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Evaluation of thiobencarb runoff from rice farming practices in a California watershed using an integrated RiceWQ-AnnAGNPS system

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Abstract

The development of modeling technology to adequately simulate water and pesticide movement within the rice paddy environment faces several challenges. These include: (1) adequately representing ponded conditions; (2) the collection/implementation of temporal/spatial pesticide application data at field scales; (3) the integration of various mixed-landuses simulation schemes. Currently available models do not fully consider these challenges and results may not be sufficiently accurate to represent fate and transport of rice pesticides at watershed scales. Therefore, in this study, an integrated simulation system, “RiceWQ-AnnAGNPS”, was developed to fully address these challenges and is illustrated in a California watershed with rice farming practices. The integrated system successfully extends field level simulations to watershed scales while considering the impact of mixed landuses on downstream loadings. Moreover, the system maintains the application information at fine spatial scales and handles varying treated paddy areas via the “split and adjust” approach. The new system was evaluated by investigating the fate and transport of thiobencarb residues in the Colusa Basin, California as a case study. Thiobencarb concentrations in both water and sediment phases were accurately captured by the calibrated RiceWQ model at the edge of field. After spatial upscaling, the integrated system successfully reflected both the seasonal pattern of surface runoff and the timing of monthly thiobencarb

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CRediT authorship contribution statement

Ruoyu Wang: Conceptualization, Methodology, Software, Writing – original draft, Writing – review & editing. **Ronald L. Bingner:** Conceptualization, Methodology, Software, Writing – review & editing. **Yongping Yuan:** Project administration, Funding acquisition, Writing – review & editing. **Martin Locke:** Project administration. **Glenn Herring:** Software, Validation. **Debra Denton:** Resources, Project administration. **Minghua Zhang:** Supervision, Writing – review & editing.

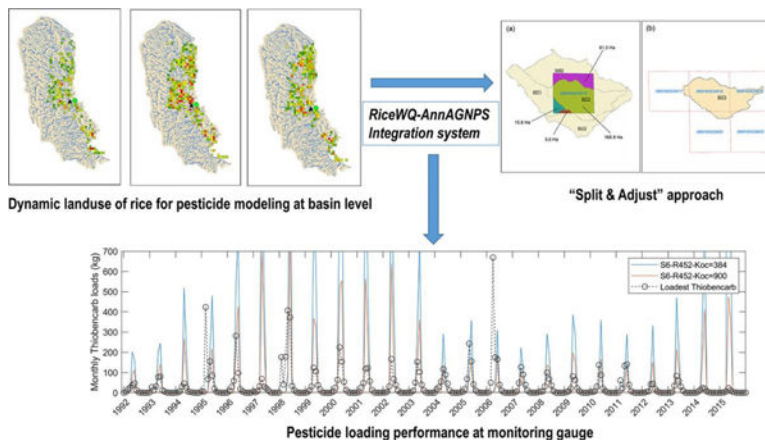
Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

loadings. Incorporating future enhancements can further improve model performance by including more detailed water drainage schedules and management practices, improving the accuracy of summer runoff estimations, and incorporating a more sophisticated in-stream process module. This integrated system provides a framework for evaluating rice pesticide impacts as part of a basin level management approach to improve water quality, which can be extended to other rice agrochemicals, or other areas with fine-scale spatial information of pesticide applications.

Graphical Abstract



Keywords

AnnAGNPS; Model integration; Pesticide modeling; Rice field; RiceWQ

1. Introduction

As a commonly grown agricultural crop, rice (*Oryza sativa*) is inevitably treated with various pesticides at different growth stages to avoid pest damage and maintain crop productivity. Rice pesticide transport into surface waterbodies negatively influences aquatic species (Rossi et al., 2020; Stadlinger et al., 2018). For example, thiobencarb, a commonly used rice herbicide controlling graminaceous weeds, had been reported to cause both acute and chronic toxicity to different non-target organisms, and is relatively persistent in both water and soil (Ceesay, 2000; Kuivila and Jennings, 2007; Quayle et al., 2006). Both laboratory and field studies exhibited negative effects of thiobencarb on aquatic invertebrates and vertebrates, including the reduced emergence success, shortened development time (Burdett et al., 2001), and significant inhibitory effects on Acetylcholinesterase activity (Fernández-Vega et al., 2002) and fecundity (Elias et al., 2020).

Monitoring systems are often applied to measure and assess the extent of water quality degradation caused by various agrochemicals. Local stakeholders have investigated rice pesticide residues in surface water via sampling and chemical analysis (Bhattacharjee et al., 2012; Carazo-Rojas et al., 2018). Monitoring results are then linked to usage and application patterns for mitigation purposes (Fabro and Varca, 2012; Wagner et al., 2019). Due to the expense and labor costs, most pesticide monitoring and usage reporting is confined to

field scales and for limited periods of time (DeMars et al., 2021). Long term, large scale monitoring and reporting usually exceeds typical research grant periods and require both funding and legislative support from the government. Currently, a highly detailed usage reporting system is only available in California, USA. State law requires farmers to report pesticide application times and amounts by crop type to the California Department of Pesticide Regulation (CDPR). Agricultural applications are recorded with sub-daily scale and are spatially organized using the Public Land Survey System (PLSS) section spatial resolution (County/Meridian/Town/Range/Section, or COMTRS, ~1 square mile), which formed the Pesticide Use Reporting (PUR) database (CDPR, 2015). The abundance of pesticide usage information provided a rare opportunity to study and develop modeling technology for rice pesticide fate and transport, given the expensive nature and limited resources for extensive water quality monitoring in California, which is the second largest US rice growing state.

Considering the complexities of rice management systems, extra cares should be taken in fate and transport simulation of rice pesticides via modeling approaches (Wang et al., 2019c). Compared to other crops, rice fields are applied with a more detailed management practices, making it a more complicated ecohydrological system. Rice fields are usually flooded during the growing season, requiring irrigation to maintain the ponded condition. Pesticides applied in paddy fields are released to agricultural ditches via controlled drainage or overflow when water depths exceed the height of the drainage gate. The alternating wet and dry environment also induces oxygen content variation of soil and water, ranging from aerobic to anaerobic conditions.

Generally, to adequately simulate water and pesticide movement within the rice paddy environment faces four challenges. The first challenge is in the representation of the appropriate processes within a rice paddy model, which should include: paddy water-soil pesticide exchange, paddy water management practices, and aquatic dissipation or metabolism degradation of pesticide residues (Luo et al., 2012; Wang et al., 2018). The second challenge is in the collection of pesticide application information. The lack of accurate spatial application information can substantially affect the accuracy of simulation results (Fohrer et al., 2014; Janney and Jenkins, 2019), but are common in most areas. The third challenge is the integrating technology at basin scale capturing the spatial aspects of the system. Usually, multiple other landuses co-exist with the rice system in the same watershed. Therefore, it requires at least two different simulation schemes to address both rice and dryland crops. The fourth challenge is specific to California: the detailed pesticide usage summery (PUR database) is not ideal for direct utilization in modeling, because of the spatial organization of the dataset. In California, usage is reported at field scale, but is spatially lumped at the COMTRS level. This means the spatial shape and location of each treated paddy field is not identifiable inside a COMTRS. Besides, the acreage of treated fields and applied amount varies from year to year. Since most models have their own basic simulation unit to represent field level processes (usually with a defined boundary), the spatial inconsistency between basic simulation units and COMTRS brings difficulties in incorporating detailed usage information for field level simulation. Further, detailed spatial information of rice treated area (COMTRS level) requires more spatially refined “subwatershed- hydrological simulation unit” schemes. Otherwise, the variation of pesticide

application/management information will be spatially unified due to the coarse simulation schemes.

