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Modeling pesticide diuron loading from the San Joaquin watershed into the Sacramento-San Joaquin Delta using SWAT

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ABSTRACT

Quantifying pesticide loading into the Sacramento-San Joaquin Delta of northern California is critical for water quality management in the region, and potentially useful for biological weed control planning. In this study, the Soil and Water Assessment Tool (SWAT) was applied to model streamflow, sediment, and pesticide diuron loading in the San Joaquin watershed, a major contributing area to the elevated pesticide levels in the downstream Delta. The Sequential Uncertainty Fitting version 2 (SUFI-2) algorithm was employed to perform calibration and uncertainty analysis. A combination of performance measures (PMs) and standardized performance evaluation criteria (PEC) was applied to evaluate model performance, while prediction uncertainty was quantified by 95% prediction uncertainty band (95PPU). Results showed that streamflow simulation was at least "satisfactory" at most stations, with more than 50% of the observed data bracketed by the 95PPU. Sediment simulation was rated as at least "satisfactory" based on two PMs, and diuron simulation was judged as "good" by all PMs. The 95PPU of sediment and diuron bracketed about 40% and 30% of the observed data, respectively. Significant correlations were observed between the diuron loads, and precipitation, streamflow, and the current and antecedent pesticide use. Results also showed that the majority (>70%) of agricultural diuron was transported during winter months, when direct exposure of biocontrol agents to diuron runoff is limited. However, exposure in the dry season could be a concern because diuron is relatively persistent in aquatic system. This study not only provides valuable information for the development of biological weed control plan in the Delta, but also serves as a foundation for the continued research on calibration, evaluation, and uncertainty analysis of spatially distributed, physically based hydrologic models.

1. Introduction

Increasing pesticide contamination of surface water has raised substantial concern, especially in the agriculturally dominated San Joaquin watershed in California. Extensive pesticide application in this region has led to water quality degradation, posing a potential threat to aquatic organisms in the watershed (Luo and Zhang, 2010; Starner and Zhang, 2011). In addition, pesticide loads exported from the San Joaquin watershed eventually drain into the waterways of the Sacramento-San Joaquin Delta, which is an ecologically rich area that also serves as a major hub of California's water supply (Healey et al., 2016; Orlando et al., 2014).

Recently, invasive aquatic weeds have dominated several areas in the Delta, blocked the waterways and severely disrupted the ecosystems (USDA-DBW, 2012a, b). Biological control is an environmentally sound and promising means of mitigating floating aquatic weed invasion (Coetzee et al., 2011; Julien, 2008). The USDA-Agricultural Research Service Delta Region Areawide Aquatic Weed Project (DRAAWP) has been initiated to develop and implement adaptive, integrated aquatic weed control strategies, including biological control. However, the effectiveness of biocontrol agents may be influenced by pesticide loading from the upstream agricultural watersheds. As part of the DRAAWP, this study

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aims to quantify pesticide loading from the San Joaquin watershed into the Delta, providing information to facilitate the development of biological weed control plans. Diuron was selected as the target pesticide because it is toxic to insects and one of the most frequently detected with the highest maximum concentrations at the inlet to the Delta (Kegley et al., 2011; Orlando et al., 2014).

Hydrologic models are increasingly used to support environmental exposure and risk assessments, pollution control planning, and decision making (Abbaspour et al., 2015; Daggupati et al., 2015; Moriasi et al., 2015b), as they are cost-effective and can be used to quantitatively predict pollutant fate and transport under a wide range of scenarios. Improved understanding of hydrology and biogeochemical processes, advances in Geographic Information System (GIS) technology, and exponential growth in computing power have led to increasingly sophisticated physically based, spatially distributed, watershed-scale models. One of the most widely used watershed models is the Soil and Water Assessment Tool, SWAT (Arnold et al., 2015a; Neitsch et al., 2011). SWAT was developed to predict water, sediment and agricultural chemical yields under varying soil, land use and management conditions (Arnold et al., 2012). The ability of SWAT in simulating streamflow (Ficklin and Zhang, 2013; Saha et al., 2014; Singh et al., 2005; Spruill et al., 2000; Van Liew and Garbrecht, 2003; Zhou et al., 2014), sediment (Abbaspour et al., 2007; Kliment et al., 2008; Lu et al., 2014; Oeurng et al., 2011; Santhi et al., 2001; Shen et al., 2009; Xu et al., 2009), and agrochemicals including pesticides (Bannwarth et al., 2014; Boithias et al., 2011; Ficklin et al., 2013; Kannan et al., 2006; Larose et al., 2007; Luo et al., 2008) on an annual or monthly basis has been demonstrated, while inadequate model performance has also been observed (Bieger et al., 2014; Fohrer et al., 2014; Gassman et al., 2007, 2014; Kim et al., 2010; Zeiger and Hubbart, 2016).

Model calibration is an inevitable process since it is almost impossible to take enough measurements that cover the entire watershed at the desired spatial and temporal resolution for a specified hydrologic process (Guzman et al., 2015), and some parameters are difficult to measure or define physically (Malone et al., 2015). Calibration should focus on the most uncertain and sensitive parameters (Malone et al., 2015), and should be justified by the actual physical knowledge of the relevant watershed processes (Arnold et al., 2012). Constraints on parameter ranges are also necessary to ensure that processes are within reasonable limits (Arnold et al., 2015b). It is beneficial to calibrate the model using different output variables at multiple sites, as this will allow for better representation of the diverse characteristics of a watershed and help reduce the problem of equifinality (Daggupati et al., 2015), i.e. an acceptable model prediction might be achieved by more than one set of parameter values (Beven, 1993).

The increasing use of numerical models for scientific inquiry and regulatory planning calls for a more rigorous procedure for model performance evaluation (Moriasi et al., 2015b). Quantitative performance measures (PMs) are used to provide objective model assessment. A combination of different PMs should be applied to overcome the bias of individual methods (Krause et al., 2005). On the other hand, subjectivity is often involved in judging the results of PMs (Bennett et al., 2013). Such limitations might be overcome by using standardized performance evaluation criteria (PEC), which provide objective indications of model adequacy across different studies (Moriasi et al., 2015a). Recently, PEC guidelines for hydrologic modeling has been developed and refined based on a meta-analysis of model performance data reported in the literature (Moriasi et al., 2007, 2015a). There are, to the authors' knowledge, no studies that apply these PEC guidelines for comprehensive evaluation of model performance.

Moreover, it is important to perform proper uncertainty analysis given the uncertainties inherent in hydrologic modeling (Beven, 1993; Guzman et al., 2015). These include uncertainties in the input and output data, model structure, and parameterization. In the past few decades, many techniques have been developed and applied to assess prediction uncertainty in hydrologic modeling (Yang et al., 2007). The Sequential Uncertainty Fitting version 2 (SUFI-2) program is one such technique that is able to perform a combined calibration and uncertainty analysis (Abbaspour et al. 1997, 2004). It accounts for all sources of uncertainties by an enhanced parameter uncertainty (Yang et al., 2008). SUFI-2 has high efficiency in achieving good prediction uncertainty ranges in terms of coverage of the observed data (Yang et al., 2008), and has been successfully applied in many modeling studies (Abbaspour et al. 2007, 2015; Ficklin et al., 2013; Schuol et al., 2008a, 2008b; Zhou et al., 2014). The limitations of SUFI-2 include lack of a rigorous statistical foundation, lack of considering parameter correlations, and inclusion of some simulations with poor objection function values (Yang et al., 2008).

