SIMULATIOAN AND EVALUATION OF STREAM FLOW AND PESTICIDE PREDICTION IN ORESTIMA CREEK WATERSHED USING THE AnnAGNPS MODEL

by

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A Thesis
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THESIS APPROVAL

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Approved by:

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TITLE: Simulation and Evaluation of Stream flow and Pesticide Prediction in Orestimba Creek Watershed using AnnAGNPS Model

MAJOR PROFESSOR: Dr. Tonny J. Oyana

Pesticides have been recognized as one major agricultural non-point source (NPS) pollution to the environment and surface water in United States. Numerous mathematical models have been developed over the last decades to simulate the fate and transport of NPS at watershed scale. Geographic Information System (GIS) combined with models extends the spatial and temporal scopes of the research by integrating a variety of climates, soils, land covers, and management practices.

The Annualized Agricultural Nonpoint Source model (AnnAGNPS) has received considerable attention in the United States for estimating runoff, sediment yield, pesticide and nutrients transport from ungauged agricultural watershed. However, few studies have been conducted on pesticide loading prediction in surface water using AnnAGNPS. In this study, the AnnAGNPS model was calibrated and validated for prediction of stream flow and chlorpyrifos loading for an agricultural dominated watershed of Orestimba Creek, in Central Valley, California. Large amounts of chlorpyrifos are applied to almonds, walnuts and other stone-fruit orchards in this area every year, which caused significant concern regarding their contamination to the San Joaquin River. Variety of data obtained from multiple sources were utilized as model input, including climate, land use, topology, soil, crop management and schedule, non-crop data, and pesticide. The model's performance was quantitatively analyzed using mean, standard deviation, coefficient of determination (r^2), coefficient of efficiency (NSE), and root mean square error (RMSE). Model's prediction was considered to be unsatisfactory if NSE < 0.36, satisfactory if 0.36 < NSE < 0.75 and good if NSE > 0.75. Monthly stream flow discharge prediction was satisfactory and fit the observed data during model calibration mode. The prediction had major improvement in validation mode with modified curve number and rainfall interception values (r^2 = 0.78 and NSE = 0.77). The AnnAGNPS predictions of chlorpyrifos concentrations in runoff water were unsatisfactory in both calibration and validation modes. Predicted chlorpyrifos concentrations at rainfall events

were 1/1000 of observed data and it was impossible to improve the results through any type of calibration. The overall results suggested the model's poor performance was most likely a result of coarse sampling resolution of observed chlorpyrifos concentrations and lack of irrigation data.

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LIST OF ACRONYMS

ACRONYM	DEFINITION
AGNPS	Agricultural Nonpoint Source pollution model
AnnAGNPS	Annualized Agricultural Non-point Source pollution model
CatchIS	Catchment Information System
CCID	Central California Irrigation District
CDPR	California Department of Pesticide Regulation
CDWR	California Department of Water Resources
CMZ	Cropping Management Zone
DWSM	Dynamic Watershed Simulation Model
GLEAMS	Groundwater Loading Effects of Agriculture Management System
HSPF	Hydrological Simulation Program – Fortran
K_{ow}	Octanol-water partition coefficient
K_{oc}	Organic carbon partition coefficient
MTRS	Meridian, Township, Range, and Section
MUSYM	Map Unit Symbol
NASIS	National Soil Information System

LIST OF ACRONYMS

ACRONYM	DEFINITION
NRCS	Natural Resources Conservation Service
NSE	Sutcliffe coefficient of efficiency
OCW	Orestimba Creek watershed
OP	Organophosphate Insecticides
POPs	Persistent organic pollutants
PRMS	Precipitation-Runoff Modeling System
PRZM	Pesticide Root Zone Model
PUR	Pesticide Use Report
RUSLE	Revised Universal Soil Loss Equation
SCS	Soil Conservation Service
(R)CN	(Runoff) Curve Number
SSURGO	Soil Survey Geographic database
SWAT	Soil and Water Assessment Tool
USDA-NASS CDL	USDA National Agriculture Statistical Survey Cropland Data Layer
WHAT	Web-based Hydrograph Analysis Tool

CHAPTER 1

INTRODUCTION

1.1 General information on pesticides

Food shortage is often defined as not enough food is grown to meet regional needs. The world's population is growing faster than expected and is predicted to reach over 8 billion in 2030 and possibly reach 10 billion by the year 2050 (Rathore and Nollet 2012). The unprecedented increase in human population has triggered an enormous increase in man's need for food. Frequent natural disasters such as drought and flood in various parts of the world on the other hand have added more pressure to food shortage. Modern agriculture techniques are needed to increase the quantity and improve the quality of food in order to match with fast population growth expected in the future.

Pesticides have emerged as one of the greatest tools to protect food against pests that attack crops. Pesticides are defined as chemical substances or mixture of substances that prevent, destroy, repel or mitigate any pest ranging from insects (i.e., insecticides), and weeds (i.e., herbicides) to microorganisms (i.e., algicides, fungicides or bactericides) (USEPA, 2013a). The history for using pesticides to protect crops against pests and diseases dates back many centuries (USEPA 2013a). Since old era, people have used sulfur as pesticides to prevent damage to their crops. The knowledge and skills for protecting crops against pests and disease have greatly improved over the centuries. Other toxic chemicals such as arsenic, mercury, and lead were applied to crops to kill pests by the fifteenth century. A dramatic breakthrough in insect control was achieved in early 1940s when dichlorodiphenyltrichloroethane (DDT) was first created with its insect killing properties. And it quickly became the most widely used pesticide in the world. Synthetic pesticides such as organochlorine and organophosphate pesticides evolved from chemicals began to thrive and became increasingly popular for pest control after the Second World War (1940-1945). Pesticide use has increased 50-fold since 1950 (Rathore and Nollet, 2012). In the United States, pesticides are used on 900,000 farms with 80% of all pesticides are applied to agriculture. In 2007, approximately 1.1 billion pounds of pesticides were used, which was 22% of the estimated 5.6 billion pounds of pesticides used worldwide (USEPA, 2011).

