(ws_obs.Cells(3, 1), ws_obs.Cells(3, 7)))
                End If
            '
            ReDim M_lk1(1 To lastrow_o, 1 To n_col1)
                If n_col1 >= 3 Then
                    For i = 1 To lastrow_o
                    ' Column for Time for runoff output data
                        M_lk1(i, 1) = Round(ws_o.Cells(2 + i, 1), 7)
                    ' Column for time step runoff, dQ (mm/h)
                        M_lk1(i, 2) = Round(ws_o.Cells(2 + i, 9), 7)
                    ' Column for cumulative runoff, Q (mm)
                        M_lk1(i, 3) = Round(ws_o.Cells(2 + i, 4), 7)
                    Next i
                End If
                '
                If n_col1 >= 5 Then
                    For i = 1 To lastrow_o
                    ' Column for Sediment concentration (g/L)
                        M_lk1(i, 4) = Round(ws_o.Cells(2 + i, 10), 7)
                    ' Column for Cumulative Sediment
                        M_lk1(i, 5) = Round(ws_o.Cells(2 + i, 11), 7)
                    Next i
                End If
                '
                If Sim_op = "Runoff & Pesticide" Then
                    If n_col1 >= 7 Then
                        For i = 1 To lastrow_o
                        ' Column for Pesticide concentration in runoff water (mg/L)
                            M_lk1(i, 6) = Round(ws_o.Cells(2 + i, 13 + n), 7)
```

```
            ' Column for pst concentration in sediment (mg/kg)
               M_lk1(i, 7) = Round(ws_o.Cells(2 + i, 14 + n), 7)
            Next i
         End If
      End If
   End If
End If
'
' Write lookup table for water content
If n_col2 >= 2 Then
   ReDim M_lk2(1 To lastrow_o, 1 To n_col2)
   For i = 1 To lastrow_o
   ' Column for Time for water content output data
      M_lk2(i, 1) = Round(ws_o.Cells(2 + i, 1), 7)
   ' Column for Samp. water content (mm3/mm3)
      M_lk2(i, 2) = Round(ws_o.Cells(2 + i, 12), 7)
   Next i
End If
'
If n_col2 >= 3 Then
   ' Columns for Water content in soil layers
   For i = 1 To lastrow_o
      For k = 1 To n_col2 - 2
         M_lk2(i, 2 + k) = Round(ws_o.Cells(2 + i, 12 + k), 7)
      Next k
   Next i
End If
'
' Write lookup table for pesticide concentration in soil
If Sim_op = "Runoff & Pesticide" Then
   If n_col3 >= 2 Then
         ReDim M_lk3(1 To lastrow_o, 1 To n_col3)
      For i = 1 To lastrow_o
         ' Column for Time for Cs output data
            M_lk3(i, 1) = Round(ws_o.Cells(2 + i, 1), 7)
         ' Column for average Cs (mg/kg)
            M_lk3(i, 2) = Round(ws_o.Cells(2 + i, 15 + n), 7)
      Next i
   End If
   '
   If n_col3 >= 3 Then
      For i = 1 To lastrow_o
      ' Columns for Csi (mg/kg)
         For k = 1 To n_col3 - 2
            M_lk3(i, 2 + k) = Round(ws_o.Cells(2 + i, 15 + n + k), 7)
         Next k
      Next i
   End If
End If
‘--------------------------------------------------------------------------------------------------------------------------------
```

Appendix 7. Monte Carlo simulations module

The typical code created for Monte Carlo simulation of Water content is shown as below,

```
‘-----------------------------------------------------------------------------------------------------------------------
Option Explicit
' For Water content in specific soil layer
Sub MonteCarlo1_WC()
    Application.ScreenUpdating = False
    Dim ws_i, ws_r, ws_o, ws_od, ws_obs, ws_MC As Worksheet
    Dim n, i, j, jj, k, Output_op, r_o_sta, la_order As Single
    Dim CN0, low_CN, high_CN, lambdai, low_lambda, high_lambda As Single
    Dim Per1, Per2, Per3, Per4, Per5 As Single
    Dim Max_NSE, WCs_op, WCr_op, WCf_op, Ks_op, CN_op, lambda_op, WC0_op As Single
    Dim T_ts, ts, n_MC, WCsi, WCri, WCfi, Ksi, WC0i As Double

    Dim StartTime, SecondsElapsed As Double
    Dim Sens_op, MC_WC_op, MC_WC_ts, OPts As String
    '
    Set ws_i = Worksheets("RUN")
    Set ws_r = Worksheets("Report")
    Set ws_o = Worksheets("Output")
    Set ws_od = Worksheets("Output_D")
    Set ws_obs = Worksheets("Obs_Data")
    Set ws_MC = Worksheets("MC_WC")
    '
 StartTime = Timer
    '
    ws_MC.Cells.ClearContents
    ws_i.Activate
    Cells(26, 5) = "Runoff"
    '
    If IsEmpty(ws_obs.Cells(3, 10)) Then
        MsgBox "Observed water content data are not available"
        Exit Sub
    End If
    '
    ' Monte Carlo Information
    ' Number of runs
        n_MC = Range("_n_MC")
    ' Number of layers
        n = ws_i.Range("_n")
        r_o_sta = 43 + n
    ' Option for input parameters
        Output_op = Range("_MC_op")
        MC_WC_op = Range("_MC_WC_op")
        MC_WC_ts = Range("_MC_WC_ts")
        OPts = Range("_OPts") ' Output time step
        '
        If OPts = "1-minute" Then
            ts = 1
            ElseIf OPts = "2-minute" Then
                ts = 2
            ElseIf OPts = "5-minute" Then
```

```
        ts = 5
      ElseIf OPts = "10-minute" Then
        ts = 10
      ElseIf OPts = "30-minute" Then
        ts = 30
      Else
        ts = 60
    End If

' Number of days or total time steps (for small ts)
    If MC_WC_ts = "Daily" Then
      T_ts = ws_i.Range("_duration")
    Else
      T_ts = ws_i.Range("_duration") * 24 * 60 / ts
    End If
    '
    If MC_WC_op = "spd" Then
      la_order = 0
    ElseIf MC_WC_op = "1" Then
      la_order = 1
    ElseIf MC_WC_op = "2" Then
      la_order = 2
    ElseIf MC_WC_op = "3" Then
      la_order = 3
    ElseIf MC_WC_op = "4" Then
      la_order = 4
    ElseIf MC_WC_op = "5" Then
      la_order = 5
    End If

' percent change from initial parameter
    Per1 = Range("_per_WCs") / 100 ' For saturated WC
    Per2 = Range("_per_WCr") / 100 ' For residual WC
    Per3 = Range("_per_WCf") / 100 ' For field capacity WC
    Per4 = Range("_per_Ks") / 100 ' For saturated hydraulic conductivity
    Per5 = Range("_per_WC0") / 100 ' For initial water content
' lower and upper values for CN and lambda
    low_CN = Range("_min_CN")
    high_CN = Range("_max_CN")
    low_lambda = Range("_min_lambda")
    high_lambda = Range("_max_lambda")