Many previous research efforts have attempted to overcome one or more of the challenges mentioned above, but not all four. For example, scientists developed many pesticide models specifically for paddy fields. Commonly used rice models include Pesticide Paddy Field Model (PADDY) (Inao and Kitamura, 1999), Rice Water Quality Model (RICEWQ) (Williams et al., 2014), Simulation Model for Pesticide Concentrations in Paddy Field (PCPF) (Watanabe et al., 2006), and Pesticide in Flooded Application Model (PFAM) (Young, 2012). However, these models are limited to the field scale and are incapable of simulating pesticide transport to downstream waterbodies, which is of great importance in pesticide ecological risk assessments (Wang et al., 2019b).

To expand simulations from field to watershed scales, researchers attempted to integrate models, or adapt rice paddy simulation modules into well-developed ecohydrological models. For example, Miao et al. (2003) coupled RICEWQ model and a stream transport model (RIVWQ) to evaluate the environmental concentration of Tricyclazole in paddy fields and adjacent water bodies. Simulation results exhibited a successful predicting of pesticide exposures in water bodies near paddies for higher tier risk assessments. However, RICEWQ-RIVWQ is more suitable for a rice dominated watershed, but not adequate for watersheds with mixed landuses. As a commonly used basin level model, Soil and Water Assessment Tool (SWAT) is also applied to evaluate the fate and transport of pesticides (Wang et al., 2019a). However, the default SWAT pothole algorithm lacks the capacity to simulate paddy fields (Wang et al., 2018). Therefore, efforts have been made to modify the default SWAT module (Sakaguchi et al., 2014; Wu et al., 2019; Xie and Cui, 2011), making it more suitable for rice simulation via algorithm improvement (e.g., pothole shape, evaporation process, overflow generation) in the SWAT hydrological component. The most recently released version is called SWAT-Paddy (Tsuchiya et al., 2018), which has been evaluated in northeastern China for hydrology and nitrate simulation (Ouyang et al., 2020), but not pesticide simulation.

To our knowledge, PCPF-1@SWAT (Boulangue et al., 2014; Tu et al., 2018) is the only successful application for rice pesticide simulation at the watershed level, with both paddy and dryland simulation systems to address the mixed landuses within a watershed. PCPF-1@SWAT not only improved the hydrological component (pothole and overflow algorithm improvement) of the SWAT model, but also utilized PCPF-1 for pesticide simulation in paddy water and shallow soil layer, and coupled with SWAT to track pesticide movement in deeper soil layers, as well as chemical transport in river channels. The main challenge of using PCPF-1@SWAT in California is how to incorporate COMTRS pesticide application information in the modeling system. The basic simulation unit, or the so-called hydrological response unit (HRU) in SWAT is decided by landuse, soil, and slope. Inside a subbasin, multiple paddy fields at different COMTRS could be treated as one HRU as long as the same slope and soil type are maintained. Therefore, rice HRU could be geographically separated with multiple fields. Each paddy field could be treated differently depending on the application date/rate summarized from its located COMTRS. However, SWAT always treats HRU as one, and applies the same management practices (Liu et al., 2019; Wang et

al., 2017) and climate information (Wang et al., 2016; Yen et al., 2018) to different fields in such HRU. The spatial simplification could be tolerated if no detailed management practices were available, but not in California, where pesticide application information is summarized in fine spatial scaled COMTRS. Besides, the HRU simplification also makes it difficult to handle the annual variation of rice planting acreages, which is also reported at COMTRS level (~1 mi², Fig. 1).

Compared to other ecohydrological models for agrochemical simulation, the Annualized Agricultural Non-Point Source pollution model (AnnAGNPS) provides spatial explicit hydrological boundaries as its basic simulation unit (AnnAGNPS cells) (Chahor et al., 2014). Therefore, accurately incorporating the detailed, COMTRS level rice pesticide application/loading information into the basin level modeling system is possible. The combination of characterization of spatial explicit information and simulation capabilities at field to basin scales using AnnAGNPS provides an effective way to link with other field level models or newly designed components (Shen et al., 2016; Yasarer et al., 2018; Yuan et al., 2007). The capability of AnnAGNPS in reflecting soil erosion and sediment transport (Chahor et al., 2014; Zema et al., 2016) is another advantage for pesticide modeling, because many pesticides are hydrophobic, which are more easily absorbed by sediments during the channel transport process.

Considering all these modeling challenges, and the advantages of AnnAGNPS, we therefore proposed a new integrated simulation system “RiceWQ-AnnAGNPS” to evaluate pesticide fate and transport appropriate for California rice paddy environment, which not only extends field level simulations into watershed scales considering mixed landuses, but also maintains the fine spatial information of pesticide application and varying acreages of rice treated areas.

The detailed objectives of this study are two folds. The first objective was to build an integration framework to investigate rice pesticide runoff with the field scale RICEWQ model and the watershed scale AnnAGNPS model, investigating pesticide runoff from paddy fields. The second objective is to demonstrate the application of this new integrated modeling system in the Colusa basin with intense rice farming, but also containing many other landuses.

2. Methodology

2.1. Study area

For this modeling research we selected a headwater subbasin in northern California, the Colusa Basin, as our study area. The Colusa basin envelopes the northern portion of Yolo County, most of Colusa County, and the lower part of Glenn County, with a total drainage area of 4137 km². Colusa basin is a typical watershed in this region, with intensive rice farming (19.93%) and other cultivated landuses (almond, spring wheat, tomato, etc) accounting for 18.08% of the drainage area. The main channel in the watershed is the Colusa basin drain, conveying tailwaters from paddy fields with pesticide residues, and eventually draining to the Sacramento river, transporting to downstream areas. Inside Colusa Basin, daily precipitation and temperature data is recorded by NOAA Global Historical

Climatology Network Daily (GHCND) Station USC00041948 (COLUSA 2 SSW, CA US). Daily flow discharges are collected by California Department of Water Resources at station A02976 (Fig. 1). Water sampling for dissolved thiobencarb is measured near A20976 by California Rice Commission and State Water Resources Control Board. Usually, water quality sampling is conducted weekly during the rice growing season (late April to July). Rice paddy fields are treated with thiobencarb each year since the early 1990s, with treated acreage and location varies every year (Fig. 1).