Pesticides are generally considered as widespread “nonpoint” pollution source from agricultural land. Once pesticides are released into the environment, the highest initial concentrations are generally present in plant leaves, soil and water to which direct applications are made. Only 0.1% of pesticides applied to agriculture reaches the target pests, the rest 99.9% enter the environment, contaminating water, soil and air (Pimentel and Levitan, 1986). Pesticides can enter surface waterway in many ways. Some pesticides, including many organophosphate insecticides (OPs) such as chlopyrifos and diazinon are readily absorbed by the soil and dissolve in irrigation or storm water runoff as it moves across treated areas (USPEA, 2006). Pesticides that are insoluble in water move offsite attached to soil particles in water runoff and eventually settle out and contaminate downstream areas. DDT, toxaphene, OPs, atrazine herbicides, these airborne pesticides are also detected in atmosphere, they may return to the earth with rainfall to further contribute to water contamination (USGS, 1995). Pesticide levels in water are monitored routinely today and pesticide residues have been detected in ground water, surface water and rainfall (Pistocchi et al., 2009; Luo and Zhang 2010; Schepper et al., 2012). According to USGS, the results of monitoring 76 pesticides and seven pesticide breakdown products in ground and surface water indicated that 90% of streams and 50% of wells tested were positive for at least one pesticide (USGS, 2006).

Excessive use of pesticides in agricultural land has indeed benefited humanity but at the same time caused considerable concern regarding environmental quality, food quality and human health. Those concerns on pesticides are mainly caused by the physicochemical properties of pesticides. Active ingredients in pesticides have the potential of poisoning insect, microorganism or plant besides the target pest. DDT was discovered preventing marine animals from production, causing birth defects in animals and humans. Exposure to persistent organic pollutants (POPs) pesticides can cause death and immune systems disruption, neurobehavioral disorders and cancers. OPs are listed as a possible human carcinogen by USEPA and exposing to them have demonstrated increased the risk to Alzheimer's disease and attention-deficit/hyperactivity disorder (ADHD) to children. Biological wise, many pesticides can persist in ecosystem for long periods and are capable of long-range transport, bioaccumulation in human and animal tissues through food chain, leading to potential significant impact on human health and the environment. For instance, depending on conditions, DDT can stay in the soil for 22 to 30 years (USEPA 2013b). POPs do not easily break down in the environment and once they are release into environment, they can travel vast long distance to remote regions, and can bio-accumulate and bio-concentrate up to 70,000 times their original concentrations (USEPA 2013c).

Modeling has become increasingly popular as a tool for evaluating the fate and transport of pesticides from agricultural land. Compared to field studies, which often involve sample collection from monitoring well and run analysis in the lab, the use of mathematical models simulating pesticide fate is less costly and easier to implement. Two types of pesticide model have been widely applied: field-scale model and watershed-scale model (Moriasi et al., 2012). The field-scale pesticide models account for hydrologic processes within fields and the simulated pesticides reflect the cropping fields with distinct agricultural activities. While watershed-scale pesticide models offer the opportunity of integrating variability in meteorological data, soil, topographic and land use characteristics to address multiple issues relate to water quality concerns and environmental assessments (Dubus et al. 2002). Pesticide models at watershed scale are useful analysis tools to identify critical areas of nonpoint source pollution and furthermore to support the decision making processes such as Best Management Practices (BMP) for high risk areas. The watershed-scale models can also help in developing total maximum daily loads (TMDLs), required by the Clean Water

Act, and reducing nonpoint source pollution problems by designing alternative land-use and BMP scenarios (National Research Council 2001).

1.2 Introduction of pesticides modeling

A wide number of watershed-scale models capable of simulating pesticides fate and transport movement have been developed over the last decades. Some of the commonly used models include: Agricultural Nonpoint Source pollution model or AGNPS (Young et al., 1987), Annualized Agricultural Nonpoint Source pollution model or AnnAGNPS (Bingner and Theurer, 2013), Catchment Information System or CatchIS (Breach et al., 1994), Dynamic Watershed Simulation Model or DWSM (Borah et al., 2002), Hydrological Simulation Program – Fortran or HSPF (Bicknell et al., 1993), the European Hydrological System model or MIKE SHE (Refsgaard and Storm, 1995), Precipitation-Runoff Modeling System or PRMS (Leavesley et al., 1983), and Soil and Water Assessment Tool or SWAT (Arnold et al., 1998 and Neitsch et al., 2002). It is difficult to choose the most suitable model for a particular watershed without comprehensive education and training with model applications to understand the potentials and limitations of a model. Several journals have reviewed and compared the general applicability of watershed-scale pesticide models and their capability to accurately predict stream flow, sediment concentration and pollutant. Borah and Bera (2003) compared 11 NPS models including those models above based on mathematical characteristics of different components of the models. In their following study (Borah and Bera, 2004), they compared more precisely SWAT, HSPF, and DWSM based on their applications. Quilbe et al. (Quilbe et al., 2006) used a multi-criteria analysis approach to characterize and classify thirty six models. Five criteria were selected and each criteria was signed a weight. The approach determines the most appropriate model by the model score which was calculated by adding the weights of satisfied criteria. In those reviews, each pesticide model has been designed for specific purpose and condition of use, and therefore has its own strength and weakness. Generally, the simple models involve less detailed information but sometimes incapable of providing desired results, and complicated models are somewhat powerful but require more detailed knowledge and much input data. The watershed models can be either stochastic or deterministic, mechanistic or empirical, research or management oriented. Some of the models are based on simple empirical relations having robust algorithms and others use physically based governing equations having computationally intensive numerical solutions (Borah and Bera, 2003). Models can be applied on short term storm event (AGNPS, DWSM and PRMS) or long term continuous basis (AnnAGNPS, HSPF, and SWAT) or both (MIKE SHE). Some of the models have all the three major components: hydrology, sediment, and chemical (AGNPS, AnnaGNPS, DWSM, HSPF, MIKE SHE and SWAT), while others only have partial components. Some models can simulate leaching and groundwater contamination in addition to surface water contamination (HSPF, SWAT and CatchIS). Quite a few models have components for ease of use (GIS, GUI, post-process tools and management tools).

1.3 GIS and Modeling

With the rapid development of Geographic Information System (GIS), its application in pesticide transport modeling has become a prospective research support for various water protection and assessment purposes (Huber et al., 2000; Wang et al., 2005; Rahman, A., 2008; and Probst et al., 2013). GIS is a powerful tool for integrating and analyzing data obtained from a wide range of sources such as soil surveys, land cover, topographic maps and census data and displaying the results in the form of vulnerability maps. An important issue in pesticide transport modeling is that most basic data in regards to pesticides transport (land use, soil, topology and climate) are geographically–referenced data and have a spatial distribution; hence by linking GIS to watershed scale hydrologic and pesticide pollution models, multiple data in simulation models can be compared and analyzed together. Coupling these watershed-scaled models with GIS also extends the spatial and temporal scopes of the research and brings visualization and spatial analysis capabilities to the assessment. It provides a more effective and economical way of developing BMPs for high risk areas and thus help reduce the pesticide pollution of watersheds (Quilbé et al., 2006).