' Read intial paramaters
    WCsi = Cells(65, 4)
    WCri = Cells(66, 4)
    WCfi = Cells(63, 4)
    Ksi = Cells(67, 4)
    WC0i = Cells(72, 4)
'
' Variables for Monte Carlo
    Dim WCs() As Double
    Dim WCr() As Double
    Dim WCf() As Double
```

```
        Dim Ks() As Double
        Dim CN() As Double
        Dim lambda() As Double
        Dim WC0() As Double
        Dim Avg_Para() As Double
        '
        ReDim WCs(1 To n_MC, 1 To 1) As Double
        ReDim WCr(1 To n_MC, 1 To 1) As Double
        ReDim WCf(1 To n_MC, 1 To 1) As Double
        ReDim Ks(1 To n_MC, 1 To 1) As Double
        ReDim CN(1 To n_MC, 1 To 1) As Double
        ReDim lambda(1 To n_MC, 1 To 1) As Double
        ReDim WC0(1 To n_MC, 1 To 1) As Double
        ReDim Avg_Para(1 To 7, 1 To 1) As Double
        '
        Dim M1() As Double      ' Input parameters
        ReDim M1(1 To 12, 1 To n_MC) As Double
        '
        Dim M2() As Double      ' Outputs
        ReDim M2(1 To T_ts, 1 To n_MC) As Double
        '
        Dim T() As Double       ' Time
        ReDim T(1 To T_ts, 1 To 1) As Double
        '
        Dim MLH_Para() As Double   ' Statistical indexs of input parameters
        ReDim MLH_Para(1 To 12, 1 To 4) As Double
        '
        Dim M_NSE() As Double      ' Lookup of input parameters
        ReDim M_NSE(1 To 9, 1 To n_MC) As Double
        '
        Dim MLH_output() As Double          ' Statistical indexs of outputs
        ReDim MLH_output(1 To T_ts, 1 To 4) As Double
   '
    For j = 1 To n_MC
        WCs(j, 1) = Round(Application.RandBetween((1 - Per1) * WCsi * 10 ^ 6, (1 + Per1) * WCsi * 10 ^ 6) /
10 ^ 6, 2)
        WCr(j, 1) = Round(Application.RandBetween((1 - Per2) * WCri * 10 ^ 6, (1 + Per2) * WCri * 10 ^ 6) /
10 ^ 6, 2)
        WCf(j, 1) = Round(Application.RandBetween((1 - Per3) * WCfi * 10 ^ 6, (1 + Per3) * WCfi * 10 ^ 6) /
10 ^ 6, 2)
        Ks(j, 1) = Round(Application.RandBetween((1 - Per4) * Ksi * 10 ^ 6, (1 + Per4) * Ksi * 10 ^ 6) / 10 ^
6, 2)
        WC0(j, 1) = Round(Application.RandBetween((1 - Per5) * WC0i * 10 ^ 6, (1 + Per5) * WC0i * 10 ^ 6)
/ 10 ^ 6, 2)
        '
        CN(j, 1) = Round(Application.RandBetween(low_CN, high_CN), 0)
        lambda(j, 1) = Round(Application.RandBetween(100 * low_lambda, 100 * high_lambda) / 100, 2)
        '
        ' Write papameters to RUN sheet
        For k = 1 To n
            ws_i.Cells(65, 3 + k) = WCs(j, 1)
            ws_i.Cells(66, 3 + k) = WCr(j, 1)
            ws_i.Cells(63, 3 + k) = WCf(j, 1)
```

```
        ws_i.Cells(67, 3 + k) = Ks(j, 1)
    Next k
    '
    ws_i.Cells(31, 5) = CN(j, 1)
    ws_i.Cells(33, 5) = lambda(j, 1)
    '
    Call Main_code
    Call Sta_WC
    '
    ' Write parameters to M1 array
        M1(6, j) = WCs(j, 1)
        M1(7, j) = WCr(j, 1)
        M1(8, j) = WCf(j, 1)
        M1(9, j) = Ks(j, 1)
        M1(10, j) = CN(j, 1)
        M1(11, j) = lambda(j, 1)
        M1(12, j) = WC0(j, 1)
        '
        ' read 5 statistic indexes of WC
            M1(1, j) = ws_r.Cells(r_o_sta + 1 + la_order, 4)
            M1(2, j) = ws_r.Cells(r_o_sta + 1 + la_order, 5)
            M1(3, j) = ws_r.Cells(r_o_sta + 1 + la_order, 6)
            M1(4, j) = ws_r.Cells(r_o_sta + 1 + la_order, 7)
            M1(5, j) = ws_r.Cells(r_o_sta + 1 + la_order, 8)
        '
        ' read WC
            If MC_WC_ts = "Daily" Then  ' Daily WC
                For jj = 1 To T_ts
                    M2(jj, j) = ws_od.Cells(2 + jj, 6 + la_order)
                Next jj

            Else                        ' small ts WC
                For jj = 1 To T_ts
                    M2(jj, j) = ws_o.Cells(2 + jj, 12 + la_order)
                Next jj

            End If
Next j
    ' Create Matrix for NSE lookup
        For i = 1 To 9  ' 9 rows
            For j = 1 To n_MC
                M_NSE(i, j) = M1(i + 3, j)
            Next j
        Next i
    '
    If MC_WC_ts = "Daily" Then
        ' read daily times
            For jj = 1 To T_ts
                T(jj, 1) = ws_od.Cells(2 + jj, 1)
            Next jj
    Else
        ' read small ts times
            For jj = 1 To T_ts
```

```
            T(jj, 1) = ws_o.Cells(2 + jj, 1)
        Next jj
    End If
    '
    With Application
        '
        ' Mean, Low, High, Median values of 5 statistical indexes and 7 parameters
            For i = 1 To 12
                MLH_Para(i, 1) = .Average(.index(M1, i, 0))
                MLH_Para(i, 2) = .Percentile(.index(M1, i, 0), 0.05)
                MLH_Para(i, 3) = .Percentile(.index(M1, i, 0), 0.95)
                MLH_Para(i, 4) = .Percentile(.index(M1, i, 0), 0.5)
            Next i
        '
        ' Mean, Low, High, Median values of outputs
            For i = 1 To T_ts
                On Error GoTo 1
                MLH_output(i, 1) = .Average(.index(M2, i, 0))
                MLH_output(i, 2) = .Percentile(.index(M2, i, 0), 0.05)
                MLH_output(i, 3) = .Percentile(.index(M2, i, 0), 0.95)
                MLH_output(i, 4) = .Percentile(.index(M2, i, 0), 0.5)
            Next i
1
        '
        ' Find optimal parameters
            Max_NSE = .Max(.index(M_NSE, 1, 0))
            WCs_op = .HLookup(Max_NSE, M_NSE, 3, 0)
            WCr_op = .HLookup(Max_NSE, M_NSE, 4, 0)
            WCf_op = .HLookup(Max_NSE, M_NSE, 5, 0)
            Ks_op = .HLookup(Max_NSE, M_NSE, 6, 0)
            CN_op = .HLookup(Max_NSE, M_NSE, 7, 0)
            lambda_op = .HLookup(Max_NSE, M_NSE, 8, 0)
            WC0_op = .HLookup(Max_NSE, M_NSE, 9, 0)
    End With
    '
    ws_MC.Activate
    '
    ' Write results
        Range(Cells(3, 7), Cells(14, n_MC + 6)) = M1
        Range(Cells(3, 3), Cells(14, 6)) = MLH_Para
        Range(Cells(21, 6), Cells(T_ts + 20, n_MC + 5)) = M2
        Range(Cells(21, 2), Cells(T_ts + 20, 5)) = MLH_output
        Range(Cells(21, 1), Cells(T_ts + 20, 1)) = T