In this study, our goal was to simulate pesticide loading from the San Joaquin watershed to the Sacramento-San Joaquin Delta. Specifically, our objectives were to: (1) perform calibration and validation of SWAT for simulating streamflow and sediment in the San Joaquin watershed, (2) calibrate SWAT for simulating diuron loading in the study area, (3) evaluate model performance using PMs and standardized PEC, and (4) carry out uncertainty analysis using the SUFI-2 algorithm to assess model prediction uncertainty. This study not only informs weed control planning and water quality management in the Delta region, but also provides a standard framework of model calibration, evaluation, and uncertainty analysis for large-scale hydrologic modeling in general.

2. Materials and methods

2.1. Study area

The San Joaquin watershed in the California's Central Valley was selected as the study area (Fig. 1). Its total area, as defined in this study, is approximately 15 000 km^2. It has a Mediterranean climate with hot, dry summers and cool, wet winters. The soils are mostly clay loams to fine sandy loams. The major land use types include cropland, pasture-based livestock farming, and forest (USDA-NASS, 2015). Land area occupied by pasture and forest was about 7400 and 1100 km^2, respectively. Almond has the largest cultivated area of 2000 km^2, followed by vineyard (1000 km^2), alfalfa (900 km^2), oat (300 km^2), corn (300 km^2), cotton (200 km^2) and tomato (200 km^2). The San Joaquin River originates in the Sierra Nevada Mountains and descends onto the valley floor, where it flows northwest before reaching the Sacramento-San Joaquin Delta. The watershed outlet is defined at the San Joaquin River at Vernalis, a United States Geological Survey (USGS) gauging station (#11303500, Table 1 and Fig. 1). Four watershed inlets were defined at the USGS stations below dams on the eastern major rivers.

2.2. Data acquisition

Spatial environmental datasets were obtained from public databases maintained by various government agencies. For topographic data, we retrieved the 1/3 arc-second (10 m) digital elevation models from the 3D Elevation Program, which has an altitude resolution of 0.001 m (USGS, 2015). Stream network data were obtained from the 1:100 000 scale National Hydrography Dataset (USGS, 2016b). The stream network dataset was superimposed onto the topography map to assist with watershed and stream network delineation in flat terrain. Land use data were extracted from the 2014 Cropland Data Layer (USDA-NASS, 2015).

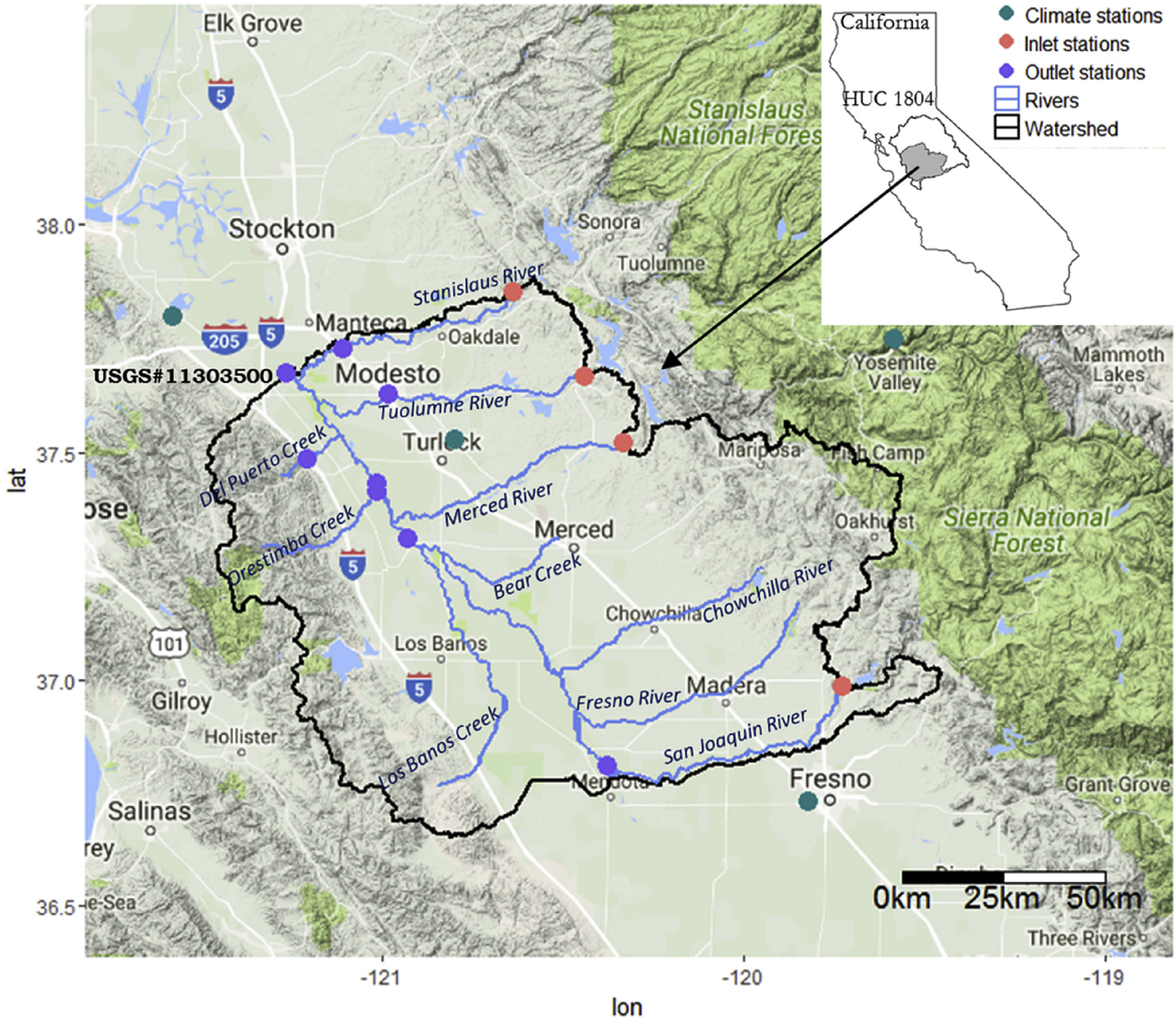

Fig. 1. Study area of the San Joaquin watershed.

Table 1
Inlet and outlet stations within the San Joaquin watershed.

USGS ID	Reach No.[a]	Name	Type	Longitude	Latitude	Area drained by reach (km^2)
11251000		San Joaquin River	Inlet	−119.72	36.98	
11270900		Merced River	Inlet	−120.33	37.52	
11289650		Tuolumne River	Inlet	−120.44	37.67	
11302000		Stanislaus River	Inlet	−120.64	37.85	
11254000	27	San Joaquin River at Mendota	Outlet	−120.38	36.81	1193
11261500	18	San Joaquin River at Fremont	Outlet	−120.93	37.31	10160
11274538	13	Orestimba Creek	Outlet	−121.02	37.41	407
11274550	11	San Joaquin River at Crows Landing	Outlet	−121.01	37.43	11960
11274630	9	Del Puerto Creek	Outlet	−121.21	37.49	188
11290000	6	Tuolumne River	Outlet	−120.98	37.63	343
11303000	3	Stanislaus River	Outlet	−121.11	37.73	261
11303500	1	San Joaquin River at Vernalis	Outlet	−121.27	37.68	14960

[a] Reach number for outlet refers to the stream that drains into the corresponding outlet. This is also the subbasin number where the reach originates.