1.4 Problem Statement

Invasive use of pesticides in agricultural land has led to great concern about their contamination to surface water. Organophosphate (OP) pesticides often refer to compounds containing any organic phosphorus, and many of them contain C-P bounds. OP pesticides are classified by the US EPA as highly or moderately toxic. OP pesticides and their metabolites can interfere with the nervous system by inhibiting an enzyme called acetylcholinesterase (AChE).

Substantial neurotoxic studies have demonstrated that exposure to OP pesticides affect neurodevelopment and cause neurologic impairment to human and animals. (USEPA 2006a). Once released into environment, OP pesticides can travel long distances and persist in cold climate. Researchers have even detected OPs in Arctic and sub-Arctic environments (Hermanson, M.H. 2005 and AMAP, 2009). In Central Valley California State, one of the most productive agricultural regions in the world, OP pesticides such as chlorpyrifos have been the most widely used pest-control agents in agriculture activities. Nut trees, vegetables, alfalfa, and field corn are accounted for more than 80 percent of total agricultural use (USEPA 2006). Chlorpyrifos has the potential of migrating with surface runoff from agricultural land and drainage to San Joaquin River and its tributaries. The San Joaquin River was listed on the 2002 Clean Water Act Section 303(d) for its toxicity due to OP pesticides, and chlorpyrifos was in the list (CEPA, 2002). Evaluations of aquatic toxicity by OP pesticides in Central Valley have been conducted by California Central Valley Water Quality Control Board since 1988 and violations have been detected (Foe, 1995, Zhang et al., 2012).

1.5 Objectives

In this study, a watershed scaled pesticide model – Annualized Agricultural Nonpoint Source Pollution Model (AnnAGNPS) was applied to Orestimba Creek watershed (OCW), an agricultural watershed of the Stanislaus County, California to evaluate the model's performance at estimating stream flow and chlorpyrifos load in surface water. Although pesticide concentrations in waterways are usually within drinking water standards, they are still high enough to cause toxicity to aquatic life. Potential risk of chlorpyrifos to ecosystem and water quality in OCW has been evaluated with different pesticide models (Luo and Zhang, 2009a, b). Luo and Zhang (2009a) studied chlorpyrifos and diazinon contamination and associated ecosystem risk in OCW using pesticide root zone model (PRZM) during 1990 through 2006. Good correlations were observed between observed and predicted monthly stream flow and both pesticide concentrations (r^2 = 0.83 and 0.723 for stream flow and chlorpyrifos). The spatiotemporal variability of pesticide distributions indicated high concentrations of dissolved pesticide were predicted during the irrigation season. The study also assessed the key factors governing spatial patterns on pesticide distribution and contamination potential to the aquatic ecosystem. In their second study (Luo and Zhang 2009b), they evaluated SWAT model for simulation fate and transport of chlorpyrifos and diazinon in OCW between 1990 and 2007. The model also showed good capability in evaluating pesticide fate and transport processes in agricultural fields (coefficient of efficiency (NSE) = 0.78 and 0.55 for stream flow and chlorpyrifos). Sensitivity analysis indicated that surface runoff, soil erosion and sedimentation were the governing processes in this study area.

In this study, the AnnAGNPS model was first calibrated for simulation of stream flow for three years (2000-2002). The model was modified and then validated for eight years (2003 – 2010). The AnnAGNPS pesticides loading routine was calibrated for years 2000 – 2002 and validated using previous modified model for years 2003 – 2006. The overall objective for this study was to evaluate the applicability of AnnAGNPS in a semi-arid environment for simulating monthly stream flow discharge and monthly pesticide losses from an agricultural watershed by comparing predicted results with observed data at a USGS gaging station. The spatial temporal distribution of pesticide runoff loadings at Orestimba Creek watershed will not be evaluated unless the validation result of pesticides loadings is satisfactory. Since AnnAGNPS was designed to be applied to ungagged watershed, there are possible sources of error and uncertainty associated with model simulation.

1.6 Organization of the Thesis

This thesis is organized into five chapters. Chapter 1 begins with an introduction to pesticides and their potential risk to environmental and surface water quality, and then move on to the concept and advantages of pesticide modeling and the role that GIS plays in the process of pesticide modeling. Chapter 2 is a literature review of studies conducted in stream flow and pesticide prediction at watershed scale using the AnnAGNPS. Discussions of the processes and algorithms included in the model and model limitations are also included in this chapter. Chapter 3 describes detailed inputs and the steps taken in this model to process the simulations, and explains the statistical analysis of model outputs. Chapter 4 presents and discusses model outputs. Chapter 5 includes summary of this study and suggests directions for future research.

CHAPTER 2

LITERATURE REVIEW

The AnnAGNPS pollution model

The AnnAGNPS (Theurer and Cronshey, 1998; Bingner and Theurer, 2005; USDA-ARS, 2006) is a continuous simulation enhancement of the single storm AGNPS model (Young et al., 1987 and 1989). It was developed by the USDA Agricultural Research Service (ARS) and Natural Resources Conservation Service (NRCS) to predict sediment and nonpoint-source pollutants delivery from ungagged agricultural dominated watersheds up to 300,000 ha (Bingner et al., 2013). The AnnAGNPS possess significant more advanced features than AGNPS, accounting for spatial variability of soil, land use and topography within a watershed by dividing the watershed into many user-specified homogenous land areas (called AnnAGNPS cells). The model simulates long-term hydrology, sediment, nutrients and pesticides leaving upland surface and shallow subsurface cells and routed through channel network to watershed outlet (Bingner and Theurer, 2002). AnnAGNPS calculates water balance based on a simple bookkeeping of input and output of water on a daily basis. Water inputs include rainfall, snowmelt, and irrigation water; while water outputs involve surface runoff, percolation, evapotranspiration, tile drainage, and input to ground water. The hydrologic process simulated in the model include interception evaporation, surface runoff, evapotranspiration, subsurface lateral flow, and surface drainage. The output of model is available in daily, monthly and annually scale. Up to 100 unique parameters for runoff volume assessment and up to an additional 80 unique parameters for sediment yield prediction are required for model implementation, including watershed physical information, crop, non-crop management data, climate, land cover and soil data. The MapWinGIS tool in the AnnAGNPS provides several GIS functions. Special land use components such as feedlots, gullies, field ponds, and point sources are also included in model input. Details about the model components are given in Figure 1:

The surface runoff from a cell is determined using the Soil Conservation Service Curve Number (SCS-CN) technique within the AnnAGNPS hydrologic sub-model (USDA-SCS, 1972). Only initial values of curve number (CN) is required for Antecedent Moisture Condition (Average AMC II) by AnnAGNPS and the model will updates the hydrologic soil moisture condition based on the daily soil moisture balance and crop cycle (Binger and Theurer 2013).

$$SM_{t+1} = SM_t + \frac{Wit - Q_t - PERC_t - ET_t - Q_{lat} - Q_{tile}}{Z}$$ (Equation 1)

where SM_t is the moisture content for each soil layer at the beginning of the time period (fraction); SM_{t+1} is the moisture content for each soil layer at the end of the period (fraction); W_{it} is water input, consisting of precipitation or snowmelt plus irrigation water (mm); Q_t is surface runoff (mm); $PERC_t$ is percolation of water out of each soil layer (mm); ET_t is potential evapotranspiration (mm); Q_{lat} is the subsurface lateral flow (mm); Q_{tile} is tile drainage flow (mm); Z is thickness for soil layer (mm); and t is the time period. Subsurface lateral flow and tile drainage are calculated using Darcy's and Hooghoudt's equations respectively and added to the reach at the same time as runoff. Runoff in channel is calculated using Manning's n equation. Base flow is not calculated in the model (Yuan et al., 2006). The peak flow is calculated by the extended TR-55 technique (Cronshey and Theurer, 1998), a modified version of original NRCS TR-55 Urban Hydrology for Small Watersheds technology.

Soil erosion from each cell is predicted for a single storm type on a daily basis by Revised Universal Soil Loss Equation (RUSLE; Renard et al., 1997) method. The Hydro-Geomorphic Universal Soil Loss Equation (HUSLE; Theurer and Clarke, 1991) is applied to calculate the sediment volume delivered from each cell to the stream network. The sediment reach routing is based on Einstein deposition equation using Bagnold suspended sediment formula for sediment transport capacity by five particle size classes (Bingner and Theurer, 2013).

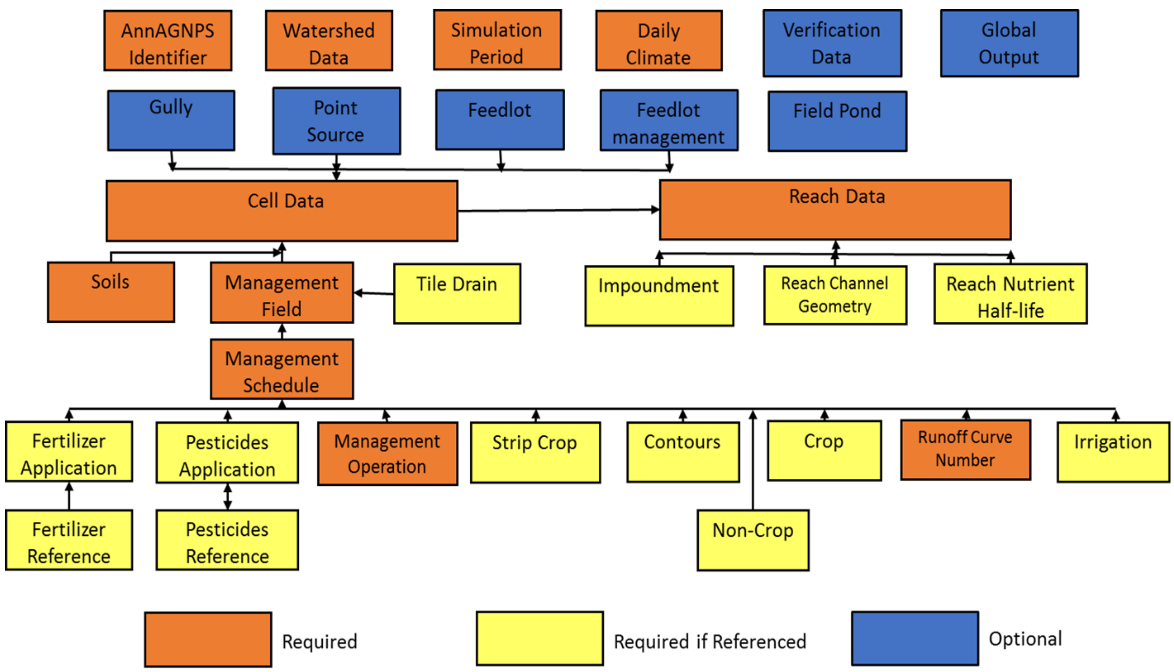

Figure 1: Overview AnnAGNPS model input (Yuan et al., 2011)

AnnAGNPS allows for any number of pesticides, each with their own independent physical and chemical properties. Each pesticide is treated separately, and independent equilibration is assumed for each pesticide. The model utilizes a modified version of Groundwater Loading Effects of Agriculture Management System (GLEAMS; Leonard et al., 1987) to simulate the transport and fate of pesticides (Bingner and Theurer, 2013). The physical and chemical process of pesticides accounted for in GLEAMS includes evaporation, degradation, foliage washoff, transport with sediment in surface runoff, vertical flux, and plant uptake (Figure 2) (Bosch et al., 2001; Bingner and Theurer 2013). Parameter pesticide half-life in soil is used to simulate volatilization, photolysis, hydrolysis, and biological degradation in the soil. While half-life in foliage is used to estimate pesticide degradation and volatilization on the canopy. The runoff of pesticides attached to the clay particles and dissolved in solution are calculated for each cell by a daily pesticide mass balance equation. The governing factors of pesticide yield are surface and subsurface runoffs caused by rainfall and irrigation, especially runoff events soon after pesticide application (Luo and Zhang 2009). Other factors influencing pesticide yield also include terrestrial factors and chemical properties of pesticides.

Pesticide distribution between the solution phase and the soil phase is $K_d = \frac{C_s}{C_w}$ (Equation 2), where K_d is the soil adsorption (mg kg^{-1}), C_s is the concentration of pesticide sorbed to the solid phase (mg kg^{-1}), and C_w is the concentration of pesticide in solution (mg L^{-1}).

K_d is calculated in GLEAMS from the relation $K_d = 0.0058K_{oc}OM$ (Equation 3), where OM is the organic content of the soil expressed as percent of total soil mass and K_{oc} is the linear adsorption coefficient for organic carbon.