        If MC_WC_ts = "Daily" Then
            Range(Cells(21, 1), Cells(20 + T_ts, 1)).NumberFormat = "mm/dd/yyyy"
        Else
            Range(Cells(21, 1), Cells(20 + T_ts, 1)).NumberFormat = "mm/dd/yyyy hh:mm"
        End If
    '
    ' Write optimal parameters
        Cells(6, 2) = Max_NSE
        Cells(8, 2) = WCs_op
```

```
   Cells(9, 2) = WCr_op
   Cells(10, 2) = WCf_op
   Cells(11, 2) = Ks_op
   Cells(12, 2) = CN_op
   Cells(13, 2) = lambda_op
   Cells(14, 2) = WC0_op
'
' Write optimal paramters to RUN sheet
ws_i.Activate
   If Output_op = 1 Then   ' Optimal value
      Cells(31, 5) = Round(CN_op, 0)
      Cells(33, 5) = Round(lambda_op, 2)
      '
      For i = 1 To n
         Cells(65, 3 + i) = Round(WCs_op, 2)
         Cells(66, 3 + i) = Round(WCr_op, 2)
         Cells(63, 3 + i) = Round(WCf_op, 2)
         Cells(67, 3 + i) = Round(Ks_op, 2)
         Cells(72, 3 + i) = Round(WC0_op, 2)
      Next i
   Else    ' average value
      Cells(31, 5) = Round(MLH_Para(10, 1), 0) ' CN
      Cells(33, 5) = Round(MLH_Para(11, 1), 2) 'lambda
      '
      For i = 1 To n
         Cells(65, 3 + i) = Round(MLH_Para(6, 1), 2) 'WCs
         Cells(66, 3 + i) = Round(MLH_Para(7, 1), 2) 'WCr
         Cells(63, 3 + i) = Round(MLH_Para(8, 1), 2) 'WCf
         Cells(67, 3 + i) = Round(MLH_Para(9, 1), 2) ' Ks
         Cells(72, 3 + i) = Round(MLH_Para(12, 1), 2) ' WC0
      Next i
   End If
'
ws_MC.Activate
'
' Write Label
   Cells(1, 1) = "Monte Carlo for Samp. water content results"
   Cells(2, 2) = "Optimal"
   Cells(2, 3) = "Mean"
   Cells(2, 4) = "Low"
   Cells(2, 5) = "High"
   Cells(2, 6) = "Median"
   Cells(2, 7) = "Monte Carlo values"
   Cells(2, 7 + n_MC) = "Initial value"
   Cells(3, 1) = "Sim. Mean"
   Cells(4, 1) = "RMSE (%)"
   Cells(5, 1) = "R² (-)"
   Cells(6, 1) = "NSE (-)"
   Cells(7, 1) = "PBIAS (%)"
   Cells(8, 1) = "WCs"
   Cells(9, 1) = "WCr"
   Cells(10, 1) = "WCf"
   Cells(11, 1) = "Ks"
```

```
         Cells(12, 1) = "CN"
         Cells(13, 1) = "lambda"
         Cells(14, 1) = "WC0"

         Cells(20, 1) = "Time"
         Cells(20, 2) = "Mean WC"
         Cells(20, 3) = "Low WC"
         Cells(20, 4) = "High WC"
         Cells(20, 5) = "Median WC"
         Cells(20, 6) = "Samp. water content"
      SecondsElapsed = Round(Timer - StartTime, 2)
      MsgBox "Monte Carlo Simulation for WC is completed in " & SecondsElapsed & " seconds",
vbInformation
   Application.ScreenUpdating = True
End Sub
‘--------------------------------------------------------------------------------------------------------------------------
```

Appendix 8. Supported module

This module for writing labels, creating output for single event, copying data to SPEC model, creating functions is shown as below,

```
‘--------------------------------------------------------------------------------------------------------------------------
Option Explicit
' Lables for SPEC outputs
Sub Label()
      Dim ws_sts, ws_h, ws_d, ws_i, ws_o, ws_od, ws_gr, ws_obs, ws_rp As Worksheet
      Dim OPtsText, Sim_op As String
      Dim i, n, lastrow_o, lastrow_od, fr_rp As Double
      '
      Set ws_sts = Worksheets("Small_TS")
      Set ws_h = Worksheets("Hourly")
      Set ws_d = Worksheets("Daily")
      Set ws_i = Worksheets("RUN")
      Set ws_o = Worksheets("Output")
      Set ws_od = Worksheets("Output_D")
      Set ws_rp = Worksheets("Report")
      Set ws_gr = Worksheets("Graph")
      Set ws_obs = Worksheets("Obs_Data")
      '
      ' Last rows
      lastrow_o = ws_o.Cells(3, 1).End(xlDown).Row
      lastrow_od = ws_od.Cells(3, 1).End(xlDown).Row
      '
      n = ws_i.Range("_n")
      OPtsText = ws_i.Range("_OPts")
      Sim_op = ws_i.Range("_sim_op").Text
' 1. Write Labels in Ouput sheet
      ws_o.Activate
         If Sim_op = "Runoff & Pesticide" Then
               ws_o.Cells(2, 13 + n) = "Crw_pst (" & ChrW(956) & "g/L)"
               ws_o.Cells(2, 14 + n) = "C_sed_pst (mg/kg)"
               ws_o.Cells(2, 15 + n) = "Samp. avg. Cs (mg/kg)"
            For i = 1 To n
               ws_o.Cells(2, 15 + n + i) = "Cs" & i & " (mg/kg)"
               ws_o.Cells(2, 15 + 2 * n + i) = "Mds" & i & " (mg)"
```