Soil data were retrieved from the Soil Survey Geographic database (SSURGO) (USDA, 2015). Precipitation and other weather information were obtained from the SWAT internal weather database. Diuron application data were retrieved from the California

Pesticide Use Reporting (PUR) database (CDPR, 2015). Physiochemical properties of diuron (Table 2) were extracted from the built-in pesticide database in SWAT and the literature (Arnold et al., 2015a; Moncada, 2004).

Daily streamflow and suspended sediment monitoring data were retrieved from the National Water Information System (NWIS) (USGS, 2016a). Streamflow data were available at eight stations while sediment data were only available at the watershed outlet (Table 1 and Fig. 1). The monitoring data for dissolved diuron concentrations were obtained from NWIS through the Water Quality Portal (NWQMC, 2016), and the California Surface Water Database (SURF) (CDPR, 2016). Sufficient pesticide data (>30 data points) were only available at the watershed outlet. A time-centered scheme was adopted to convert concentration to monthly load based on the time of sample collection (Du et al., 2006; Jaynes et al., 1999). The inflow at the four watershed inlets is dominated by high-quality snow melt from the Sierra Nevada mountain range. Therefore, inflow is assumed to be free of pesticides.

2.3. Model setup

The SWAT version 2012 and its ArcSWAT interface were selected. The study area was delineated into 27 subbasins using a threshold of 550 km^2. A total of 647 hydrologic response units (HRUs) were defined by overlaying topography, soil and land use maps based on a threshold of 5%, which was used to eliminate minor slope, soil and land use classes based on their percent coverage of the subbasin. The simulation was performed from 2001 to 2014, with the first 2 years as the warm-up period. The model was calibrated and validated using a temporal split-sample approach. Flow and sediment were calibrated and validated using data from 2003 to 2008, and 2009 to 2014, respectively. Annual precipitation during the study period ranged from 234 to 450 mm, with average annual precipitation of 336 and 361 mm for the calibration and validation periods, respectively. The study period was considered as slightly wetter than average, considering the latest 30-year average precipitation of 325 mm over the San Joaquin Valley (NOAA, 2017). As the monitoring data for diuron were only available after 2009, we calibrated pesticide for this period, and thus no validation was performed for pesticide due to data limitation. Pesticide calibration was performed by changing only the pesticide parameters while keeping the calibrated flow and sediment parameters unchanged. The modeling results were evaluated at monthly time steps.

The curve number method was selected for estimating surface runoff. The automatic irrigation operation routine was enabled to simulate irrigation water use based on soil water content, due to the lack of actual irrigation data on a daily basis. SWAT supports two types of water routing methods: the variable storage routing method and the Muskingum routing method. We selected the Muskingum method because the variable storage method tended to overestimate streamflow. For sediment routing, the physically based simplified Bagnold equation (CH_EQN-1) was selected. Preliminary comparison of CH_EQN-1 and the default simplified Bagnold equation (CH_EQN-0) showed that CH_EQN-1 matched the observations better. Further details about this are described in the Results and Discussion sections.

2.4. Model calibration and uncertainty analysis using the SUFI-2 algorithm

The SUFI-2 algorithm in the SWAT-CUP (Calibration and Uncertainty Procedures) program was applied for model calibration and uncertainty analysis (Abbaspour, 2015). In SUFI-2, parameter uncertainties are described by uniform distributions and are propagated through the model to produce prediction uncertainty quantified by a 95% prediction uncertainty band (95PPU). We selected ϕ (= 0–1) as the objective function since it is not dominated by the worst events (Krause et al., 2005; Schuol et al., 2008b):

$$\text{Maximize} : \phi = \begin{cases} |b|R^2 & if\,|b| \le 1 \\ |b|^{-1}R^2 & if\,|b| > 1 \end{cases}$$

where b is the gradient of the regression line, R^2 is the coefficient of determination, and ϕ is the weighted R^2. The procedure continues until a desired fit between the observed data and the 95PPU is obtained, as judged by the *P-factor* and *R-factor*. The *P-factor* is the percentage of the observed data bracketed by the 95PPU, and the *R-factor* is the normalized thickness of the 95PPU. A balance must be reached between the two as a larger *P-factor* can be found at the expense of a larger *R-factor* (Abbaspour et al., 2015).

We took the following steps to calibrate SWAT for the San Joaquin watershed. First, SWAT was set up using measured and estimated site-specific parameters when possible. The default SWAT was then tested for streamflow simulation, which showed a promising outcome especially for the watershed outlet ($NSE = 0.9$). It is crucial to start with a good default model; otherwise the optimization algorithm might be lost in seaching the parameter space. Secondly, parameters for calibration were selected based on physical watershed understanding, plotting results of one-at-a-time sensitivity analysis, and the literature (Abbaspour et al., 2015; Arnold et al., 2012; Luo et al., 2008; Veith et al., 2010). Calibration was focused on the most uncertain and sensitive parameters (Table 3). Parameter values were also constrained to the published or physically realistic ranges (Malone et al., 2015). Relative changes were assigned to distributed spatial parameters in order to preserve their spatial variation and to keep the number of parameters small (Li et al., 2010). Thirdly, SWAT was spatially calibrated for streamflow at each outlet station by freezing the

Table 2
Physiochemical properties of diuron as SWAT input parameters.

Parameter name	Description	Value	Data source
SKOC	Soil adsorption coefficient normalized for soil organic carbon (ml/g)	480	SWAT built-in pesticide database
WOF	Wash off fraction	0.45	
HLIFE_F	Degradation half-life of the chemical on the foliage (days)	30	
HLIFE_S	Degradation half-life of the chemical on the soil (days)	90	
WSOL	Solubility of the chemical in water (mg/L)	42	
HENRY	Henry's Law Constant	2.09E-08	(Moncada, 2004)
CHPST_REA	Pesticide reaction coefficient in reach (day^{-1})	0.001271	
SEDPST_REA	Pesticide reaction coefficient in reach bed sediment (day^{-1})	0.000696	
CHPST_VOL	Pesticide volatilization coefficient in reach (m/day)	0	
CHPST_KOC	Pesticide partition coefficient between water and sediment in reach (m^3/g)	2.15E-05	

Table 3
Sensitive SWAT parameters and their final calibrated ranges.