2.2. Model introduction

2.2.1. RiceWQ—The RICEWQ model is the field level pesticide exposure model specifically designed for paddy environment (Williams et al., 2014). RICEWQ considers ponded water conditions in paddy fields, simulating water movement and pesticide fate associated with rice water management practices (e.g., irrigation, controlled drainage, overflow).

The principle of mass balance is utilized to track the change of water volume, as well as the pesticide residues in three phases, which are plant foliage, water layer and paddy sediment. After pesticide application, some chemicals may be intercepted by crop leaves, while most of them are maintained in paddy water or absorbed to paddy sediments. Model simulates the chemical partitioning between water and sediment through the process of direct partitioning, diffusion, the settling and resuspension of suspended sediment.

Pesticide residues in both water and sediment are further simulated via the decay to solar radiation (photolysis), the reaction with other chemicals in water layer (hydrolysis), and the degradation by micro-organisms (biolysis). RICEWQ provides pesticide and water loadings at the edge of the field. Users can adjust the water depth to implement irrigation or discharge. When paddy water is released, flow discharge with pesticide residue in the water phase is removed from the simulation system. When paddy water is recharged, then pesticide residues will be re-distributed between the sediment compartment and recharged water layer.

In this study, RiceWQ was used to simulate the thiobencarb loadings in both paddy water and sediment at the field level. Pesticide loadings and water discharged from paddy fields were then lumped at the COMTRS level. Due to the limitations of overserved data, we conducted the calibration at one rice field in Glenn County which had adequate measurement collected by Ross and Sava (1986). The purpose of this field level calibration was to evaluate RiceWQ performance in representing physiochemical processes of thiobencarb in both paddy water and soil compartments, while considering more spatially explicit information, such as soil properties, climate inputs, and water/pesticide management practices. The field-level modeling performance can be found in the “Results and Discussions” section.

2.2.2. AnnAGNPS—Designed and developed by USDA-ARS, AnnAGNPS is a process-based, daily time scale model for hydrological and water quality simulation at the watershed scale (Yuan et al., 2003; Yuan et al., 2007). AnnAGNPS employs GIS technology to divide the watershed into various sub-areas with explicit hydrological boundaries (i.e AnnAGNPS

cells) and generate a reach network to route overland flows from AnnAGNPS cells. Each AnnAGNPS cell is the basic spatial simulation unit associated with a single climate, landuse, soil type and management throughout the cell.

Daily soil moisture balance is maintained via the simulation of applied water (precipitation and irrigation), runoff, evapotranspiration and percolation. The rainfall-runoff processes at cell level are simulated using the NRCS Curve Number (CN) approach as part of the method to determine runoff, and the TR-55 approach to determine peak flow rate (Bosch et al., 1998). Surface runoff can also be a result of irrigation management and snowmelt processes. Potential Evapotranspiration (PET) is simulated using the Penman-Monteith equation. Actual evapotranspiration is adjusted based on PET, crop coefficients at different growth stages (Allen et al., 1998), and the available soil moisture in each AnnAGNPS cell. Sheet and rill soil erosion is determined by the Revised Universal Soil Loss Equation (RUSLE) (Renard, 1997). Pesticide simulation at the cell level is adapted from the GLEAMS model (Knisel and Douglas-Mankin, 2012). Both soluble and sediment attached pesticides can be simulated within AnnAGNPS.

Daily load of water, sediment, nutrient and pesticide is transported from AnnAGNPS cells to reaches, moving from upstream to downstream, and eventually to watershed's main outlet (Taguas et al., 2012). Reach routing is conducted when runoff is generated in an AnnAGNPS cell. Sediment in the channel is composed of sheet/rill, gully and bed/bank sediments, and is routed based on the Bagnold equation (Bagnold, 1966; Yen et al., 2017). Pesticide residues are transported by both sediment and water in the reach network. The pesticide in transport is degraded based on their half-life, water temperature, and reach travel time. The soluble portion can be further reduced by water infiltration at channel bottoms. The sediment-attached portion are adjusted by changes in clay sediment from the upstream to downstream. Pesticide equilibration is conducted at the beginning (upstream) and the end of the routing (downstream).

In this study, AnnAGNPS was used to simulate all non-rice landuses in Colusa Basin. Surface runoff from all landuse types, and rice pesticide loadings provided by RiceWQ were routed to downstream areas through the channel network delineated by AnnAGNPS. Detailed model integration approach could be found in the next section.

2.3. Model integration

The spatial inconsistency in RiceWQ and AnnAGNPS simulation units/scales requires an integrated modeling system for watershed level simulation. AnnAGNPS conducts simulation in AnnAGNPS cells with hydrological boundaries. Only one dominate management is assigned to each AnnAGNPS cell. RiceWQ, on the other hand, summarize rice field results (pesticide loadings and paddy water discharge) at the COMTRS level. To include rice pesticide runoff into the AnnAGNPS simulation scheme (Fig. S1), a step-wise approach (Split & Adjust approach) was proposed for integration:

1. Simulate paddy water discharge/thiobencarb loadings at the edge of the field by RiceWQ.

RiceWQ was used to simulate all paddy fields located in COMTRS. Daily loadings from each section could be directly taken from RiceWQ results as $W_RICEWQ_{section,n,t}$ and $P_RICEWQ_{section,n,t}$ which explained by Eqs. (2), (3) respectively in detail in the later section.

2. Divide water and pesticide loadings at COMTRS section level into different AnnAGNPS cells.

Rice pesticide loadings lumped at the COMTRS section scale finally entered the channel streams which is associated with AnnAGNPS cells. If the grid section is overlaid with several cells, then both water discharge and pesticide loadings (daily time series data) from one COMTRS section (06M16N03W16 in Fig. 2a) need to be separated into several intersected AnnAGNPS cells (ID: 6582,5671, 6573, 6572 in Fig. 2a).

Pesticide loadings distributed to each AnnAGNPS cell was controlled by “split ratio”, which is computed based on the overlaid area inside each COMMTR (represented in multiple colors at 06M16N03W16 in Fig. 2a). Eq. (1) was used to distribute pesticide loadings from one section into several AnnAGNPS cells over the entire simulation.

$$Ratio_{split} = \frac{AreaInter_{cellID}}{\sum_1^m AreaInter_{cellID}} \quad (1)$$

Where $AreaInter_{cellID}$ is the intersected area for a specific AnnAGNPS cell, m is the total cells intersected with the grid section under scrutiny, in Fig. 2a, $m = 4$. $Ratio_{split}$ is the split ratio. The denominator part of Eq. (1) equals to the area of COMTRS 06M16N03W16.

For example, the intersected area for AnnAGNPS cell “6852”, “6571”, “6573” and “6572”, are 61.3, 15.8, 168.9, 5.0 hectares respectively (represented as purple, green, brown and olive polygons in Fig. 2a), then the split ratio for cell 6573 is $168.9 / (61.3 + 15.8 + 168.9 + 5.0) = 67.3\%$, which means 67.3% of the loadings from paddy fields in COMMTR 06M16N03W16 will contribute to AnnAGNPS cell 6573.