Pesticide available for loss in runoff is based on the equation: $C_{av}B = C_w + C_sB$ (Equation 4), where C_{av} is the runoff-available pesticide concentration in the surface soil layer (mg kg^{-1}), B is the soil mass per unit volume of overland flow (kg L^{-1}), C_w is the pesticide concentration in solution (mg L^{-1}), and C_s is pesticide concentration in the soil or solid phase (mg kg^{-1}). More detailed information regarding pesticide transport equation for AnnAGNPS can be found in Leonard et al. (1987).

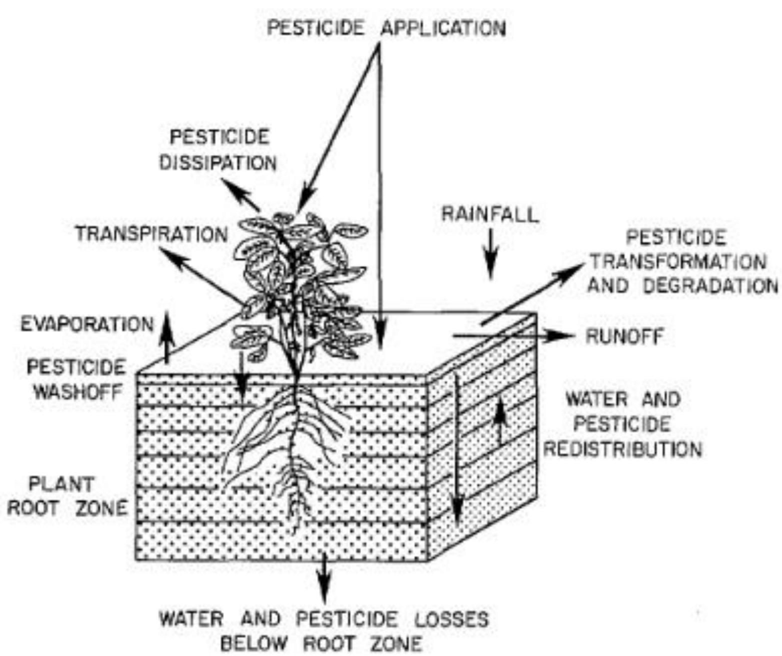

Figure 2: The physical system and process presented in GLEAMS (Leonard et al., 1987).

Some limitations of the model that are acknowledged by the developers are listed below (Bosch et al., 1998):

- All runoff and associated sediment, nutrient, and pesticide loads for a single day are routed to the watershed outlet before the next day simulation begins (regardless of how many days this may actually take);
- There are no mass balance calculations tracking inflow and outflow of water; There is no tracking of nutrients and pesticides attached to sediment deposited in stream reaches from one day to the next;
- Point sources are limited to constant loading rates (water and nutrients) for entire simulation period;

AnnAGNPS has been successfully used for predicting hydrology, sediment and nutrient loading over a wide range of environments in the United States and all over the world (Yuan et al., 2001, 2002, 2003, 2008, 2011; Suir, 1999, Suttles et al., 2003; Shrestha et al., 2006; Polyakov et al., 2007; Licciardello et al., 2007; Hua et al., 2012; Zema et al., 2012). Yuan et al. (2003) applied AnnAGNPS to the Deep Hollow watershed in Mississippi to evaluate nitrogen loading and poor correlation was reported for monthly prediction to the observed values. The poor prediction was attributed to the simplification of the nitrogen process in model 2.0 version. Nitrogen processes in the model have subsequently been refined in version 4.0 (Binger et al., 2007). conducted simulation of annual runoff, sediment, and nutrient loads in the 333 km^2 Little River research watershed in south central Georgia and found simulated results were all under-predicted in the upper part of the watershed, while in the lower part of the watershed, predicted runoff was close to the observed data, but sediment and nutrients were overestimated. Suttle et al. (2003) concluded that overestimation of forest areas that caused an underestimation of runoff was the reason for under-prediction in upper part of the watershed. Over-prediction in the lower portion of the watershed was likely caused by not adequately quantifying the riparian and wetland areas. Parajuli et al. (2009) compared the performance of AnnAGNPS and SWAT for prediction of flow, sediment and total phosphorus in Red Rock Creek and Goose Greek watersheds in south-central Kansas. Both calibration and validation results were satisfactory for AnnAGNPS runoff prediction (NSE = 0.69). Model efficiencies for AnnAGNPS sediment predictions were also good (NSE = 0.64 at validation phase). Prediction of total phosphorus performed unsatisfactory results for validation phase (NSE = -2.38). On a global base, Hua et al. (2012) conducted simulations with AnnAGNPS in the 4184 km^2

Daning River watershed in the Three-Gorge region of the Yangtze River of China and found good prediction (r^2 = 0.93) for monthly runoff volume. The model's prediction of annual average sediment yield also achieved satisfactory agreement with observed data. Hua et al. (2012) concluded that AnnAGNPS has considerable potential as a research and management tool for long term estimation of runoff and sediment yields. The AnnAGNPS model was utilized in a Belgian agriculture watershed to assess its prediction capacity of runoff, peak flow and sediment yield (Zema et al., 2012). The model performed well in predicting large runoff volumes (r^2 = 0.92 and NSE = 0.89), however the prediction capability of peak flow and sediment yield was poor. Zema et al. (2012) pointed out that the internal model deficiencies (incomplete representation of watershed complex process) and the quality of recorded data were probably the reasons for inaccurate results.

Application of the pesticide transport portion of AnnAGNPS model has been very limited, and there has been only two peer-reviewed journal articles (Heathman et al., 2008 and Zuercher et al., 2011) and one PhD dissertation (Tagert, 2006). Other than these three studies, there have been no calibration and validation of the pesticide routines in the model.