Parameter	Lower limit	Upper limit
Parameters calibrated for streamflow		
Outlet 1, San Joaquin River at Vernalis		
v__CH_N2.rte________1-2,4-5,7-8,10	0.015	0.055
Outlet 9, Del Puerto Creek		
v__CH_K2.rte________9	65.5	81.7
r__SOL_AWC().sol________9	0.53	0.65
r__CN2.mgt________9	−0.66	−0.53
Outlet 11, San Joaquin River at Crows Landing		
v__CH_N2.rte________11-12,14-17	0.010	0.041
v__CH_K2.rte________11-12,14-17	8.8	17.7
Outlet 13, Orestimba Creek		
r__CN2.mgt________13	−0.25	0.00
v__CH_K2.rte________13	0.0	25.4
Outlet 18, San Joaquin River at Fremont		
v__CH_N2.rte________18-26	0.026	0.065
v__CH_K2.rte________18-26	0.0	39.6
Outlet 27, San Joaquin River at Mendota		
v__CH_K2.rte________27	1.5	30.9
r__CN2.mgt________27	0.01	0.31
Parameters calibrated for sediment load		
Outlet 1, San Joaquin River at Vernalis		
v__PRF_BSN.bsn	0.24	0.75
v__SPEXP.bsn	1.1	1.3
v__SPCON.bsn	0.00010	0.00032
Parameters calibrated for pesticide load		
Outlet 1, San Joaquin River at Vernalis		
v__AP_EF.pest.dat	0.75	0.93
v__HLIFE_S.pest.dat	90	381
v__PERCOP.bsn	0.69	0.94

CH_K2: effective hydraulic conductivity in the main channel alluvium.
CH_N2: Manning's N value for the main channel.
CN2: initial curve number for moisture condition II.
SOL_AWC: available water capacity of the soil layer.
PRF_BSN: peak rate adjustment factor for sediment routing in the main channel.
SPEXP: exponent parameter for calculating sediment transport capacity.
SPCON: linear parameter for calculating sediment transport capacity.
AP_EF: application efficiency.
HLIFE_S: degradation half-life of diuron in the soil.
PERCOP: pesticide percolation coefficient.
Parameter identifier is specified as x__⟨parname⟩.________⟨subbsn⟩, where x__ is the code to indicate the type of change to be applied to the parameter. v__ means the existing parameter is replaced by a given value, and r__ means an existing parameter value is multiplied by (1+ a given value); ⟨parname⟩ is the name of the parameter; is the file extension code for the file containing the parameter; ⟨subbsn⟩ is the subbasin number. Modification is applied only to the parameter(s) associated with the specified subbasin(s). For more details please refer to (Abbaspour, 2015).

parameter(s) in the upstream subbasin(s). This procedure was only feasible for streamflow, as sufficient monitoring data for other constituents were only available at the watershed outlet. Regionalization of parameters helps to ensure that the variability for each subbasin is captured and to improve the efficiency of the subsequent multi-site calibration. Finally, multi-site calibration (i.e. including all stations within the watershed) was performed with 500 times per iteration by calibrating flow, sediment, and pesticide sequentially.

2.5. Model performance evaluation and statistical analysis

The following PMs were applied to assess SWAT with the best calibrated parameters: (1) model-to-data hydrograph, (2) coefficient of determination (R^2), (3) Nash-Sutcliffe efficiency (*NSE*), and (4) percent bias (*PBIAS*). For R^2, *NSE* and *PBIAS*, the corresponding PEC were established according to a recent review (Moriasi et al., 2015a) (Table 4). In addition, the Pearson correlation analysis was performed to examine the linear relationship between dissolved diuron loads and the three other variables: precipitation, streamflow and diuron use. All the statistical analysis and data visualization were performed in R, a flexible and powerful language for statistical computing and graphics (Kahle and Wickham, 2013; R Development Core Team, 2015).

3. Results

3.1. Simulation of streamflow

The sensitivity analysis identified 12 parameters that played a significant role in streamflow simulation (Table 3). The hydrograph shape and volume were most sensitive to channel parameters of Manning's N value for the main channel (CH_N2) and effective hydraulic conductivity in the main channel alluvium (CH_K2), while the peak flow was most sensitive to landscape parameters of initial curve number for moisture condition II (CN2) and available water capacity of the soil layer (SOL_AWC). The sensitivity of these parameters varies spatially. For the mainstem of the San Joaquin River (reach number = 1, 11, 18, 27, Table 1), the most sensitive parameters were those that govern channel routing. For the small tributaries on the western side (reach number = 9, 13), streamflow was most sensitive to landscape parameters and CH_K2, suggesting the importance of surface runoff generation and in-stream leakage. For the large eastside tributaries, no parameters were found to be highly sensitive.

At the watershed outlet, monthly streamflow calibration was judged as at least “good” based on all PMs (Table 5). During the validation period, the model was rated as “very good” based on R^2 and *NSE*, but “unsatisfactory” based on *PBIAS* (18%). For other stations along the San Joaquin River and the major eastern tributaries (Stanislaus River and Tuolumne River), the model also attained reasonable performance ratings during both calibration and validation periods. The two major peaks in the San Joaquin River were underestimated in April of 2006 and 2011 (Fig. 2f, g and h). Streamflow was less accurately simulated in the western tributaries (Del Puerto Creek and Orestimba Creek).

On average, more than 50% and 60% of the variation in streamflow was bracketed by the 95PPU for stations along the San Joaquin River and the major eastern tributaries during the calibration and validation periods, respectively, confirming that streamflow simulation was satisfactory. The *P-factor* was lower for the western streams, and generally increased from upstream to downstream. The *R-factor* was less than 1 for all stations, suggesting acceptable thickness of the 95PPU envelope.

3.2. Simulation of sediment

The CH_EQN-0 (Bagnold) model significantly overestimated sediment load at the watershed outlet during peak events (Fig. 3a). The CH_EQN-1 (physically based Bagnold) model produced better matches between predictions and observations (Fig. 3b). The two major peaks in sediment discharge were overestimated using CH_EQN-1 in April of 2006 and March of 2011. Only the CH_EQN-1 model was selected for subsequent analyses. In the CH_EQN-1 model, sediment load was most sensitive to a few channel parameters: PRF_BSN, SPCON and SPEXP. PRF_BSN is the peak rate adjustment factor for sediment routing in the main channel. In SWAT, sediment transport capacity is a function of the peak channel velocity. PRF_BSN was incorporated to calculate peak flow rate based on the mean daily flow, because SWAT is not able to directly simulate subdaily hydrograph when daily precipitation is used as the input. SPCON and SPEXP are the linear and exponent parameters for calculating sediment transport capacity, respectively.

During the calibration period, model performance was rated as at least “satisfactory” based on R^2 and *NSE* but “unsatisfactory” based on *PBIAS*, while during the validation period, the result was

Table 4
Evaluation metrics and associated performance ratings (adapted from Moriasi et al., 2015a).