Similarly, split ratios from other sections (06M16N03W15, 06M16N03W17, 06M16N03W21, 06M16N03W22) are computed, which are also intercepted with the cell 6573, and will contribute water and loadings to this AnnAGNPS cell.

3. Aggregate water and pesticide loadings from different sections into one AnnAGNPS cell.

Based on daily water and loading from step1 and split ratio from step 2, for any given AnnAGNPS cell, aggregated water loadings from paddy fields was computed by Eq. (2)

$$W_RICEWQ_{cell,t} = \sum_1^n (Ratio_{split} * W_RICEWQ_{section,n,t}) \quad (2)$$

where $W_RICEWQ_{cell,t}$ is the total water loadings aggregated to a specific AnnAGNPS cell in day t (m^3). $W_RICEWQ_{section,n,t}$ is the water total loadings (m^3) lumped at the grid

section n for day t (provided by RiceWQ daily results). n is the total number of sections contributing pesticide runoff to a specific AnnAGNPS cell. In the case of Fig. 2b, $n=5$.

Similarly, the pesticide loadings in water phase for a specific AnnAGNPS cell was computed based on Eq. (3)

$$P_{RICEWQ_{cell,t}} = \sum (Ratio_{split} * P_{RICEWQ_{section,n,t}}) \quad (3)$$

where, $P_{RICEWQ_{cell,t}}$ is the pesticide loadings in paddy water aggregated to a specific AnnAGNPS cell in day t (mg). $P_{RICEWQ_{section,n,t}}$ is the pesticide loadings (mg) lumped at the grid section n for day t (provided by RiceWQ daily results).

The dissolved pesticide loadings transported by runoff was computed by Eq. (4)

$$P_{d-RICEWQ_{cell,t}} = \sum (Ratio_{split} * P_{RICEWQ_{cell,t}} * F_{DW_{cell}}) * 10^{-6} \quad (4)$$

where, $F_{DW_{cell}}$ is the dissolved fraction of RICEWQ pesticide in water. The coefficient 10^{-6} is the conversion of loadings from mg kg.

$$F_{DW_{cell}} = 1/(1 + K_{oc} * F_{oc} * C_{ss} * 10^9) \quad (5)$$

K_{oc} is the organic carbon partition coefficient (m^3/mg) of thiobencarb, which may vary from 384 ml/g to 1435 ml/g (Fisheries, 2012). F_{oc} is the fraction of organic carbon. C_{ss} represents the sediment concentration of the RICEWQ water load (Mg/m^3), which is assumed to be all clay. A default value of 30 ppm ($0.00003 Mg/m^3$) is derived from personal contact with the RICEWQ developers.

The pesticide loadings attached with suspended sediment was then computed by Eq. (6)

$$P_{a-RICEWQ_{cell,t}} = P_{RICEWQ_{cell,t}} - P_{d-RICEWQ_{cell,t}} \quad (6)$$

4. Adjust AnnAGNPS cell area.

Rice paddy fields not only provide pesticide runoff to a specific cell, but also take a considerable acreage. Actually, we can image treated paddy fields as point sources in the integrated modeling system, which also occupy certain acreage in the watershed. The area of AnnAGNPS cell need to be adjusted to avoid double counting when non-rice fields are simulated.

The treated rice area in a specific AnnAGNPS cell was computed by Eq. (7)

$$AITA_{cellID} = \sum_1^n (Ratio_{split} * AreaTreated_{section,n}) \quad (7)$$

Where $AreaTreated_{section,n}$ is treated rice area (m^2) lumped at the grid section n , $AITA_{cellID}$ is the total treated rice area (m^2) for a specific AnnAGNPS cell.

Therefore, the non-treated area for a specific AnnAGNPS cell was computed by Eq. (8)

$$NTA_{cellID} = Area_{cellID} - AITA_{cellID} \quad (8)$$

where $Area_{cellID}$ is the total area of one AnnAGNPS cell, NTA_{cellID} is the non-treated area in such cell, which is simulated by AnnAGNPS in the next step.

5. Model non-rice landuse by AnnAGNPS. Integrate water/pesticide from all landuses, and route them from fields to channels.

If an AnnAGNPS cell is not intersected with any rice sections, then this entire cell was simulated by AnnAGNPS. Otherwise, NTA_{cellID} was computed based on Eq. (8) to decide the proportion of the cell for AnnAGNPS simulation. Flow/pesticide from paddy fields and flow/sediment from other landuse in AnnAGNPS cells eventually transported to channels. Pesticide was redistributed between water and sediment during the channel transport process using AnnAGNPS in-stream process algorithm.

3. Results and discussions

3.1. RiceWQ simulation results at the field scale

Field level evaluation was conducted for unit area loadings in the paddy water and soil phases (Fig. 3a and b). The thiobencarb concentration in released drainage was also evaluated (Fig. 3c). Evaluation of field level modeling is based on measurement in a paddy field (40 ha) at Glenn County, California (Ross and Sava, 1986). Thiobencarb was applied on May 30th (9 days after rice seedling) with the rate of 4.48 kg/ha. After application, water was held for six days at average depth of 25 cm. Then, water with thiobencarb residues was rapidly drained from the field after holding. Detailed information on parameter set comparisons between the equilibrium test and the field level calibration is recorded in Wang et al. (2019b). RICEWQ was able to mimic the pesticide loadings in both paddy water and soil phases after calibration, as well as the thiobencarb concentration in discharged water. After thiobencarb application in late May, pesticide was distributed between both water phase and soil phase. Loadings in both paddy water and paddy soil reached to their peak values around a week after application. Then loadings in water drops substantially in middle June due to releasing paddy water from the field (Fig. 3a). Since thiobencarb was strongly attached to soil particles, loadings in the soil phase were not significantly affected by the water release in Middle June. The dissipation process is slow in paddy soil, reflected by a considerable measured value in early July (Fig. 3b). Satisfactory model performance provided confidence in the accuracy of pesticide mass and concentration values at the edge of the field, which is a prerequisite for subsequent watershed level integration. We then extended the calibrated parameter settings from the test plot to all paddy fields in the Colusa basin. Daily water and thiobencarb loadings are both coupled with AnnAGNPS based on our proposed “split & adjust” integration method.

3.2. Observed surface runoff and monthly thiobencarb loadings

Currently, no groundwater module has been developed within AnnAGNPS to represent the contribution of return flow to total streamflow discharge. Therefore, AnnAGNPS only represents surface runoff, not including baseflow conditions (Zema et al., 2016). Separating surface runoff from daily observations at CDWR station A02976 is useful for model performance evaluation. The baseflow-surface runoff separation was conducted by the automated digital filter, which has been widely employed to split high-frequency and low-frequency signals (Arnold and Allen, 1999; Lee et al., 2018). The baseflow ratio is around 54% for the entire period (Fig. 4).