Heathman et al. (2008) applied SWAT and AnnAGNPS to the streamflow and atrazine loss prediction in 707 km^2 Cedar Creek watershed in northeastern Indiana. Although pesticide components in both models were adapted from GLEAMS, the atrazine estimates differed from two models to a great degree. Without calibration, neither model simulations were satisfactory. AnnAGNPS produced poor prediction for both monthly stream flow and atrazine loss (NSE = 0.13 and -0.64 respectively), and the simulated atrazine concentration values were approximately 1/100 of measured. As there was only one literature source on atrazine prediction by AnnnAGNPS at that time, Heathman et al. (2008) did not discuss the possible reasons contributing to AnnAGNPS's poor performance, but he suggested use more detailed automated event-based water quality sampling data might improve model's performance. Inspired by Heathman's finding, Zuercher et al. (2011) analyzed runoff and atrazine concentration simulation by AnnAGNPS in Cedar Creek watershed and Matson Ditch sub-catchment in northeastern Indiana in uncalibrated, calibrated and validation modes. Flow discharge for both watersheds were well matched with observed values in model calibration and validation. A source code error of unit conversion in the runoff value being input to the pesticide routine was found and later being corrected. Zuercher et al. (2011) mentioned AnnAGNPS version 5.00 with corrected source code has been released in 2010. The corrected AnnAGNPS model could be satisfactorily predict atrazine concentration in Matson Ditch watershed if applying 100% of the atrazine to foliage. Prediction of atrazine concentration in Cedar Creek watershed was poor even with 100% foliage application fraction. Zuercher et al. (2011) concluded coarse sampling method might be the reason for poor atrazine prediction in Cedar Creek watershed. Tagert et al. (2006) also found poor correlation of AnnAGNPS prediction of atrazine and metolachlor concentrations with measured data (r^2 = 0.09 and 0.06 respectively) in 13,200 ha Upper Pearl River basin. Tagert et al. (2006) concluded that low pesticide sampling intensity and few matching observed and simulated events were likely the causes for much of the deviation in the study.

CHAPTER 3

MATERIALS AND METHODS

3.1 Site selection

The State of California was first chosen as an experimental site for three reasons. First, California is known as the western powerhouse of agriculture with approximately 43 million acres agriculture land. It is reported as the nation's number one and the world's fifth largest supplier of diverse agriculture commodities, producing more than 400 different crops and half of the U.S. fruits and vegetables (OPR, 2003). Second, California ranked number one regarding pesticide use and accounted for 22% of all agricultural pesticide use in the United States (EPA, 2005). The Central Valley Region in California ranks as one of the world's most productive agricultural regions. It is the most significant contributor to pesticide use in California because of its high agricultural production. Large amount of pesticides released into environment has raised scientific concern regarding their impact to the ecology and human health. Numerous studies have been conducted in the past decades about the fate and transport of pesticides in Central Valley, and pesticide residues have been routinely detected in water quality monitoring projects in this area. (Sparling et al., 2001; Chu and Marino 2004; Amweg et al., 2005; Luo and Zhang 2009, 2010; Saleh et al., 2011). Third, California State pesticides dataset is accessible, complete and sufficient to my study. The California Department of Pesticide Regulation (CDPR) maintains a full pesticide use data since 1990. It covers annual pesticide use amount by Mercator, township, pesticide type, area and by commodity. The CPUR data has been successfully used in a number of pesticide related environmental risk studies (Nuckols, et al., 2007; Luo, et al., 2008; Luo and Zhang 2009, 2010). Within California this study focus on Orestimba Watershed in Stanislaus County because following reasons: First, it's located in the Central Valley, large amounts of organophosphate insecticides are applied to nut trees and fruit orchard in the Orestimba Creek watershed (Cryer et al., 2001). Previous studies have discussed the residual levels of organophosphate insecticides, especially chlorpyrifos in this area (Ross et al., 1999; Kratzer et al., 2002; Domagalski and Munday, 2003; Luo et al., 2008a, b). Second, the valley floor (western side) of Orestimba Creek Watershed emerges out onto flatter croplands (eastern side), forming a wide undefined alluvial fan. This alluvial fan is composed of geologic materials with low hydraulic conductivity which lead to potential pesticide contamination (Luo and Zhang 2008).

3.2 Site description

Orestimba Creek watershed (OCW) is located in western Stanislaus County, near the center of California's San Joaquin Valley which, together with the Sacramento Valley 600 km to the north forms the Great Central Valley (Figure 3). Orestimba creek originates in the mountains of the Diablo Coast Range in the western portion of the county and flows in a northeasterly direction through agriculture lands in San Joaquin Valley and emerges into the San Joaquin River at river mile 109. Highway 33, Interstate Highway I-5, the California Aqueduct, the Delta-Mendota Canal, the Northern California Railroad (NCRR), and the Central California Irrigation District (CCID) Main Canal are intersected with Orestimba Creek. Elevations in OCW vary from forest and rangeland regions (about 3600 feet) to croplands (45 feet). This area has a semi-arid climate, with 80% of precipitation is observed during late winter, which is normally from December through March. Irrigation water is accounted for low flows during the summer months. Almonds, walnuts, and fruit orchard are the leading agriculture crops in this area and represent about 50% of the agricultural acres and 29% of the agricultural value (Cryer et al., 2001). Other primary agricultural products in Stanislaus County include tomatoes, dry beans, winter wheat, cotton, and corn.