```
               ws_o.Cells(2, 15 + 3 * n + i) = "Msw" & i & " (mg)"
               ws_o.Cells(2, 15 + 4 * n + i) = "Mbio" & i & " (mg)"
               ws_o.Cells(2, 15 + 5 * n + i) = "Mper" & i & " (mg)"
               ws_o.Cells(2, 19 + 6 * n + i) = "MEr" & i & " (%)"
            Next i
               ws_o.Cells(2, 16 + 6 * n) = "Mrw_pst (mg)"
               ws_o.Cells(2, 17 + 6 * n) = "Msed_pst (mg)"
               ws_o.Cells(2, 18 + 6 * n) = "Mpho (mg)"
               ws_o.Cells(2, 19 + 6 * n) = "Mvol (mg)"
         End If
      ' Label sheet title
            ws_o.Cells(1, 1).Value = OPtsText & " output"
            ws_o.Cells(1, 1).Font.Bold = True
            ws_o.Cells(1, 1).Font.Color = RGB(0, 176, 80)
            ws_o.Cells(1, 1).Font.Size = 16
      ' Label row title
            ws_o.Cells(2, 1) = "Time"
            ws_o.Cells(2, 2) = "Rainfall (mm)"
            ws_o.Cells(2, 3) = "Cum. rainfall (mm)"
            ws_o.Cells(2, 4) = "Cum. runoff (mm)"
            ws_o.Cells(2, 5) = "Runoff (mm)"
            ws_o.Cells(2, 6) = "Cum. infiltration (mm)"
            ws_o.Cells(2, 7) = "Infiltration (mm)"
            ws_o.Cells(2, 8) = "Rainfall (mm/h)"
            ws_o.Cells(2, 9) = "Runoff (mm/h)"
            ws_o.Cells(2, 10) = "Sed. conc. (g/L)"
            ws_o.Cells(2, 11) = "Sed. yield (g)"
            ws_o.Cells(2, 12) = "Samp. avg. " & ChrW(952) & " (mm³/mm³)"
         '
         For i = 1 To n
            ws_o.Cells(2, 12 + i) = ChrW(952) & i & " (mm³/mm³)"
         Next i
      '
      ' Format row title
               ws_o.Range(Cells(2, 1), Cells(2, 19 + 7 * n)).WrapText = True
               ws_o.Range(Cells(2, 1), Cells(2, 19 + 7 * n)).Font.Bold = True
               ws_o.Range(Cells(2, 1), Cells(2, 19 + 7 * n)).HorizontalAlignment = xlCenter
               ws_o.Range(Cells(2, 1), Cells(2, 19 + 7 * n)).VerticalAlignment = xlTop
               '
               ' Font size for all outputs
               ws_o.Range(Cells(2, 1), Cells(lastrow_o, 19 + 7 * n)).Font.Size = 8
               ws_o.Range(Cells(2, 1), Cells(2, 19 + 7 * n)).Rows.AutoFit
               ws_o.Range(Cells(2, 1), Cells(lastrow_o, 1)).ColumnWidth = 13
               ws_o.Range(Cells(2, 2), Cells(lastrow_o, 19 + 7 * n)).ColumnWidth = 7
               ws_o.Range(Cells(2, 6), Cells(lastrow_o, 7)).ColumnWidth = 8
               ws_o.Range(Cells(2, 12), Cells(lastrow_o, 12 + n)).ColumnWidth = 8
'
' 2. Write Labels in OuputD sheet
      ws_od.Activate
         If Sim_op = "Runoff & Pesticide" Then
               ws_od.Cells(2, 7 + n).Value = "Crw_pst (" & ChrW(956) & "g/L)"
               ws_od.Cells(2, 8 + n).Value = "Csed_pst (mg/kg)"
               ws_od.Cells(2, 9 + n).Value = "Samp. avg. Cs (mg/kg)"
```

```
        For i = 1 To n
          ws_od.Cells(2, 9 + n + i) = "Cs" & i & " (mg/kg)"
        Next i
          ws_od.Cells(2, 10 + 2 * n).Value = "Mrw_pst (mg)"
          ws_od.Cells(2, 11 + 2 * n).Value = "Msed_pst (mg)"
      End If
    '
    ' Label Title
      ws_od.Cells(1, 1).Value = "Daily output"
      ws_od.Cells(1, 1).Font.Bold = True
      ws_od.Cells(1, 1).Font.Color = RGB(0, 176, 80)
      ws_od.Cells(1, 1).Font.Size = 16
    '
    ' Label first row
      ws_od.Cells(2, 1).Value = "Date"
      ws_od.Cells(2, 2).Value = "Rainfall (mm)"
      ws_od.Cells(2, 3).Value = "Runoff (mm)"
      ws_od.Cells(2, 4).Value = "Sed. conc. (g/L)"
      ws_od.Cells(2, 5).Value = "Sed. yield (g)"
      ws_od.Cells(2, 6).Value = "Samp. avg. " & ChrW(952) & " (mm³/mm³)"
    '
    For i = 1 To n
      ws_od.Cells(2, 6 + i) = ChrW(952) & i & " (mm³/mm³)"
    Next i
    '
    ' Format row title
      ws_od.Range(Cells(2, 1), Cells(2, 11 + 2 * n)).WrapText = True
      ws_od.Range(Cells(2, 1), Cells(2, 11 + 2 * n)).Font.Bold = True
      ws_od.Range(Cells(2, 1), Cells(2, 11 + 2 * n)).HorizontalAlignment = xlCenter
      ws_od.Range(Cells(2, 1), Cells(2, 11 + 2 * n)).VerticalAlignment = xlTop
    '
    ' Font size & Border outputs
      ws_od.Range(Cells(2, 1), Cells(lastrow_od, 11 + 2 * n)).Font.Size = 8
      ws_od.Range(Cells(2, 1), Cells(2, 11 + 2 * n)).Rows.AutoFit
      ws_od.Range(Cells(2, 1), Cells(lastrow_od, 1)).ColumnWidth = 9
      ws_od.Range(Cells(2, 2), Cells(lastrow_od, 11 + 2 * n)).ColumnWidth = 7
      ws_od.Range(Cells(2, 6), Cells(lastrow_od, 6 + n)).ColumnWidth = 8
'
' 3. Write Labels in Report sheet
    fr_rp = 5           ' first row's position for "Report" sheet
    ws_rp.Activate
        ws_rp.Cells(1, 1).Value = "SPEC REPORT SUMMARY"
        ws_rp.Cells(fr_rp - 2, 1).Value = "General information"
        ws_rp.Cells(fr_rp - 1, 1).Value = "Pesticide and location"
        ws_rp.Cells(fr_rp + 0, 1).Value = "Textural class"
        ws_rp.Cells(fr_rp + 1, 1).Value = "Starting day of simulation"
        ws_rp.Cells(fr_rp + 2, 1).Value = "Ending day of simulation"
        ws_rp.Cells(fr_rp + 3, 1).Value = "Output time step"
        ws_rp.Cells(fr_rp + 5, 1).Value = "Dataset"
        ws_rp.Cells(fr_rp + 5, 3).Value = "time step"
        ws_rp.Cells(fr_rp + 6, 1).Value = "Rainfall"
        ws_rp.Cells(fr_rp + 7, 1).Value = "Temperature"
        ws_rp.Cells(fr_rp + 8, 1).Value = "Evapotranspiration"
```