Thiobencarb measurements were conducted via water sampling near CDWR station A02976, reported as instantaneous concentrations. However, infrequent instantaneous concentration values cannot be used directly for model performance evaluation. It is better using the mass (loadings) of chemical constituent as observed measurement, which considers both instantaneous concentration and continuous flow discharge. Therefore, the USGS Load Estimator (LOADEST) was utilized to calculate the constituent loadings in streams via multiple regression equations (Runkel et al., 2004), when a time series of observed streamflows and instantaneous thiobencarb concentrations was provided. Fig. 5a shows the flow discharges and instantaneous concentrations of thiobencarb at station A02976. The peaks of flow discharge and thiobencarb concentration are detected at different time periods, with peak discharge occurring in winter, but higher concentrations occurring in summer, when paddy fields released ponded water into the ditches. Compared to other years, the late 1990s and early 2000s experienced higher concentrations, which were consistent with the overall pesticide application pattern in this area (CDPR, 2015). Peak loadings of thiobencarb in each year occurred in the summer months (Fig. 5b). In addition, similar to the peak concentration pattern, the higher loadings were also found in the period of 1995–2002. The highest loadings happened in 2006 due to the higher flow discharge in the summer months of that year, since measured concentrations were at lower levels in 2006. The monthly loadings generated by USGS LOADEST (Fig. 5b) were used to evaluate model performance of thiobencarb simulation in the following section.

3.3. Coupling results at reach segment

The integrated modeling system did a good job in capturing monthly surface runoff for the entire 23-year period (Fig. 6a), especially for runoff caused by winter storms, though the system showed modest overestimation of winter peak flows. The average monthly discharges for observed and simulated surface runoff are 10.21 m³/s and 11.08 m³/s, respectively. Monthly statistics of Mass Balance Error, R-squared and the Nash-Sutcliffe Coefficient (Nash and Sutcliffe, 1970) are 7.1%, 0.859 and 0.704, respectively, which are adequate based on the standard model performance evaluation criteria recommended by Moriasi et al. (2015). For summer months, the integrated model systematically underestimated the surface runoff (Fig. 6b), noting the change in the Y axis from a linear scale (Fig. 6a) into a log scale. For the summer months, Mass Balance Error and R-squared values are -8.7% and 0.432, respectively, while the Nash-Sutcliffe Coefficient is negative (-1.283). We attribute the poor performance of surface runoff in the summer months to three factors: 1) the uncertainty of irrigation information in summer months for dryland crops; 2)

the uncertainty of water releases from rice fields; and 3) the uncertainty in baseflow-surface runoff separation.

Agricultural lands in California must be irrigated in summer, since most precipitation events occur in the winter and spring. Irrigation-runoff is the dominant source of summer surface runoff in California. The irrigation schedule applied in this study was estimated based on crop evapotranspiration, which is a water-use efficient method for deriving irrigation amounts and times. This approach may underestimate the irrigation amount (Fig. 6c), resulting in the generation of less tailwater from dryland crop fields. Therefore, summer surface runoff is underestimated as shown. In addition, the amount of water released from rice fields was also uncertain. In current model settings, the schedule of water release was mainly dependent on the rice pesticide management requirement (Wang et al., 2019b). For thiobencarb, paddy water was released only once after application in RiceWQ. However, paddy water could actually be released multiple times during the rice growing season (Kim et al., 2006), which is not completely captured by RiceWQ. Another factor causing the underestimation of summer surface runoff is the limitation of the observed data. The surface runoff was actually the processed data after applying the automated digital filter, which separated the high frequency signal (surface runoff) from the low frequency signal (baseflow). In other words, the baseflow separation was based on signal analysis instead of physically-based laws, which may introduce uncertainties into the surface runoff estimations (Zhang et al., 2013).

Two scenarios are compared to examine the sensitivity of K_{oc} in controlling the dissolved loadings of thiobencarb at station A02976 (Fig. 7). Based on Eqs. (4), (5), K_{oc} is the adjustable parameter for altering the relative portions of soluble and absorbed components of the pesticide. We selected two K_{oc} values (384 vs. 900 ml/g) to test the responses of dissolved loadings to the parameter selection. The seasonal trend of dissolved thiobencarb is successfully captured by the “RiceWQ-AnnAGNPS”, with the timing of peaks being accurately reflected. However, although the simulated thiobencarb mass is at the same order of magnitude as the observation, the model substantially overestimated the monthly loadings. Adjusting the K_{oc} value from 384 to 900 ml/g was a promising way to reduce the peak loadings. For some specific years (1993, 2004–2013), the adjusted loadings matched very well with the monthly overserved loadings, but for other years (e.g., 1994–2003, 2014–2015), the model still substantially overestimated the monthly loadings. For the entire simulation period, the monthly statistics of Mass Balance Error, R-squared and the Nash-Sutcliffe Coefficient are 24.3%, 0.189, and -1.289 respectively (Table S1). Although the Mass Balance Error is not huge for the entire period, poor Nash-Sutcliffe Coefficient indicates the significant mismatch of several years’ loadings. The statistic value of R-square is much better than Nash-Sutcliffe Coefficient, implying that simulated data have the same trend with observed data (LOADEST estimation) in time, but not at a proportionate rate (Wang and Kalin, 2011).

Thiobencarb is moderately to slightly mobile in sediment, with a K_{oc} range from 384 to 1435 ml/g (Fisheries, 2012). Therefore, we can further adjust K_{oc} , tweaking it beyond 900 ml/g to further reduce the loadings in the 1990s. However, this strategy may lead to underestimation after year 2004. We attribute the poor performance of dissolved thiobencarb

loading to several uncertainties and errors: 1) the uncertainty caused by paddy water releases as AnnAGNPS inputs; 2) the uncertainty in generating monthly observed loadings; 3) the structural uncertainty of model in-stream processes; and 4) accumulated errors from the summer flow simulation.

Thiobencarb is an herbicide used only in rice paddy fields, so thiobencarb residues detected in Colusa channels should all come from released paddy water. Since the paddy water drainage schedule was estimated based on the purpose of rice pesticide management, water release from rice fields may not completely captured and provided to AnnAGNPS as accurate input. Another factor affecting the accuracy of water releasing is related to tailwater management practices. The model treated the released paddy water as point sources, with direct discharge from the edge of fields to channels. However, rice growers in California may apply a “recirculating tailwater recovery system” to facilitate the reuse of drainage water and avoid direct pesticide runoff to public waterways (UCCE, 2015). Currently, there are no available records summarizing farms which applied the “recirculating tailwater recovery system” in their paddy fields. Therefore, the model does not consider any loading reduction due to tailwater management practice, which could substantially reduce observed thiobencarb residues in channel segments.

The mismatch between observed and simulated loadings may also be impacted by the uncertainty in estimating monthly thiobencarb loadings via LOADEST. Note that the ground truth measurements of thiobencarb are instantaneous concentrations, but not mass loadings. The load estimation process is complicated, and may experience various sources of error, such as retransformation bias, data censoring and non-normality (Jiang et al., 2014; K. Jha et al., 2007). The regression equations applied by LOADEST first build a relationship between instantaneous concentration and flow discharge, and then loadings are estimated. Thiobencarb sampling is always conducted in summer months under low-flow conditions, making its loading estimations inaccurate under high-flow conditions. This factor could explain the abrupt appearance of high loadings in 2006 (Fig. 7), when instantaneous concentration water samplings were not high (Fig. 5a). The extreme high loading can be caused by the imprecision and bias of USGS LOADEST in the extrapolation to high flow conditions. Besides, the instantaneous concentrations of water quality data are not error free either, but associated with measurement uncertainty (Moriassi et al., 2007; Yen et al., 2016), which are usually caused in sample collection, sample storage/preservation, and chemical analysis (Harmel et al., 2006). Therefore, the uncertainty in monthly thiobencarb loadings is further exaggerated by measurement errors.