Performance rating	Streamflow	Sediment	Pesticide[a]
$R^2 = \left(\frac{\sum_{i=1}^{n}(y_i-\bar{y})(\hat{y}_i-\bar{\hat{y}})}{\sqrt{\sum_{i=1}^{n}(y_i-\bar{y})^2}\sqrt{\sum_{i=1}^{n}(\hat{y}_i-\bar{\hat{y}})^2}}\right)^2$			
Very good	$R^2 > 0.85$	$R^2 > 0.80$	$R^2 > 0.70$
Good	$0.75 < R^2 \leq 0.85$	$0.65 < R^2 \leq 0.80$	$0.60 < R^2 \leq 0.70$
Satisfactory	$0.60 < R^2 \leq 0.75$	$0.40 < R^2 \leq 0.65$	$0.30 < R^2 \leq 0.60$
Unsatisfactory	$R^2 \leq 0.60$	$R^2 \leq 0.40$	$R^2 \leq 0.30$
$NSE = 1 - \frac{\sum_{i=1}^{n}(y_i-\hat{y}_i)^2}{\sum_{i=1}^{n}(y_i-\bar{y})^2}$			
Very good	$NSE > 0.80$	$NSE > 0.80$	$NSE > 0.65$
Good	$0.70 < NSE \leq 0.80$	$0.70 < NSE \leq 0.80$	$0.50 < NSE \leq 0.65$
Satisfactory	$0.50 < NSE \leq 0.70$	$0.45 < NSE \leq 0.70$	$0.35 < NSE \leq 0.50$
Unsatisfactory	$NSE \leq 0.50$	$NSE \leq 0.45$	$NSE \leq 0.35$
$PBIAS = \frac{\sum_{i=1}^{n}(\hat{y}_i-y_i)}{\sum_{i=1}^{n}y_i} \times 100$ (%)			
Very good	$\|PBIAS\| < 5$	$\|PBIAS\| < 10$	$\|PBIAS\| < 15$
Good	$5 \leq \|PBIAS\| < 10$	$10 \leq \|PBIAS\| < 15$	$15 \leq \|PBIAS\| < 20$
Satisfactory	$10 \leq \|PBIAS\| < 15$	$15 \leq \|PBIAS\| < 20$	$20 \leq \|PBIAS\| < 30$
Unsatisfactory	$\|PBIAS\| \geq 15$	$\|PBIAS\| \geq 20$	$\|PBIAS\| \geq 30$

Note: y_i and $\hat{y}_i$ are the ith observed and simulated values, $\bar{y}$ and $\bar{\hat{y}}$ is the average of the observed and predicted values, and n is the sample size.
[a] Criteria for pesticides were adopted from those for nitrogen.

rated as at least “good” based on R^2 and *PBIAS* but “unsatisfactory” based on *NSE* (Table 5). Respectively, about 30% and 50% of the measured data were bracketed by the 95PPU during the calibration and validation periods, with *R-factor* below 1, but larger than those of streamflow.

3.3. Simulation of pesticide

Pesticide diuron was predominantly applied over the winter season (November through February), which coincided with the rainy season in California (Fig. 4). On average, 20,737 kg of diuron was applied annually on agricultural land in the San Joaquin watershed from 2009 to 2014. Application efficiency (AP_EF), pesticide percolation coefficient (PERCOP), and degradation half-life of diuron in the soil (HLIFE_S) were identified as the most sensitive parameters for pesticide simulation (Table 3).

At the watershed outlet, pesticide calibration was rated as “good” by all PMs (Table 5). Compared to the monitoring data, the first peak of diuron load was well captured by SWAT, while the second peak was overestimated (Fig. 4). For uncertainty analysis, 31% of the measured data were bracketed by the 95PPU, and the *R-factor* was 0.85, which was larger than the values of streamflow.

Significant correlations were observed between the observed and simulated diuron load, and precipitation and streamflow (Table 6). The observed diuron load was strongly correlated with the one-month and two-month antecedent diuron use, while the simulated diuron load was more related to diuron application in the current month and one month earlier. According to model

Table 5
Calibration, evaluation, and uncertainty analysis for monthly streamflow, sediment, and pesticide loads in the San Joaquin watershed.

Station	*P-factor*	*R-factor*	R^2	R^2 rating	*NSE*	*NSE* rating	*PBIAS* (%)	*PBIAS* rating
Calibration of streamflow and sediment (2003-2008)								
Streamflow								
San Joaquin River at Vernalis	0.50	0.37	0.91	Very good	0.89	Very good	−5	Good
Stanislaus River	0.47	0.00	0.99	Very good	0.99	Very good	−3	Very good
Tuolumne River	0.21	0.00	0.99	Very good	0.98	Very good	−14	Satisfactory
Del Puerto Creek	0.07	0.20	0.12	Unsatisfactory	−2.16	Unsatisfactory	82	Unsatisfactory
San Joaquin River at Crows Landing	0.71	0.67	0.78	Good	0.74	Good	−7	Good
Orestimba Creek	0.29	0.78	0.00	Unsatisfactory	−0.59	Unsatisfactory	−42	Unsatisfactory
San Joaquin River at Fremont	0.82	0.79	0.59	Unsatisfactory	0.57	Satisfactory	17	Unsatisfactory
San Joaquin River at Mendota	0.32	0.35	0.79	Good	−0.99	Unsatisfactory	40	Unsatisfactory
Sediment								
San Joaquin River at Vernalis	0.28	0.78	0.71	Good	0.52	Satisfactory	−32	Unsatisfactory
Validation of streamflow and sediment, and calibration of pesticide (2009-2014)								
Streamflow								
San Joaquin River at Vernalis	0.82	0.47	0.91	Very good	0.89	Very good	18	Unsatisfactory
Stanislaus River	0.49	0.00	0.98	Very good	0.98	Very good	0	Very good
Tuolumne River	0.38	0.00	1	Very good	0.99	Very good	−7	Good
Del Puerto Creek	0.10	0.13	0	Unsatisfactory	−4.61	Unsatisfactory	102	Unsatisfactory
San Joaquin River at Crows Landing	0.92	0.84	0.85	Good	0.81	Very good	25	Unsatisfactory
Orestimba Creek	0.18	1.27	0	Unsatisfactory	−1.27	Unsatisfactory	85	Unsatisfactory
San Joaquin River at Fremont	0.90	1.27	0.6	Unsatisfactory	0.49	Unsatisfactory	74	Unsatisfactory
San Joaquin River at Mendota	0.38	0.79	0.74	Satisfactory	−1.75	Unsatisfactory	54	Unsatisfactory
Sediment								
San Joaquin River at Vernalis	0.47	0.98	0.78	Good	0.38	Unsatisfactory	0	Very good
Pesticide								
San Joaquin River at Vernalis	0.31	0.85	0.69	Good	0.58	Good	19.5	Good