```
    ws_rp.Cells(fr_rp + 9, 1).Value = "Solar radiation"
    ws_rp.Cells(fr_rp + 11, 1) = "Simulation option"
    ws_rp.Cells(fr_rp + 11, 3) = Range("_Sim_op")
    ws_rp.Cells(fr_rp + 12, 1) = "Runoff control"
    ws_rp.Cells(fr_rp + 12, 3) = Range("_RO_op")
    ws_rp.Cells(fr_rp + 13, 1) = "Use CN constant?"
    ws_rp.Cells(fr_rp + 13, 3) = Range("_CN_op")
    ws_rp.Cells(fr_rp + 15, 1).Value = "Soil layer"
    ws_rp.Cells(fr_rp + 16, 2).Value = "Value"
    ws_rp.Cells(fr_rp + 16, 3).Value = "Unit"
    ws_rp.Cells(fr_rp + 17, 1).Value = "Number of layers"
    ws_rp.Cells(fr_rp + 18, 1).Value = "Total depth"
    ws_rp.Cells(fr_rp + 17, 3).Value = "layer"
    ws_rp.Cells(fr_rp + 18, 3).Value = "mm"
'
For i = 1 To n
    ws_rp.Cells(fr_rp + 18 + i, 1).Value = "Layer " & i & "'s depth"
    ws_rp.Cells(fr_rp + 18 + i, 3).Value = "mm"
Next i
    ws_rp.Cells(fr_rp + n + 20, 1) = "Calibrated parameters"
    ws_rp.Cells(fr_rp + n + 20, 2) = "Value"
    ws_rp.Cells(fr_rp + n + 20, 3) = "Unit"
    ws_rp.Cells(fr_rp + n + 21, 1) = "Runoff"
    ws_rp.Cells(fr_rp + n + 22, 1) = "lambda"
    ws_rp.Cells(fr_rp + n + 22, 2) = Range("_lambda")
    ws_rp.Cells(fr_rp + n + 22, 3) = "-"
    ws_rp.Cells(fr_rp + n + 23, 1) = "Initial CN"
    ws_rp.Cells(fr_rp + n + 23, 2) = Range("_CN2")
    ws_rp.Cells(fr_rp + n + 23, 3) = "-"
    ws_rp.Cells(fr_rp + n + 24, 1) = "Final CN"
    ws_rp.Cells(fr_rp + n + 24, 3) = "-"
    ws_rp.Cells(fr_rp + n + 25, 1) = "Sediment"
    ws_rp.Cells(fr_rp + n + 26, 1) = "K_MULSE_coef"
    ws_rp.Cells(fr_rp + n + 27, 1) = "K_MULSE"
    ws_rp.Cells(fr_rp + n + 26, 2) = Range("_K_coef")
    ws_rp.Cells(fr_rp + n + 26, 3) = "-"
    ws_rp.Cells(fr_rp + n + 27, 3) = "0.01 ton.acre.h/(acre.ft-ton.in)"
    ws_rp.Cells(fr_rp + n + 28, 1) = "Pesticide"
    ws_rp.Cells(fr_rp + n + 29, 1).Value = "Q10"
    ws_rp.Cells(fr_rp + n + 30, 1).Value = "HLpho"
    ws_rp.Cells(fr_rp + n + 31, 1).Value = "HLbio"
    ws_rp.Cells(fr_rp + n + 32, 1).Value = "Koc"
    ws_rp.Cells(fr_rp + n + 33, 1).Value = "e_coef"
    ws_rp.Cells(fr_rp + n + 34, 1).Value = ChrW(&H3B1)
    ws_rp.Cells(fr_rp + n + 35, 1).Value = ChrW(&H3B2)
    ws_rp.Cells(fr_rp + n + 33, 2).Value = Range("_e_coef")
    ws_rp.Cells(fr_rp + n + 34, 2).Value = Range("_alpha")
    ws_rp.Cells(fr_rp + n + 35, 2).Value = Range("_beta")
'
If Sim_op = "Runoff & Pesticide" Then
    ws_rp.Cells(fr_rp + n + 29, 3).Value = "-"
    ws_rp.Cells(fr_rp + n + 30, 3).Value = "d"
    ws_rp.Cells(fr_rp + n + 31, 3).Value = "d"
```

```
    ws_rp.Cells(fr_rp + n + 32, 3).Value = "L/kg"
    ws_rp.Cells(fr_rp + n + 33, 3).Value = "-"
    ws_rp.Cells(fr_rp + n + 34, 3).Value = "-"
    ws_rp.Cells(fr_rp + n + 35, 3).Value = "-"
End If
'
    ws_rp.Cells(fr_rp + n + 37, 1).Value = "Model performance"
    ws_rp.Cells(fr_rp + n + 38, 1).Value = "Output"
    ws_rp.Cells(fr_rp + n + 38, 2).Value = "Unit"
    ws_rp.Cells(fr_rp + n + 38, 3).Value = "Obs. mean"
    ws_rp.Cells(fr_rp + n + 38, 4).Value = "Sim. mean"
    ws_rp.Cells(fr_rp + n + 38, 5).Value = "RMSE (%)"
    ws_rp.Cells(fr_rp + n + 38, 6).Value = "R² (-)"
    ws_rp.Cells(fr_rp + n + 38, 7).Value = "NSE (-)"
    ws_rp.Cells(fr_rp + n + 38, 8).Value = "PBIAS (%)"
    ' Clear comments
    ws_rp.Cells(fr_rp + n + 38, 5).ClearComments
    ws_rp.Cells(fr_rp + n + 38, 6).ClearComments
    ws_rp.Cells(fr_rp + n + 38, 7).ClearComments
    ws_rp.Cells(fr_rp + n + 38, 8).ClearComments
    ' Add comments
    ws_rp.Cells(fr_rp + n + 38, 5).AddComment "Root Mean Squared Error"
    ws_rp.Cells(fr_rp + n + 38, 6).AddComment "Coefficient of determination(R²)"
    ws_rp.Cells(fr_rp + n + 38, 7).AddComment "Nash - Sutcliffe Efficiency"
    ws_rp.Cells(fr_rp + n + 38, 8).AddComment "Percent Bias"
Dim xComment As Comment
    For Each xComment In Application.ActiveSheet.Comments
        xComment.Shape.TextFrame.AutoSize = True
    Next
    '
    ' Bold cells
        ws_rp.Cells(1, 1).Font.Bold = True
        ws_rp.Cells(fr_rp - 2, 1).Font.Bold = True
        ws_rp.Range(Cells(fr_rp + 5, 1), Cells(fr_rp + 5, 3)).Font.Bold = True
        ws_rp.Cells(fr_rp + 11, 1).Font.Bold = True
        ws_rp.Range(Cells(fr_rp + 15, 1), Cells(fr_rp + 16, 3)).Font.Bold = True
        ws_rp.Range(Cells(fr_rp + n + 20, 1), Cells(fr_rp + n + 20, 3)).Font.Bold = True
        ws_rp.Range(Cells(fr_rp + n + 37, 1), Cells(fr_rp + n + 38, 8)).Font.Bold = True
    '
    ' Alignment cells
        ws_rp.Range(Cells(fr_rp + 3, 3), Cells(fr_rp + n + 35, 7)).HorizontalAlignment = xlCenter
        ws_rp.Cells(fr_rp + 16, 2).HorizontalAlignment = xlCenter
        ws_rp.Range(Cells(fr_rp + n + 38, 2), Cells(fr_rp + n + 38, 8)).HorizontalAlignment = xlCenter
        ws_rp.Cells(fr_rp + 11, 3).HorizontalAlignment = xlLeft
        ws_rp.Range(Cells(fr_rp + n + 22, 1), Cells(fr_rp + n + 35, 2)).HorizontalAlignment = xlRight
        ws_rp.Cells(fr_rp + n + 25, 1).HorizontalAlignment = xlLeft
        ws_rp.Cells(fr_rp + n + 28, 1).HorizontalAlignment = xlLeft
        ws_rp.Cells(fr_rp + n + 27, 3).HorizontalAlignment = xlLeft
    '
    ' Column Width
        ws_rp.Cells(1, 1).ColumnWidth = 23
        ws_rp.Cells(1, 2).ColumnWidth = 6
        ws_rp.Range(Cells(1, 3), Cells(1, 4)).ColumnWidth = 11
```