Model structure uncertainty is another factor potentially resulting in loading overestimation. The in-stream process module of AnnAGNPS for pesticide transport is relatively simple, mainly based on a first order equation to demonstrate the equilibration of dissolved and absorbed pesticide at a reach segment. However, the real natural process is more complicated. Seepage, diffusion, sediment settling, and resuspension processes all affect the relative portions of dissolved and absorbed pesticide. Therefore, module enhancements of the in-stream process will help improving model performance as well.

Accumulated error is the last possible reason for inaccurate prediction of pesticide loadings. Model performance of dissolved pesticide is directly related to flow, while model's accuracy in representing particulate pesticide is also related to the sediment fate and transport. The interdependencies among the constituents are due to their shared transport processes. Although the integrated modeling system successfully captured the surface runoff for the entire period, model performance for thiobencarb loadings was more dependent on summer surface runoff. Therefore, the inaccuracy in summer surface runoff estimation (Fig. 6b) may introduce additional errors in pesticide loading predictions.

4. Summary and conclusions

In this study, an integrated modeling system, "RiceWQ-AnnAGNPS", was designed for rice pesticide simulation at the watershed level. We applied it to the Colusa basin, California, evaluating its ability to capture surface runoff and thiobencarb loadings. The integrated system overcomes three common modeling difficulties in rice pesticide simulation at the watershed level, including the representation of appropriate processes for paddy fields with ponded water, the collection and implementation of pesticide application information, and the handling of mixed/multiple landuse simulation. It also resolves one challenge specific for areas like California: the spatial inconsistency between the organization of pesticide application information and basic hydrological simulation units for watershed level modeling. The "split & adjust" approach has been successfully implemented by the integrated system to maintain the most spatially explicit pesticide application information, and to handle the dynamic treated rice acreage which varies from year to year. Since the integrated modeling system extends field level simulation into basin scale with mixed land uses. Therefore, the effect of several non-structural conservation practices (e.g., reduced rate, water holding) in controlling pesticide loadings can also be evaluated at downstream water bodies via the help of this new designed system.

Based on our modeling results, the thiobencarb concentrations in both water and sediment phases were well captured by the calibrated RiceWQ at the edge of field. After including the rice pesticide runoff loadings from COMTRS to AnnAGNPS simulation schema, the integrated modeling system successfully reflected the seasonal pattern of surface runoff, especially the runoff caused by winter storms. However, summer surface runoff is not well reflected due to the uncertainty in irrigation of dryland crops, inaccurate estimation of paddy released water, and potential limitations in baseflow-surface runoff separation by the recursive digital filter. The integrated modeling system was able to reflect the timing of monthly thiobencarb loadings, but not the amount estimated by LOADEST. Adjusting the K_{oc} value was a promising strategy to avoid loading overestimation for several years, but not for all years. Further enhancements can be incorporated into the integrated system for future studies, such as including more detailed water drainage schedules and management practices of paddy fields, conducting more accurate summer runoff estimations, and developing a more sophisticated module representing thiobencarb in-stream processes.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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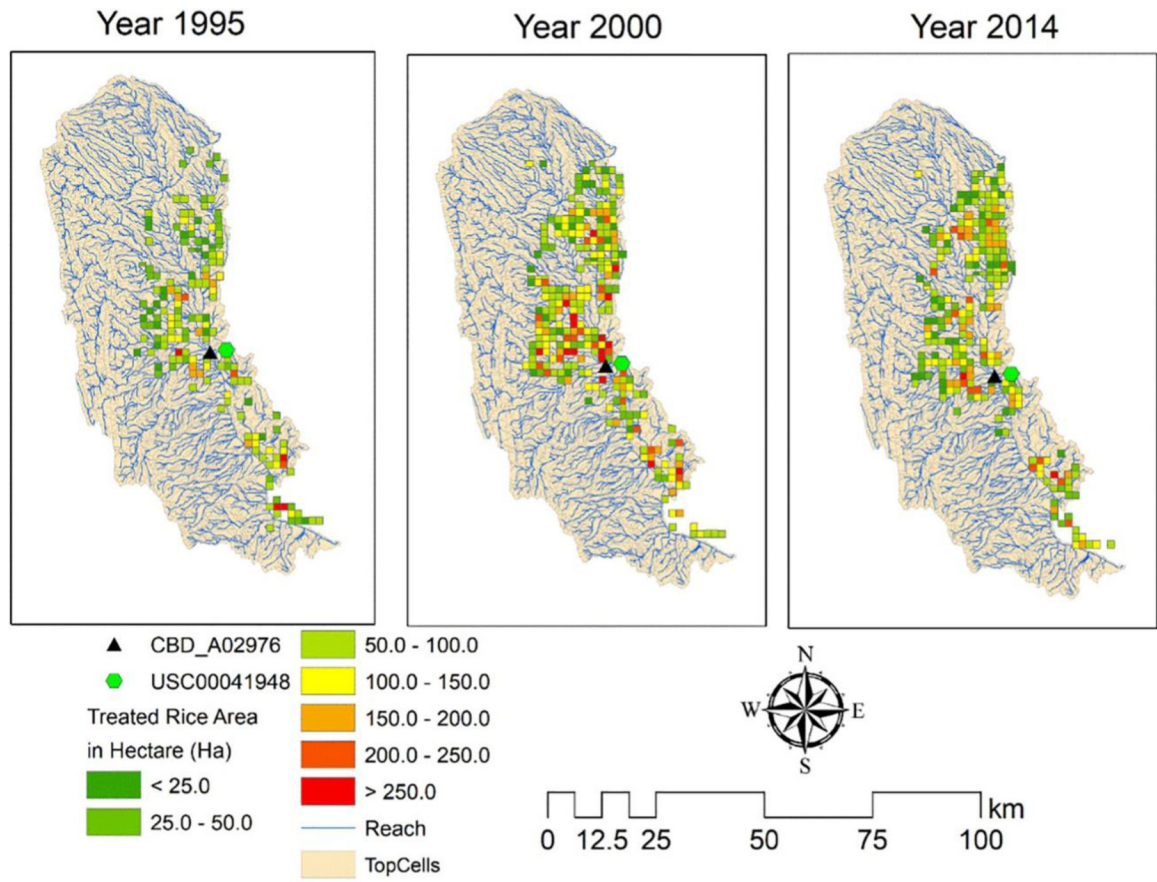


Fig. 1. The variation of thionecarb treated acreages (COMTRS level) in Colusa Basin.