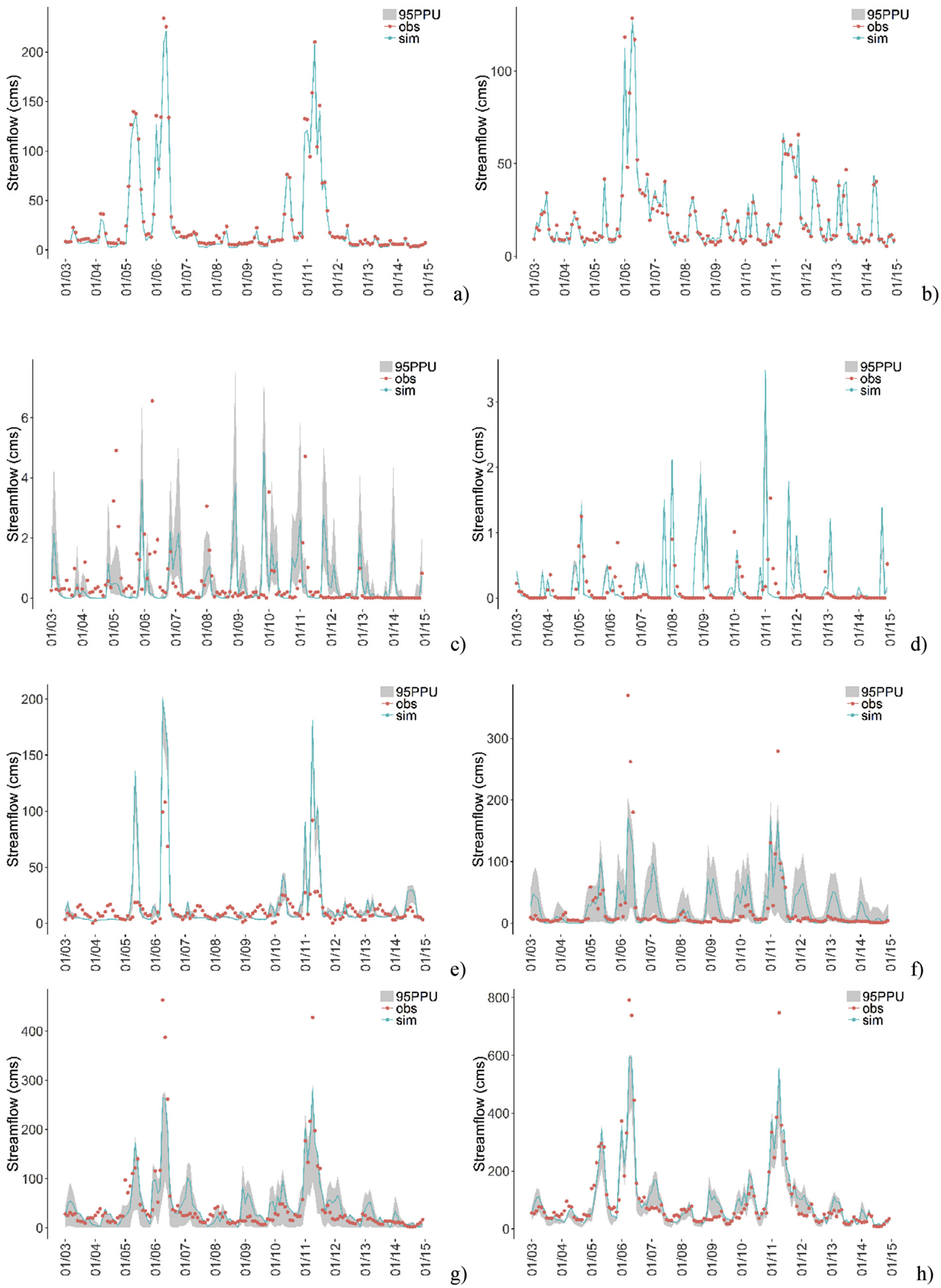

Fig. 2. Observed (obs), simulated (sim), and the 95% prediction uncertainty (95PPU) of monthly average streamflow for a) the Tuolumne River, b) the Stanislaus River, c) the Orestimba Creek, d) the Del Puerto Creek, e) the San Joaquin River at Mendota, f) the San Joaquin River at Fremont, g) the San Joaquin River at Crows Landing, and h) the San Joaquin River at Vernalis.

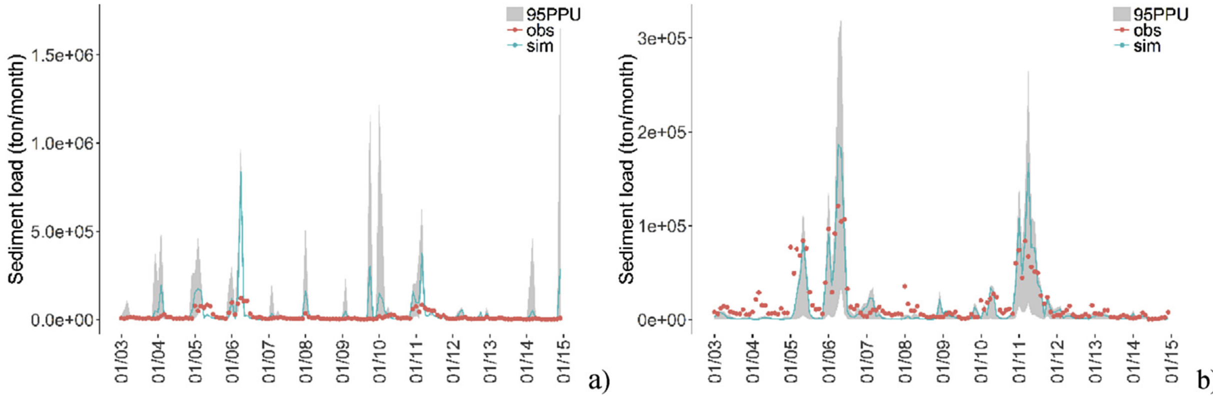

Fig. 3. Observed (obs), simulated (sim), and the 95% prediction uncertainty (95PPU) of monthly sediment load for the San Joaquin River at Vernalis using a) CH_EQN-0 (Bagnold) and b) CH_EQN-1 (physically based Bagnold).

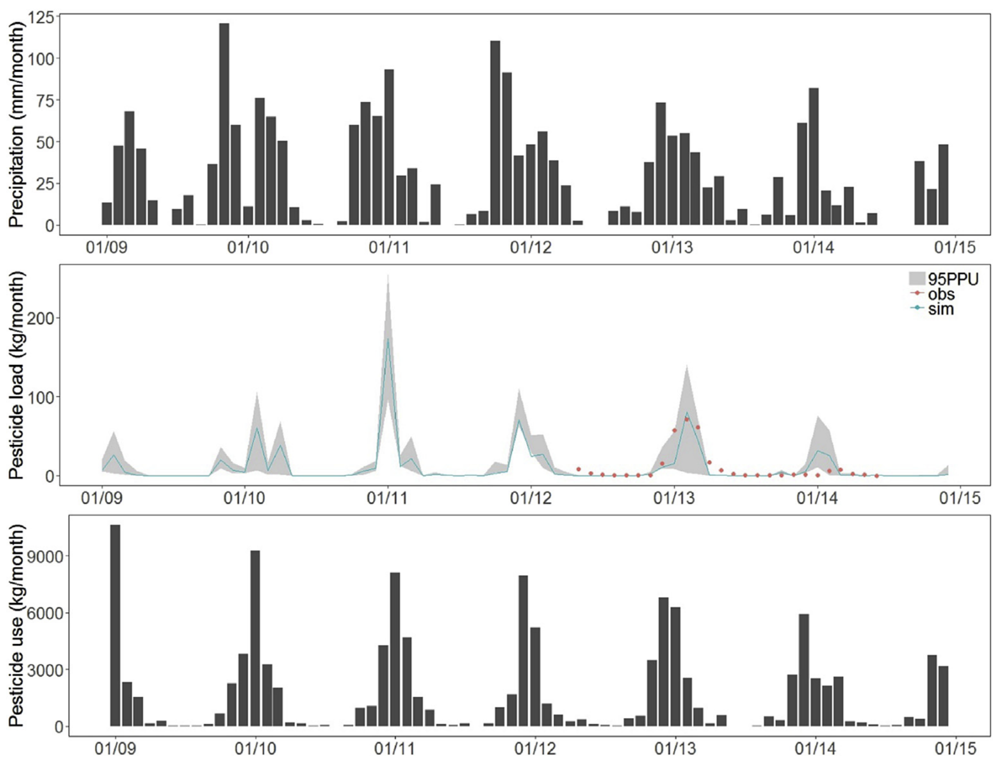

Fig. 4. Observed (obs), simulated (sim), and the 95% prediction uncertainty (95PPU) of monthly dissolved diuron load for the San Joaquin River at Vernalis (middle), monthly precipitation averaged across four weather stations within the study area (top), and monthly diuron use summed over the study area (bottom).