```
          ws_rp.Cells(1, 5).ColumnWidth = 9
          ws_rp.Range(Cells(1, 6), Cells(1, 8)).ColumnWidth = 8
        With ws_rp
          .Cells.Font.Size = 10
        End With
          ws_rp.Cells(1, 1).Font.Size = 14
'
' 4. Write Labels in Graph sheet
    ws_gr.Activate
      ws_gr.Cells(1, 1).Value = "SPEC REPORT IN CHARTS"
      ws_gr.Cells(1, 1).Font.Size = 14
      ws_gr.Cells(1, 1).Font.Bold = True
 End Sub
' Write Lookup values for single event
Sub Event_Lookup()
' Lookup runoff data for rainfall event
'
Application.ScreenUpdating = False
    Dim ws_i, ws_o, ws_obs, ws_rp, ws_o_event As Worksheet
    Dim OPtsText, Sim_op, RC As String
    Dim i, j, k, n, lastrow_o, lastrow1, duration As Double
    Dim o_col As Integer
    Set ws_i = Worksheets("RUN")
    Set ws_o = Worksheets("Output")
    Set ws_obs = Worksheets("Obs_Data")
    Set ws_rp = Worksheets("Report")
    Set ws_o_event = Worksheets("O_event")
    '
    n = ws_i.Range("_n")
    OPtsText = ws_i.Range("_OPts")
    Sim_op = ws_i.Range("_sim_op").Text
    RC = ws_i.Range("_RO_op")
    duration = ws_i.Range("_e_date") - ws_i.Range("_s_date")
    o_col = 0   ' offset columns in O_event
    '
    Dim n_col1, n_col2, n_col3, r_o_sta As Integer ' number of columns in observed runoff
    r_o_sta = 43 + n
    ' Check obs water contents exist
    If IsEmpty(ws_obs.Cells(3, 10)) = False Then
      n_col2 = Application.Count(ws_obs.Range(ws_obs.Cells(3, 10), ws_obs.Cells(3, 16)))
    Else
      n_col2 = 1
    End If
    ' Check obs Cs exist
    If IsEmpty(ws_obs.Cells(3, 18)) = False Then
      n_col3 = Application.Count(ws_obs.Range(ws_obs.Cells(3, 18), ws_obs.Cells(3, 24)))
    Else
      n_col3 = 1
    End If
    '
    Dim M_lookup() As Double    ' Matrix for required simulated data in runoff
    Dim M1() As Double          ' Matrix for observed data in runoff
    Dim M1o() As Double         ' Matrix for found simulated data in runoff
```

```
        Dim M1_col As Integer       ' Additional No of columns in Matrix 1 for pest conc in runoff and on sediment
        '
        If Sim_op = "Runoff" Then
            M1_col = 0
        Else
            M1_col = 2
        End If
        '
    If RC = "On" And duration = 1 And IsEmpty(ws_obs.Cells(3, 1)) = False Then    ' Lookup only when time in runoff differs to zero
            ' Find lastrow of output data, lastrow1 of obs data in runoff
            lastrow_o = ws_o.Cells(Rows.Count, 1).End(xlUp).Row - 2
            lastrow1 = ws_obs.Cells(Rows.Count, 1).End(xlUp).Row - 2
            '
            If lastrow_o = 0 Or lastrow1 = 0 Then
                Exit Sub
            End If
            '
                ReDim M_lookup(1 To lastrow_o, 1 To 7 + M1_col)
                ReDim M1(1 To lastrow1, 1 To 7)
                ReDim M1o(1 To lastrow1, 1 To 7 + M1_col) As Double
            '
            ' Write required simulated data from output sheet to Matrix M_lookup
            For i = 1 To lastrow_o
                ' Column for Time
                    M_lookup(i, 1) = Round(ws_o.Cells(2 + i, 1), 7)
                ' Column for rainfall (mm/h)
                    M_lookup(i, 2) = Round(ws_o.Cells(2 + i, 8), 7)
                ' Column for cumulative rainfall (mm)
                    M_lookup(i, 3) = Round(ws_o.Cells(2 + i, 3), 7)
                ' Column for time step runoff, dQ (mm/h)
                    M_lookup(i, 4) = Round(ws_o.Cells(2 + i, 9), 7)
                ' Column for cumulative runoff, Q (mm)
                    M_lookup(i, 5) = Round(ws_o.Cells(2 + i, 4), 7)
                ' Column for Sediment concentration (g/L)
                    M_lookup(i, 6) = Round(ws_o.Cells(2 + i, 10), 7)
                ' Column for Cumulative Sediment
                    M_lookup(i, 7) = Round(ws_o.Cells(2 + i, 11), 7)
                '
                If Sim_op = "Runoff & Pesticide" Then
                    ' Column for Pesticide concentration in runoff water (micro g/L)
                        M_lookup(i, 8) = Round(ws_o.Cells(2 + i, 13 + n), 7)
                    ' Column for Pest concentration on sediment (mg/kg)
                        M_lookup(i, 9) = Round(ws_o.Cells(2 + i, 14 + n), 7)
                End If
            Next i
            '
            ' Observed data in runoff
                For i = 1 To lastrow1
                    For k = 1 To 7
                        M1(i, k) = Round(ws_obs.Cells(2 + i, k), 7)
                    Next k
```

```
   Next i
' Look up simulated data
   With Application
      If RC = "On" And IsEmpty(ws_obs.Cells(3, 1)) = False Then
            For i = 1 To lastrow1
               For k = 1 To 7
                  M1o(i, k) = .VLookup(M1(i, 1), M_lookup, k, 0)
               Next k
               If M1_col <> 0 Then
                     M1o(i, 8) = .VLookup(M1(i, 1), M_lookup, 8, 0)
                     M1o(i, 9) = .VLookup(M1(i, 1), M_lookup, 9, 0)
               End If
            Next i
      End If
   End With
'
ws_o.Activate
   ' Find row order of starting rainfall
      Dim start_RF_row, sum_RF As Double
      Dim start_RO_row, sum_RO As Double
      Dim Time_RF_start, Time_RO_start As Double
      sum_RF = 0
   For j = 1 To lastrow_o
         sum_RF = sum_RF + Cells(2 + j, 2)
      If sum_RF = 0 Then
         start_RF_row = 2 + j
      End If
   Next j
   '
   Time_RF_start = Round(Cells(start_RF_row, 1), 9)
      '
      For j = 1 To lastrow_o
            sum_RO = sum_RO + Cells(2 + j, 4)
         If sum_RO = 0 Then
            start_RO_row = 3 + j
         End If
      Next j
   '
   Time_RO_start = Round(Cells(start_RO_row, 1), 9)
   ' Time for runoff event
      Dim Time_ro() As Double
      ReDim Time_ro(1 To lastrow1, 1 To 1) As Double
      Dim LapseTime0 As Double
      Dim LapseTime() As Double
      ReDim LapseTime(1 To lastrow1 + 2, 1 To 1) As Double
      Dim base_ro As Range
      '
      Set base_ro = ws_obs.Cells(2, 1)
      '
   For j = 1 To lastrow1
      Time_ro(j, 1) = Round(base_ro.Offset(j, 0), 9) 'Application.Text(base_ro.Offset(j, 0), "hh:mm")
   Next j
   '
```