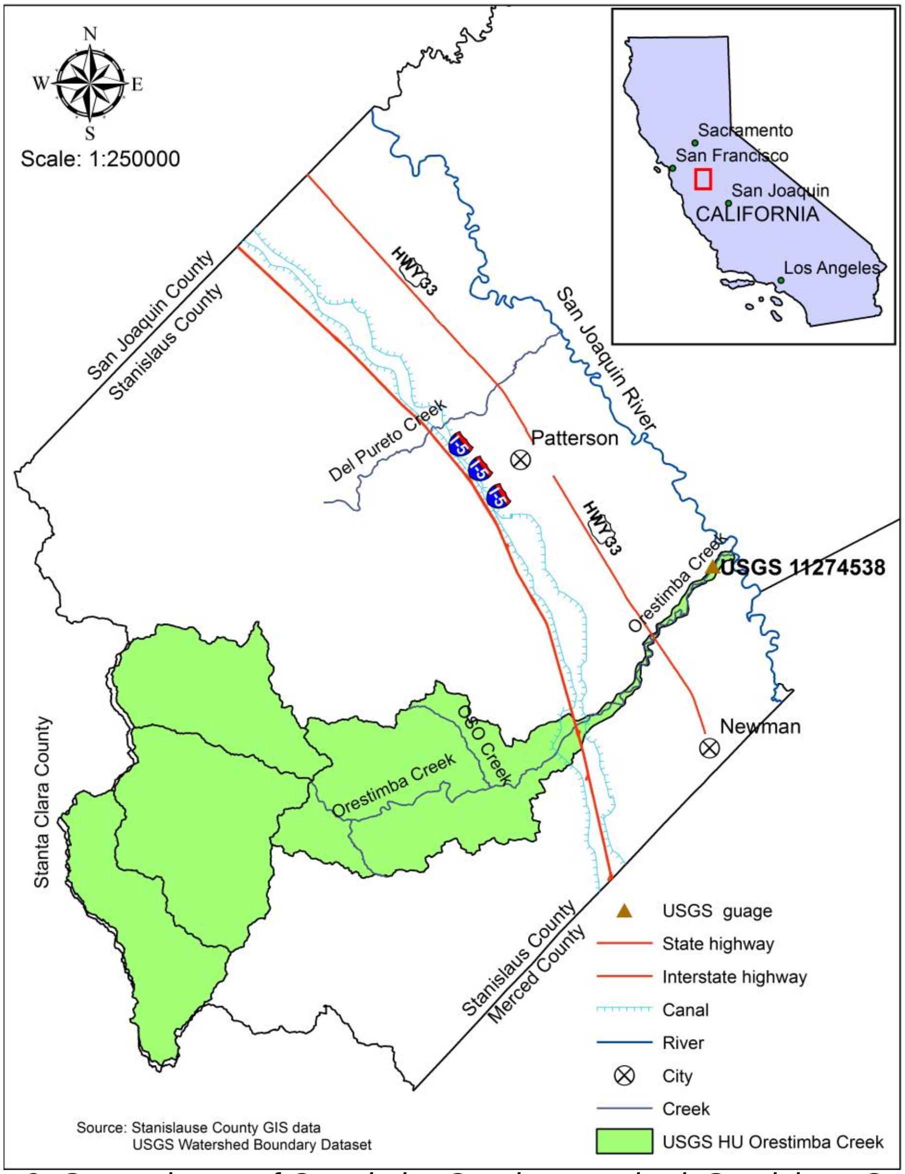

Figure 3: General map of Orestimba Creek watershed, Stanislaus County, California

3. 3 AnnAGNPS Input Preparation

Version 5.4 (32 bit and 64 bit) of the AnnAGNPS were used for this study. The AnnAGNPSA requires more than 400 input parameters in 34 data categories, including hydrology, topology, land use, soil, filed management, field operation and climate. A customized MapWinGIS interface was used to prepare the majority of data input of AnnAGNPS using GIS digital data layer of digital elevation model, soils, and land use. Input files developed using a MapWinGIS interface included physical information of watershed and subwatershed (AnnAGNPS cell), the boundary, size, and land slope, slope direction, stream and channel reach (AnnAGNPS reach). The MapWinGIS interface also performed to intersect each generated cell with land use and soil GIS layer, and assigned land use type and soil class to each cell. Additional steps to provide other input files include establishing different crop operation and management data, and developing pesticide properties data, and weather data. Those inputs can be organized using AnnAGNPS Input Editor, a graphical user interface designed to aid users in selecting appropriate input parameters. The AnnAGNPS Input Editor contains a spreadsheet of all the data collected from cell and reach, such as daily climate, land cover, and crop management practice. Once those parameters are imported in to the Input Editor, The Input Editor will automatically sort all the information within each cell and reach and calculate erosion, sediment yield, runoff, and transport of various chemicals and pollutants. Management information includes various field management operations such as planting, cultivation, pesticides, fertilization and harvesting, much of which can be obtained from Revised Universal Soil Loss Equation (RUSLE) database or actual activities implemented. Climate data for AnnAGNPS simulation can be historically measured, synthetically generated using climate generation model (GEM) (USDA-ARS, 2005), or created through a combination of the two. The AnnAGNPS Pollutant Loading module was set to run for three initialization years before beginning the simulation period, which was Jan 1, 2000 through Dec 31, 2010. The hydrology and event results at gaging station were extracted and summarized using “STEAD Editor” (Summarization Tool to Evaluate AnnAGNPS Data), a front-end graphical user interface. Figure 4 and table 1below provides a brief summary of the sources of information and simulation process applied for the AnnAGNPS pollutant loading model with this study. More details about the information used within the AnnAGNPS model are described in the next sections.

Table 1**:** *Summary of AnnAGNPS input data source*

AnnAGNPS Required Input Data	Source of Data	Resolution / Scale
Climate	Full climate dataset from 2000 - 2010 were obtained from Patterson weather station maintained by California Irrigation Management Information System (CIMS) (CDWR, 2013a).	Non-spatial
DEM	National Elevation Dataset (UTM 1983) of Stanislaus County was downloaded from USGS (USGS, 2013a).	1 - arcsecond
Crop and non-crop information	USLE2 database (Zone 34) from AnnAGNPS reference (USDA-SCS, 1986)	Non-spatial
Crop Management schedule and operation	USLE2 database (Zone 34) from AnnAGNPS reference (USDA-SCS, 1986)	Non-spatial
Land use	Land use shapefile provided by California Department of Water Resources was used to obtain land use information between 2000 and 2006 (CDWR, 2004). Land use information from 2007-2010 was captured from USDA National Agriculture Statistical Survey Cropland Data Layer (USDA-NAS CDL 2007, 2008, 2009, 2010)	N/A
Soil	Spatial files was obtained from 2003 Natural Resources Conservation Service Soil Survey Geographic database (SSURGO) (USDA, 2003) Soil properties were updated with National Soil Information System (NASIS) (USDA, 2003).	1:24000
Pesticides	Chlorpyrifos properties were obtained from chemical property database for the CalTOX4.0 model. Chlorpyrifos apply rates in MTRS geographic units from 2000 – 2006 were obtained from California Department of Pesticide Regulation (CDPR-PUR, 2013).	Non-spatial
Historical stream flow and pesticide loading	Observed stream flow discharge and pesticide concentration were obtained from USGS gaging station #11274538 (USGS, 2013b).	Non-spatial

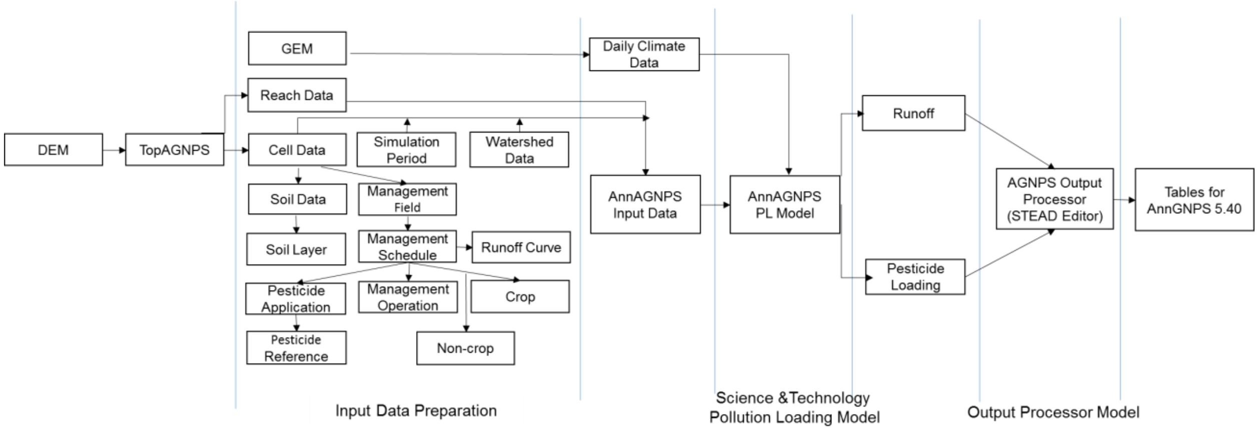

Figure 4: Flow chart for data preparation, simulation, processing and output of this study