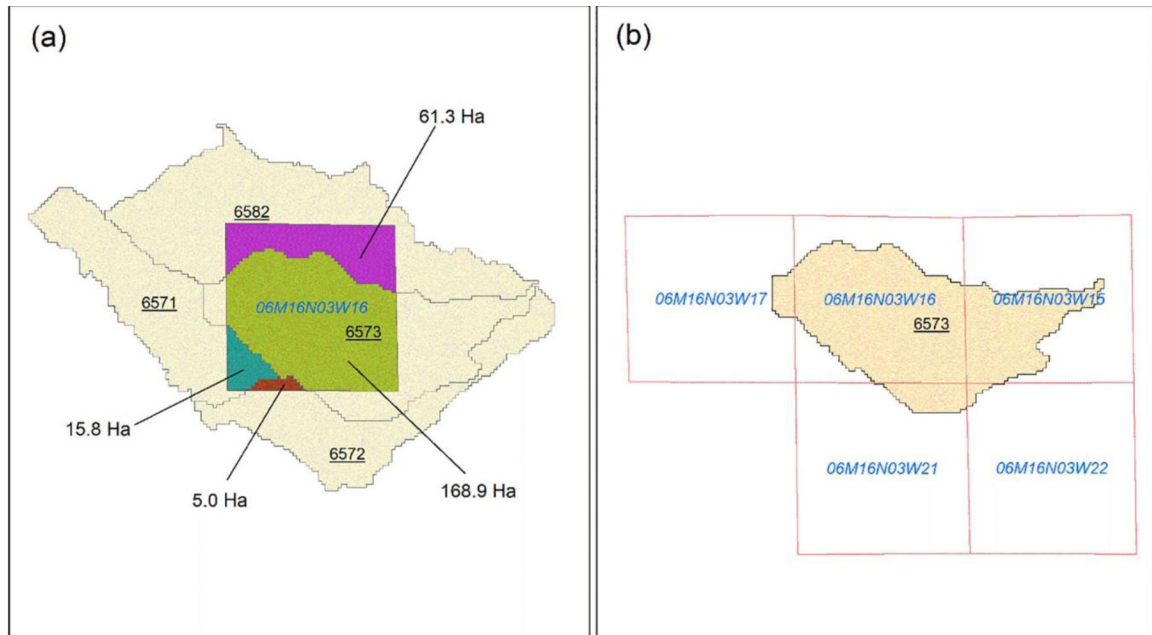


Fig. 2. RiceWQ-AnnAGNPS coupling schema. Fig. 2a exhibited the pesticide runoff from COMTRS “06M16N03W16” is distributed to four AnnAGNPS cells. The “split ratio” is decided by intercepted area. Fig. 2b indicated each AnnAGNPS cell (e.g. “6573”) can receive pesticide runoff from multiple intercepted COMTRS.

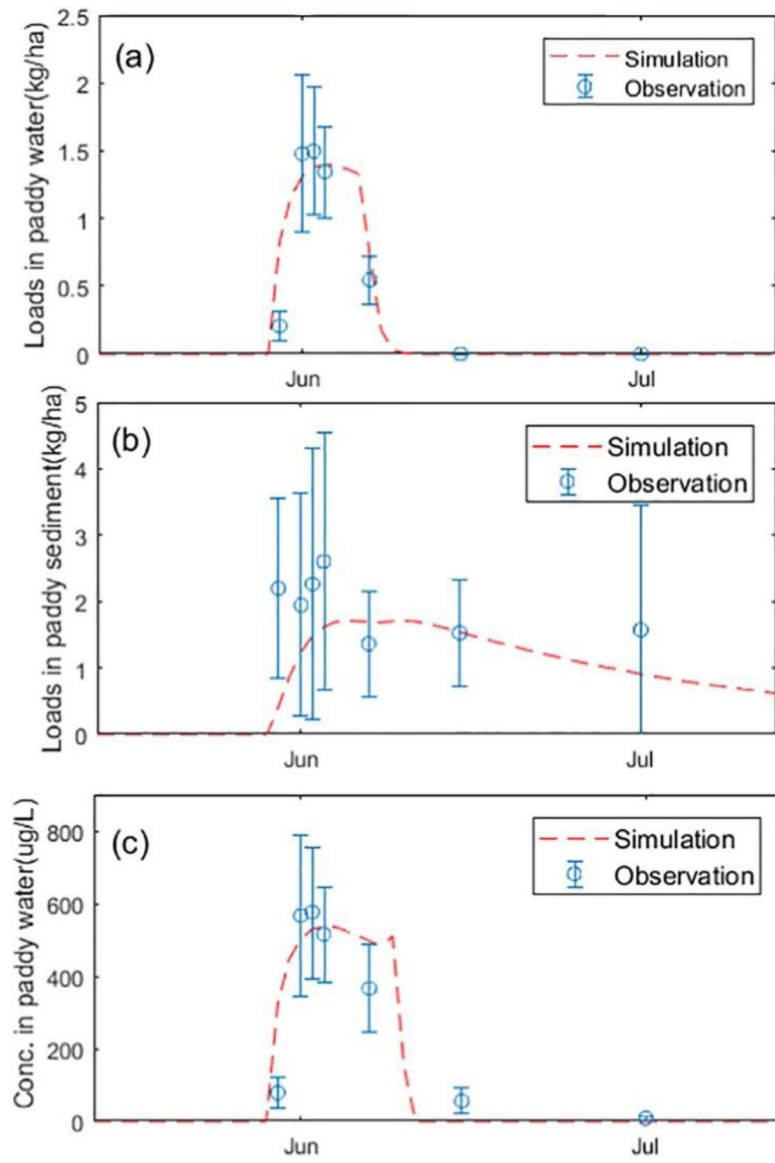


Fig. 3.
RiceWQ simulation results in paddy water & sediment at field level

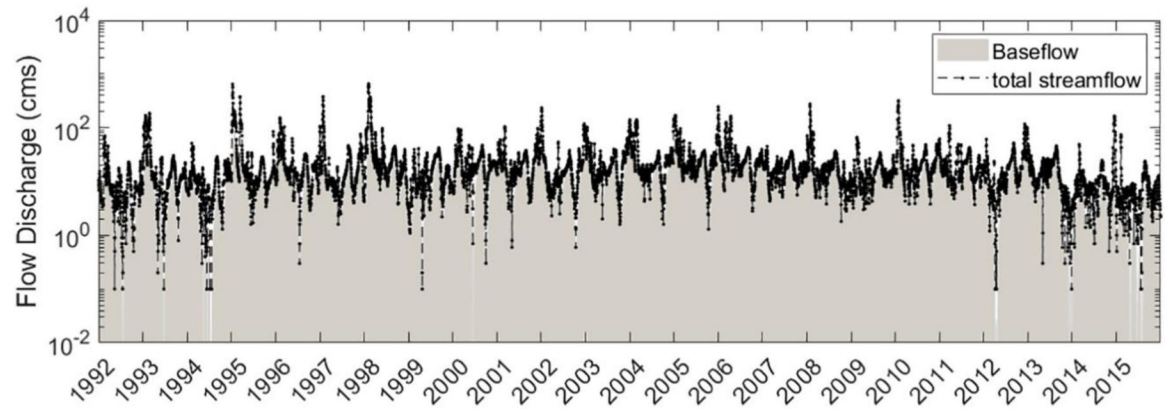


Fig. 4.
Baseflow separation from observed streamflow discharge data via digital filter