```
      LapseTime0 = Time_RF_start
      LapseTime(1, 1) = 0
      LapseTime(2, 1) = Round((Time_RO_start - LapseTime0) * 1440, 0)
    For j = 1 To lastrow1
      LapseTime(j + 2, 1) = Round((Time_ro(j, 1) - LapseTime0) * 1440, 0)
    Next j
'
' Write found outputs in runoff to Obs_Data sheet
ws_o_event.Visible = xlSheetVisible
ws_o_event.Activate
  Cells(1, 1 + o_col) = "Runoff output for rainfall event only"
  'Range(Cells(1, 1 + o_col), Cells(1, 3 + o_col)).Interior.ColorIndex = 6
  Cells(2, 1 + o_col) = "Time"
  Cells(2, 2 + o_col) = "Rainfall (mm/h)"
  Cells(2, 3 + o_col) = "Cum. Rainfall (mm)"
  Cells(2, 4 + o_col) = "Obs. dQ (mm/h)"
  Cells(2, 5 + o_col) = "Sim. dQ (mm/h)"
  Cells(2, 6 + o_col) = "Obs. Q (mm)"
  Cells(2, 7 + o_col) = "Sim. Q (mm)"
  Cells(2, 8 + o_col) = "Obs. C_sed (g/L)"
  Cells(2, 9 + o_col) = "Sim. C_sed (g/L)"
  Cells(2, 10 + o_col) = "Obs. Sed (g)"
  Cells(2, 11 + o_col) = "Sim. Sed (g)"
  Cells(2, 12 + o_col) = "Obs. C_rw_pst (" & ChrW(956) & "g/L)"
  Cells(2, 13 + o_col) = "Sim. C_rw_pst (" & ChrW(956) & "g/L)"
  Cells(2, 14 + o_col) = "Obs. C_sed_pst (mg/kg)"
  Cells(2, 15 + o_col) = "Sim. C_sed_pst (mg/kg)"
' Row 3rd
  Cells(3, 2 + o_col) = 0
  Cells(3, 3 + o_col) = 0
  Cells(3, 5 + o_col) = 0
  Cells(3, 7 + o_col) = 0
  Cells(3, 9 + o_col) = 0
  Cells(3, 11 + o_col) = 0
  Cells(3, 13 + o_col) = 0
  Cells(3, 15 + o_col) = 0
' Row 4th
  Cells(4, 2 + o_col) = ws_o.Cells(start_RO_row, 1).Offset(0, 7)
  Cells(4, 3 + o_col) = ws_o.Cells(start_RO_row, 1).Offset(0, 2)
  Cells(4, 5 + o_col) = ws_o.Cells(start_RO_row, 1).Offset(0, 8)
  Cells(4, 7 + o_col) = ws_o.Cells(start_RO_row, 1).Offset(0, 3)
  Cells(4, 9 + o_col) = ws_o.Cells(start_RO_row, 1).Offset(0, 9)
  Cells(4, 11 + o_col) = ws_o.Cells(start_RO_row, 1).Offset(0, 10)
  '
  With Application
      Range(Cells(5, 2 + o_col), Cells(lastrow1 + 4, 2 + o_col)) = .index(M1o, , 2)
      Range(Cells(5, 3 + o_col), Cells(lastrow1 + 4, 3 + o_col)) = .index(M1o, , 3)
      Range(Cells(5, 4 + o_col), Cells(lastrow1 + 4, 4 + o_col)) = .index(M1, , 2)
      Range(Cells(5, 5 + o_col), Cells(lastrow1 + 4, 5 + o_col)) = .index(M1o, , 4)
      Range(Cells(5, 6 + o_col), Cells(lastrow1 + 4, 6 + o_col)) = .index(M1, , 3)
      Range(Cells(5, 7 + o_col), Cells(lastrow1 + 4, 7 + o_col)) = .index(M1o, , 5)
      Range(Cells(5, 8 + o_col), Cells(lastrow1 + 4, 8 + o_col)) = .index(M1, , 4)
      Range(Cells(5, 9 + o_col), Cells(lastrow1 + 4, 9 + o_col)) = .index(M1o, , 6)
```

```
               Range(Cells(5, 10 + o_col), Cells(lastrow1 + 4, 10 + o_col)) = .index(M1, , 5)
               Range(Cells(5, 11 + o_col), Cells(lastrow1 + 4, 11 + o_col)) = .index(M1o, , 7)
            '
            If Sim_op = "Runoff & Pesticide" Then
               ' sim values
               ' Row 4th
               Cells(4, 13 + o_col) = ws_o.Cells(start_RO_row, 1).Offset(0, 12 + n)
               Cells(4, 15 + o_col) = ws_o.Cells(start_RO_row, 1).Offset(0, 13 + n)
               Range(Cells(5, 12 + o_col), Cells(lastrow1 + 4, 12 + o_col)) = .index(M1, , 6)
               Range(Cells(5, 13 + o_col), Cells(lastrow1 + 4, 13 + o_col)) = .index(M1o, , 8)
               Range(Cells(5, 14 + o_col), Cells(lastrow1 + 4, 14 + o_col)) = .index(M1, , 7)
               Range(Cells(5, 15 + o_col), Cells(lastrow1 + 4, 15 + o_col)) = .index(M1o, , 9)
            End If
         End With
      ' Time of runoff
         Range(Cells(3, 1 + o_col), Cells(lastrow1 + 4, 1 + o_col)) = LapseTime
         Range(Cells(2, 2 + o_col), Cells(2, 17 + o_col)).WrapText = True
         ' Format font size
         Cells(1, 1 + o_col).Font.Size = 16
         Cells(1, 1 + o_col).Font.Bold = True
         Cells(1, 1 + o_col).Font.Color = RGB(0, 176, 80)
         Range(Cells(2, 1 + o_col), Cells(100, 17 + o_col)).Font.Size = 8
         Range(Cells(2, 1 + o_col), Cells(2, 17 + o_col)).HorizontalAlignment = xlCenter
         Range(Cells(2, 1 + o_col), Cells(2, 17 + o_col)).Font.Bold = True
      '
      ' Find Time to first runoff (in minute)
         Call Sta_FRT
         ws_o_event.Visible = xlSheetVisible
   Else
         ws_o_event.Visible = xlSheetVisible
         ws_o_event.Activate
            Range(Cells(1, 1 + o_col), Cells(100, 17 + o_col)).Clear
            Range(Cells(1, 1 + o_col), Cells(1, 3 + o_col)).Interior.ColorIndex = 0
         ws_o_event.Visible = xlSheetVeryHidden
   End If
   Application.ScreenUpdating = True
End Sub
' This sub for copying data to SPEC model
Sub DataCopy()
   Dim wb1, wb2 As Workbook
   Dim ws_i1, ws_sts1, ws_H1, ws_D1, ws_obs1, ws_i2, ws_sts2, ws_H2, ws_D2, ws_obs2 As Worksheet
   Dim MyPath, MyWB, sFile As String
   '
   Set wb1 = ThisWorkbook
   Set ws_i1 = wb1.Sheets("RUN")
   Set ws_sts1 = wb1.Sheets("Small_TS")
   Set ws_H1 = wb1.Sheets("Hourly")
   Set ws_D1 = wb1.Sheets("Daily")
   Set ws_obs1 = wb1.Sheets("Obs_Data")
   '
      MyPath = ActiveWorkbook.Path & "\DataSet\"
      MyWB = ws_i1.Cells(4, 10) & ".xlsx"
      sFile = MyPath & MyWB
```