Table 6
Pearson correlation coefficient matrix for monthly diuron simulation at the watershed outlet.

	Precipitation	Streamflow[a]	Use-0[b]	Use-1[b]	Use-2[b]	Use-3[b]
Simulated diuron load	0.50**	0.37**	0.51**	0.52**	0.30*	0.10
Observed diuron load	0.46*	0.42*	0.34	0.68**	0.76**	0.46*

**Significant at 0.01 level; * significant at 0.05 level; others non-significant (p > 0.05).
[a] Simulated and observed streamflow for simulated and observed diuron load, respectively.
[b] Use-0, Use-1, Use-2, and Use-3: current, one-month, two-month, and three-month antecedent diuron use.

prediction, the diuron load accounted for approximately 0.95% of the total agricultural use in the San Joaquin watershed during 2009–2014. The exportation rate of diuron ranged from 0.003 to 239 kg per month, and the peak loads (from December to February) accounted for more than 70% of the annual yield.

4. Discussion

4.1. Simulation of streamflow

Calibration of a physically based model should focus on matching the model to processes occurring in the watershed; lack of realistic representation of the system being modelled will likely result in a model calibrated for a particular dataset rather than for the watershed (Abbaspour et al., 2007; Malone et al., 2015; White and Chaubey, 2005). In this study, we found that regionalization of parameters was important as the dominant processes and sensitivity of associated parameters varied spatially. For the San Joaquin River, streamflow was heavily dependent on upstream reservoir releases. Therefore, parameters associated with channel routing played a key role in determining streamflow (Table 3). For the ephemeral creeks on the western side, streamflow is mainly driven by winter storm events. Consequently, landscape parameters related to rainfall-runoff processes have greater impacts on streamflow prediction.

Understanding the interaction of surface water and groundwater is also important in surface water modeling. In SWAT, parameter CH_K2 is used to describe the relationship between streams and the groundwater system. A stream may be characterized as a losing or a gaining stream according to the contribution from groundwater. For losing streams, CH_K2 is used to quantify the rate of seepage toward the groundwater table. In the San Joaquin watershed, most western tributaries are ephemeral, lacking a continuous groundwater contribution. In addition, regional groundwater pumping has forced groundwater to flow away from the San Joaquin River. In our study, the San Joaquin River was parameterized as a losing stream up to Crows Landing, and as a gaining stream in its lower reaches, according to a recent study by Traum et al. (2014). It should be noted that representing the surface water and groundwater interaction with a constant factor is admittedly an oversimplification of the real situation, as the status (loss or gain) of a particular reach changes with the variation in flow, groundwater levels, climatic conditions, and other factors (Faunt, 2009; Traum et al., 2014).

Performance ratings show that SWAT was able to simulate monthly streamflow with reasonable accuracy, especially at stations near the watershed outlet (Table 5 and Fig. 2). Similarly, the *P-factor* increased as the flow traveled downstream. A possible explanation is that the uncertainties associated with flow prediction were balanced out as they propagated downstream (Piniewski and Okruszko, 2011). Consequently, the hydrograph was much smoother and easier for SWAT to capture. For the ephemeral creeks on the western side, the timing of the monthly peaks fit in generally quite well, indicating that SWAT was able to simulate rainfall-induced runoff during the winter season. However, the performance ratings were “unsatisfactory” based on all metrics. This could be attributed to the transient nature of these small rivers in response to local rainfall. Moreover, discrepancies might also result from the lack of data on actual irrigation and water management practices (Luo et al., 2008).

Underestimation of peak flow was observed at stations along the San Joaquin River. In fact, SWAT has been repeatedly reported to underestimate peak flow during extreme events (Feyereisen et al., 2007; Gassman et al., 2014; Zeiger and Hubbart, 2016; Zhou et al., 2014). This problem might be inherent in the model structure. Kim and Lee (2010) found that peak streamflow was underestimated using the SWAT built-in Muskingum routing method, and the prediction was improved by using a newly-developed nonlinear storage routing method (Kim and Lee, 2010; Kim et al., 2010). This method was tested in a watershed located in South Korea though it has not been incorporated into SWAT 2012.

4.2. Simulation of sediment

Results show that the more physically based CH_EQN-1 model outperformed the default CH_EQN-0 model (Fig. 3). The CH_EQN-0 model assumes unlimited sediment supply from channel erosion and that erosion is only dependent on sediment transport capacity. If the incoming load is less than the transport capacity, then channel erosion is assumed to meet this deficit. In CH_EQN-1, sediment supply from channel erosion is no longer unlimited. Given sufficient transport capacity, erosion only occurs when the shear stress on the bed and/or bank is more than the critical shear stress needed to dislodge the sediment particle (Neitsch et al., 2011). Consequently, CH_EQN-1 predicted less sediment yield (42% of the amount predicted by CH-EQN-0) and better match to observations.

Sediment simulation was judged as at least “satisfactory” based on two PMs during both calibration and validation periods. The *P-factor* was lower while the *R-factor* was higher compared to streamflow. The greater uncertainty associated with sediment simulation might result from the lack of knowledge about actual agricultural management practices that impact erosion and sediment transport. Most of the data missing the 95PPU were from the small loads, which was also observed in previous studies (Abbaspour et al., 2007; Ficklin et al., 2013). This could be attributed to the model's deficiencies in the groundwater component (Ficklin et al., 2013). On the other hand, the peak sediment discharge was overestimated despite the underestimation of peak streamflow (Figs. 2h and 3b). This might be due to SWAT's inability to represent the “second-storm” effect, which means that it is more difficult to mobilize sediment particles after a storm event, since there is less sediment available and the remaining surface layer is more stable (Abbaspour et al., 2007). As this phenomenon is not considered in SWAT, the model is likely to overpredict sediment load during the second and subsequent events.

4.3. Simulation of pesticide

The most sensitive pesticide parameters were AP_EF, PERCOP, and HLIFE_S (Table 3). By increasing AP_EF and PERCOP, more pesticide mass is input to the system and partitioned into surface runoff and lateral flow. HLIFE_S governs the decay rate of pesticide in the soil. As this value increases, the degradation process is slower and hence more pesticide is available for subsequent runoff events. Pesticide fate and behavior are also related to the soil adsorption coefficient (SKOC) which defines the partitioning of pesticide between soluble and sorbed phases. This parameter was found to be insensitive in our study. One possible explanation is that SKOC has dual impacts on the dissolved load of pesticide. A lower SKOC value partitions more pesticide into the soluble phase while accelerates pesticide migration to groundwater via leaching so that less pesticide is retained on the top soil for subsequent runoff events. Consequently, these two impacts could have been neutralized, resulting in overall low sensitivity of SKOC.

For pesticide simulation, it is of utmost importance that hydrology is well calibrated (Holvoet et al., 2005; Luo et al., 2008). In this study, pesticide calibration was based on the well calibrated parameters for streamflow and sediment, which contributed to the “good” performance ratings of pesticide simulation (Table 5). In addition, the spatial and temporal distribution of pesticide application proved to be a key factor for appropriate modeling results, and was often estimated because the exact location and date of application are often unknown (Bannwarth et al., 2014; Boithias et al., 2011; Fohrer et al., 2014; Vazquez-Amabile et al., 2006). In this study, the PUR system in California provides us with reliable pesticide use record at 1.0 $\times$ 1.0 mi spatial resolution and hourly time steps, resulting in less uncertainty in the input data.