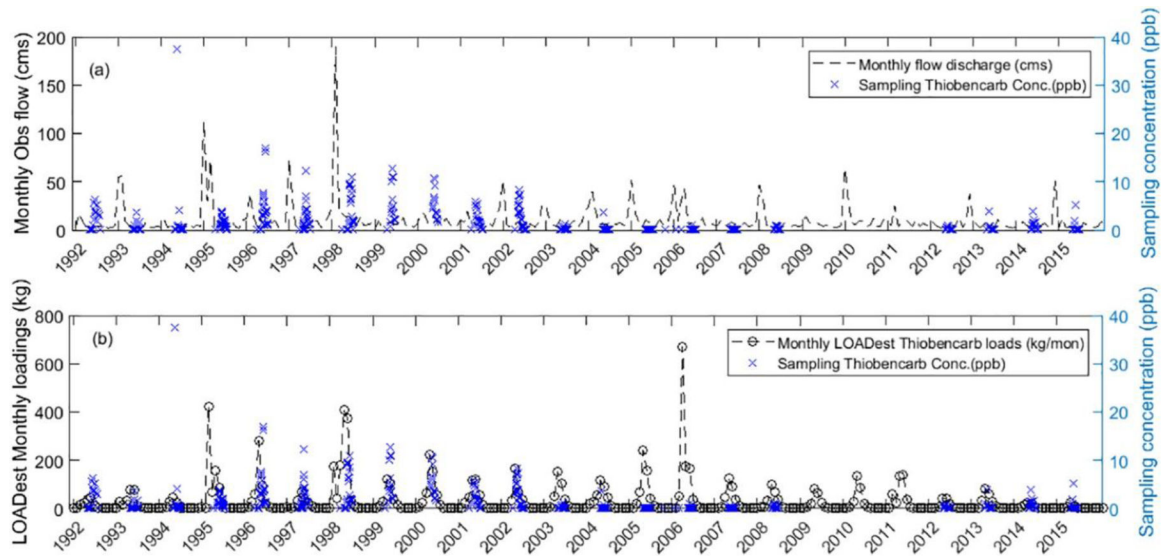


Fig. 5.
Monthly thiobencarb loadings generated by USGS LOADEST

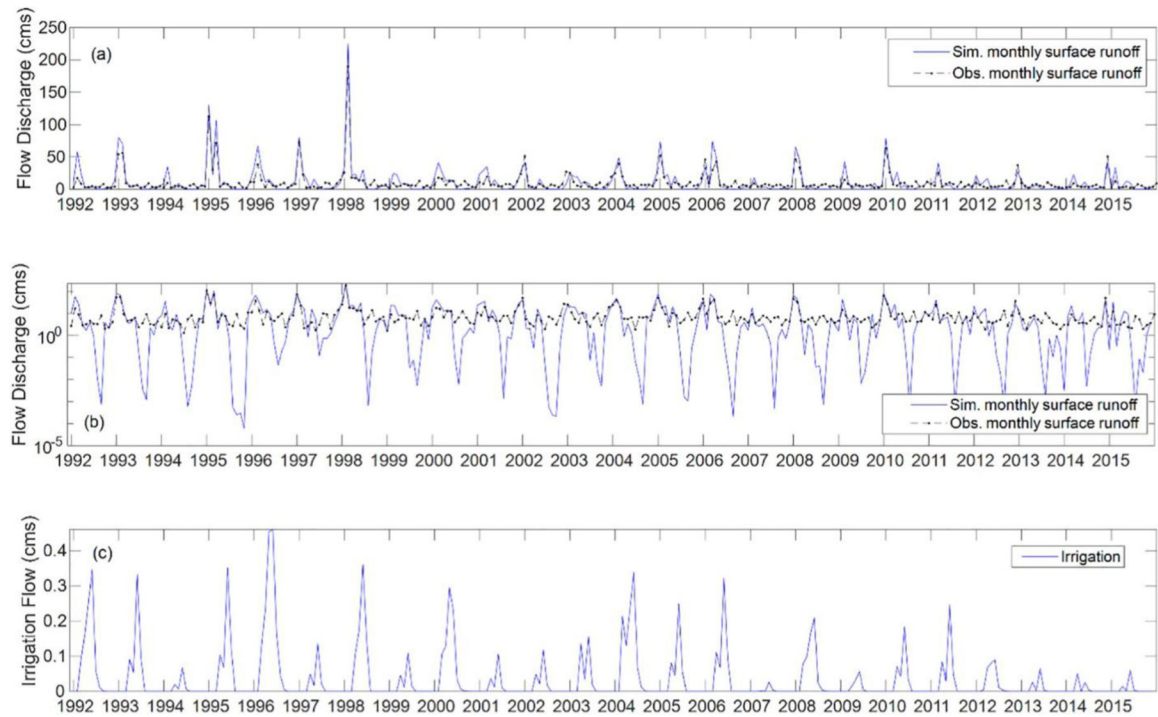


Fig. 6. Hydrologic performance of “RiceWQ-AnnAGNPS”. Fig. 6a exhibited simulated and observed surface runoff in linear scale (peak flow comparison); Fig. 6b exhibited surface runoff in log scale (baseflow comparison); Fig. 6c showed AnnAGNPS predicted irrigation

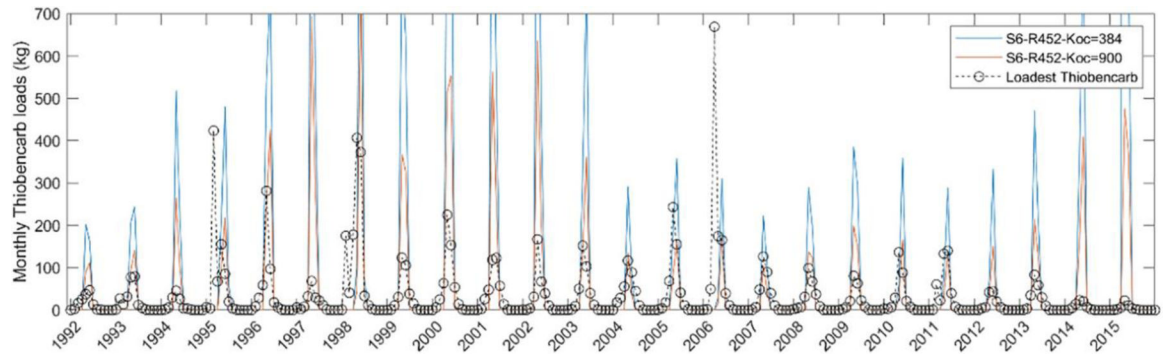


Fig. 7.
Sensitivity of Koc on monthly dissolved thiobencarb loads from the integrated modeling system