```
      'MsgBox (MyWB)
      Application.ScreenUpdating = False
      '
      If IsWorkBookOpen(sFile) Then
      Else
         On Error GoTo 1
         Workbooks.Open (sFile)
      End If
      '
      Set wb2 = Workbooks(MyWB)
      Set ws_i2 = wb2.Sheets("RUN")
      Set ws_sts2 = wb2.Sheets("Small_TS")
      Set ws_H2 = wb2.Sheets("Hourly")
      Set ws_D2 = wb2.Sheets("Daily")
      Set ws_obs2 = wb2.Sheets("Obs_Data")
   '
   'Copy and Paste Data on Small_TS sheet
      ws_sts2.Range("A:B").Columns.Copy
      ws_sts1.Cells(1, 1).PasteSpecial xlPasteValues
   'Copy and Paste Data on Hourly sheet
      ws_H2.Range("A:S").Columns.Copy
      ws_H1.Cells(1, 1).PasteSpecial xlPasteValues
   'Copy and Paste Data on Daily sheet
      ws_D2.Range("A:S").Columns.Copy
      ws_D1.Cells(1, 1).PasteSpecial xlPasteValues
   'Copy and Paste Data on Obs_Data sheet
      ws_obs2.Range("A:Z").Columns.Copy
      ws_obs1.Cells(1, 1).PasteSpecial xlPasteValues
   'Copy and Paste Data on RUN sheet
      ws_i2.Range(ws_i2.Cells(4, 4), ws_i2.Cells(6, 4)).Copy
      ws_i1.Range(ws_i1.Cells(4, 4), ws_i1.Cells(6, 4)).PasteSpecial xlPasteValues
      ws_i2.Range(ws_i2.Cells(8, 4), ws_i2.Cells(24, 5)).Copy
      ws_i1.Range(ws_i1.Cells(8, 4), ws_i1.Cells(24, 5)).PasteSpecial xlPasteValues
      ws_i2.Range(ws_i2.Cells(26, 4), ws_i2.Cells(28, 5)).Copy
      ws_i1.Range(ws_i1.Cells(26, 4), ws_i1.Cells(28, 5)).PasteSpecial xlPasteValues
      ws_i2.Range(ws_i2.Cells(37, 4), ws_i2.Cells(46, 5)).Copy
      ws_i1.Range(ws_i1.Cells(37, 4), ws_i1.Cells(46, 5)).PasteSpecial xlPasteValues
      ws_i2.Range(ws_i2.Cells(48, 4), ws_i2.Cells(50, 5)).Copy
      ws_i1.Range(ws_i1.Cells(48, 4), ws_i1.Cells(50, 5)).PasteSpecial xlPasteValues
      ws_i2.Range(ws_i2.Cells(54, 4), ws_i2.Cells(55, 5)).Copy
      ws_i1.Range(ws_i1.Cells(54, 4), ws_i1.Cells(55, 5)).PasteSpecial xlPasteValues
      ws_i2.Range(ws_i2.Cells(61, 4), ws_i2.Cells(63, 23)).Copy
      ws_i1.Range(ws_i1.Cells(61, 4), ws_i1.Cells(63, 23)).PasteSpecial xlPasteValues
      ws_i2.Range(ws_i2.Cells(68, 4), ws_i2.Cells(73, 23)).Copy
      ws_i1.Range(ws_i1.Cells(68, 4), ws_i1.Cells(73, 23)).PasteSpecial xlPasteValues
   '
   Application.CutCopyMode = False
   Application.ScreenUpdating = True
   '
   'Close source data workbook
   wb2.Close SaveChanges:=False
1:
   If Err = 1004 Then
```

```
    'ReasonForError.Show
    MsgBox "File doesn't exist! Please enter a valid file name with its extentsion!", vbExclamation
    Exit Sub
  End If
  MsgBox "Source Data were successfully copied!"
End Sub
' Additional VBAs
Function XLMod(A, b)
  ' This replicates the Excel MOD function
  XLMod = A - b * Int(A / b)
End Function
Function Max2(A, b)
  ' This replicates the Excel MAX function for 2 numbers
  If A >= b Then
    Max2 = A
  Else
    Max2 = b
  End If
End Function
Function Max3(A, b, C)
  ' This replicates the Excel MAX function for 3 numbers
  If A >= b And A >= C Then
    Max3 = A
  ElseIf b >= A And b >= C Then
    Max3 = b
  Else
    Max3 = C
  End If
End Function
Function Min2(A, b)
  ' This replicates the Excel MIN function for 2 numbers
  If A <= b Then
    Min2 = A
  Else
    Min2 = b
  End If
End Function
Function Min3(A, b, C)
  ' This replicates the Excel MIN function for 3 numbers
  If A <= b And A <= C Then
    Min3 = A
  ElseIf b <= A And b <= C Then
    Min3 = b
  Else
    Min3 = C
  End If
End Function
Function LinInterp(x, xValues, yValues) As Double
  ' This generate Linear Interpolation
  ' x is a given value to find y
  ' xValues, yValues are given as a lookup table
  Dim x1, x2, y1, y2 As Double
  x1 = Application.index(xValues, Application.Match(x, xValues, 1))
```

```
    x2 = Application.index(xValues, Application.Match(x, xValues, 1) + 1)
    '
    y1 = Application.index(yValues, Application.Match(x, xValues, 1))
    y2 = Application.index(yValues, Application.Match(x, xValues, 1) + 1)
    '
    If x = x1 Then
        LinInterp = y1

    ElseIf x = x2 Then
        LinInterp = y2

    Else
        LinInterp = y1 + (y2 - y1) * (x - x1) / (x2 - x1)
    End If
End Function
' https://www.exploreexcelvba.com/ExcelVBA/create-vlookup-function/
Function myVLookup(lookup As Variant, table As Range, index As Double, _
Optional partialMatch As Boolean = True) As Variant
Dim Cell As Range
Dim L As Double

For Each Cell In table.Columns(1).Cells
    If Cell.Value = lookup And partialMatch = False Then
        myVLookup = Cell.Offset(0, index - 1).Value
        Exit Function
    ElseIf partialMatch = True Then
        L = Len(lookup)
        If Left(lookup, L - 1) = Left(Cell.Value, L - 1) Or _
            Left(lookup, L - 1) = Cell.Value Then
            myVLookup = Cell.Offset(0, index - 1).Value
            Exit Function
        End If
    End If
Next
    myVLookup = "not found"
End Function
‘-----------------------------------------------------------------------------------------------------------------------------
```