Even with satisfactory performance ratings, it remains a challenge to fully capture the variation in diuron loads (Table 5 and Fig. 4). This could be partially explained by the uncertainty in the monitoring data. Monthly diuron monitoring data were aggregated from grab samples taken every 2–3 weeks. Those limited and intermittent sampling data might not be representative of pesticide yield during the entire month (Luo et al., 2008) and could have failed to capture the simulated peaks. Expanding the parameter ranges beyond the constraints may increase the *P-factor*, but may also result in unrealistic model parameterization (Abbaspour et al., 2007).

Pesticide fate and transport at the watershed scale strongly depends on pesticide physiochemical properties, agricultural management practices, and environmental conditions (Bannwarth et al., 2014; Ficklin et al., 2013; Fohrer et al., 2014; Gassman et al., 2014; Holvoet et al., 2005; Larose et al., 2007; Larson et al., 1997; Luo et al., 2008). Diuron has a low tendency to adsorb to soils and sediment and is predominantly transported via the water phase. Therefore, the occurrence of diuron in surface water was significantly correlated with precipitation and streamflow (Table 6). Significant strong correlations were found between the observed diuron load and the one-month and two-month antecedent use. This is probably due to the relatively long hydrolysis and aqueous photolysis half-lives of diuron (Moncada, 2004). On the other hand, the model predicted weaker association between load and antecedent use. This could be attributed to the overestimation of diuron transport in surface runoff and leachate during the first several events. It is likely that the curve number method for runoff generation, the storage routing method for soil water movement and the simplified groundwater component of SWAT have limitations in representing the mechanism of pesticide transport to surface water (Boithias et al., 2011; Fohrer et al., 2014). Further improvements in these algorithms should be investigated. However, even with some deficiencies, SWAT is still able to reasonably simulate pesticide load during the calibration period in our study and also during the validation periods in many others (Bannwarth et al., 2014; Ficklin et al., 2013; Larose et al., 2007; Luo et al., 2008).

According to model simulation, about 0.95% of the applied diuron was exported at the watershed outlet. This result was in agreement with previous studies, where the reported loss ranged from 0.05 to 1.6% for pesticides with properties similar to diuron (Boithias et al., 2011; Jaynes et al., 1999). The majority of diuron loads (>70%) were exported during major peaks, which could be up to 239 kg per month. Most of the peaks occurred during the winter months (December to February), when the current biological control agents of water hyacinth, and potential future agents of other aquatic weeds, are in quiescent life stages awaiting warming temperatures and new weed growth in late spring and summer. This timing will likely limit direct exposure of biocontrol agents to agricultural diuron runoff. Nevertheless, diuron is relatively persistent in aquatic system, therefore posing a potential threat in the warm season. The fate and transport of diuron within the Delta waterways requires further modeling efforts. Moreover, experimental determination of plant uptake of diuron and the associated impacts on the ability of insect biocontrol agents to damage aquatic weeds, should be topics for additional studies. Results from this study could also inform the design of monitoring programs. Under current climate conditions and diuron use patterns, the diuron monitoring program in the San Joaquin watershed should perform intense sampling from December to February, when peak loading of diuron occurs.

4.4. Conflicting performance ratings

Conflicting performance ratings were observed in this study. For instance, sediment simulation was judged as at least “satisfactory” based on two metrics but “unsatisfactory” based on the other (Table 5). This could be explained by the fact that each of the metrics captures a distinct aspect of model performance. R^2 quantifies the degree of linear correlation, *NSE* assesses how well the model-to-data plot fits the 1:1 line, while *PBIAS* is sensitive to systematic error. Therefore, the results indicate that the goodness-of-fit of SWAT varies across those aspects. It should be mentioned that in our study, *PBIAS* generated mostly lower ratings compared to R^2 and *NSE* (Table 5). This is probably due to the choice of ϕ as the objective function, which does not account for systematic over- and underestimation. It might be helpful to combine different (weighted) criteria into one overall objective function (Dai et al., 2010). However, this functionality is not supported in SWAT-CUP currently.

4.5. Sources of uncertainty

At the watershed scale, hydrologic modeling is often challenging due to the uncertainties in the large number of input data, spatial and temporal heterogeneity of parameters, and processes not represented in the models (Ficklin et al., 2013; Guzman et al., 2015; Schuol et al., 2008a). Inadequate land use representation is a potential uncertainty source in this study, as temporally varying land use were considered as constant throughout the simulation (Baffaut et al., 2015; White and Chaubey, 2005). However, stationary land use maps are commonly used in watershed-scale hydrologic modeling, because updating land use maps would require redefining HRUs and associated parameter values, which could significantly increase the complexity of the modeling process. The contribution of uncertainty in monitoring data has been recently emphasized (Bieger et al., 2014; Guzman et al., 2015; Panagopoulos et al., 2011), and efforts have been made to estimate uncertainty in discharge, sediment, nitrogen and phosphorus data (Harmel et al., 2009, 2014; Harmel and Smith, 2007; Harmel et al., 2014). However, quantifying uncertainties in measured values remains a demanding task, and transformation and/or aggregation of the monitored data could introduce additional uncertainties.

Model parameterization is another source of uncertainty. Often, the user's subjective judgement is involved in model parameterization. On the other hand, the knowledge of the model user is critical during parameterization (Abbaspour et al., 2015; Arnold et al., 2015b; Malone et al., 2015). Therefore, proper documentation and reporting of the modeling processes is important and increases the scientific credibility of results (Dharmendra et al., 2015; Moriasi et al., 2015b). In this study, ranges of each parameter adjusted during calibration were presented, and calibration and validation strategies were elaborated. It is believed that standardized reporting will help form the basis for future studies that simulate hydrology and flow-transported constituents such as sediment and pesticide (Arnold et al., 2012).

5. Conclusion

In this study, hydrologic modeling of streamflow, sediment, and pesticide diuron was performed in the San Joaquin watershed using SWAT. We found that regionalization of parameters was important as the dominant processes and sensitivity of associated parameters varied spatially. Streamflow of the San Joaquin River was most sensitive to channel parameters while streamflow of the western tributaries was mainly influenced by landscape parameters. Diuron simulation was rated as “good” by all PMs based on standardized PEC, benefiting from the “satisfactory” simulation of streamflow and sediment as well as the high-resolution PUR database. Significant correlations were observed between diuron load, and precipitation, streamflow and pesticide use. Compared to the simulated diuron load, the observed diuron load was more correlated with the antecedent diuron use, suggesting that SWAT might overestimate pesticide transport in surface runoff and leachate during the first several events. Uncertainty sources in this study include lack of knowledge about actual agricultural management practices, inadequate representations of land use, and pesticide monitoring data. We found that the majority of diuron transport (>70%) occurred during winter months, when the current biocontrol agents are in the state of dormancy. This timing limits direct exposure of biocontrol agents to agricultural diuron runoff, whereas exposure in the dry season could be a concern given the persistence of diuron in aquatic system. This study is expected to facilitate the advancement in large-scale water quality modeling, as well as in our understanding of diuron transport into the Delta region, potentially informing biological weed control planning.

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