3. 3.1 Climate data

Six daily climate parameters precipitation, maximum & minimum temperature, drew point temperature, solar radiation, wind speed as well as sky cover are required by AnnAGNPS simulation (Darden and Justice 2013). A large set of climate data is required to accurately run the model. This data can be historically measured or estimated using the climate generator program GEM. The GEM is a stochastic weather generator that simulates statistically represented time series of daily weather values based on the location of the site. GEM software consists of two parts: preGEM and agGEM. preGEM allows the user to develop the GEM statistical parameters when historical data is available. agGEM then uses the output of preGEM as input and produces the same information in AnnAGNPS format. During this process, the program agGEM also incorporates the former standalone program “Solar_to_Skycovrer” and generates sky cover data. The validity of the statistical parameters generated depends heavily on the data quality and number of years available, and the statistical reliability declines rapidly with fewer dataset. The nearest weather station to Orestimba Creek Watershed is Newman station (37°16’48’’N, 121°1’12’’W). Initial attempt to apply climate data from National Oceanic and Atmospheric Administration National Climate Data Center (NOAA–NCDC) for Newman station was unsuccessful because of many missing records. Final daily historical data were retrieved from Patterson station (37°26’24N, 121°08’20’’W) 11 miles away from creek outlet operated by California Irrigation Management Information System (CIMIS, 2013). Because there has been no precipitation from July to September over the simulation period, 0.01 inch rainfall was manually assigned to July 25, Aug. 5, Aug. 25 and Sept.15 every year in order to obtain sky cover data from agGEM (personal contact with USDA professionals). The agGEM output (.inp) file was text formatted into files climate_station.csv and climate_daily.csv and then imported into the AnnAGNPS Input Editor. Preliminary rainfall data analysis from historical Patterson weather data indicated that annual average precipitation is rainfall events occur manly during winter (December through March) associated with the Mediterranean climate of the region, accounting for around 80% of annual rainfall.

3.3.2 Topography data

The watershed and subwatershed boundaries were delineated by using TopAGNPS and AgFlow programs integrated with AnnAGNPS MapWinGIS interface. Digital elevation model (DEM) is required for creating AnnAGNPS cell and reach parameters and providing basic input data for pesticide losses in runoff. An AnnAGNPS cell is a grid within the watershed that contains a homogenous soil type, land use cover, management practice, and topographical (slope, length, and elevation) characteristics. For this study, the National Elevation Dataset (NED) with 1- arcsecond grids of Stanislaus County from U.S. Geological Survey (USGS) was used for hydrologic modeling and analysis. The NED grids were resampled to a resolution of 30m. The TopAGNPS program (Topographic AGNPS) which is included with the AnnAGNPS is an automated digital landscape analysis tool for topographic evaluation, drainage identification, watershed segmentation and subwatershed parameterization. The TopAGNPS consists of seven programs, three main programs are: (1) Digital Elevation

Drainage Network Model (DEDNM), (2) RASter PROperties (RASPRO), and (3) Raster FORmatting (RASFOR) (Gabrecht and Martz, 1999).

The program DEDNM pre-processes the elevation data, performs the hydrographic watershed segmentation and defines the drainage network. DEM dataset was first cleaned and filled any sinks and depressions to eliminate inherent raster errors before being analyzing in TopAGNPS. Delineation of Orestimba Creek Watershed was first attempted with the stream networks from the National Hydrography Dataset (NHD) using Arc Hydro 2.0 extension for ArcGIS 10 to obtain a reference boundary outline of the watershed. A “Clip DEM” tool has been added to the latest AnnAGNPS GIS Tools Version 5.41 for selecting user-defined sub-DEM (Darden, et al., 2013). The watershed shapefile was later applied to the Stanislaus County DEM to clip the area of interest DEM rather than using the entire county DEM. Point shapefile of watershed outlet (USGS gauge # 11274538) was intersect with clipped DEM using the Spatial Analyst Extension in ArcGIS, and the watershed outlet location was interactively defined as row 22 and column 1305. The values were later adjusted to row 20, column 1302 in DEDNM program. DEM processing in DEDNM is based on an outlet location and two user-defined network parameters: the critical source area

(CSA) and the minimum source channel length (MSCL). It is recommended that the minimum CSA should not be less than ten times of DEM cell size squared and MSCL should not be less than the DEM cell size. The density of delineated subwatersed decreases as the MSCL parameter is increased and short source channels (1st order channels) are removed. The default CSA and MSCL are 8.0 ha and 130 m. Various combinations of CSA and MSCL were tried for watershed delineation and comparison on the results of watershed at different CSA and MSCL settings is shown in Table.

Table 2*: Number of cell and reach at different CSA and MSCL*

CSA (ha)	8	5	10	15	20	40
MSCL (m)	130	50	80	100	130	250
Area (ha)	40733.1	40733.1	40733.1	40733.1	40733.1	40733.1
Number of cell	12797	8504	4739	3189	2379	1160
Number of reach	5607	3647	1963	1300	1963	470

Table 2 shows there is no impact of CSA on watershed area. The area was approximately the same at different CSA and MSCL settings. The stream network became sparser and a decreasing trend of cell number was observed with increasing CSA and MSCL values. For my study, the ideal CSA and MSCL values should not only capture Orestimba Creek network with National Hydrography Data of stream network as reference, but more importantly could best characterize the variation of land use and soil. CSA = 15 hectares and MSCL = 100 meters setting was finally chosen for AnnAGNPS model simulation for Orestimba Creek Watershed. This combination generated an average 40733.1 hectares of land for each subwatershed and total of 3189 subwatersheds or AnnAGNPS cells and 1300 reaches. The program RASPRO derives additional spatial topographic information and parameters from the basic raster produced by program DEDNM. Examples of new raster information include, but are not limited to, location and extent of depressions and flat surfaces in the DEM; flow travel distance to the next channel and to the watershed outlet; elevation drop from each cell to the next channel and to the watershed outlet; elevation reclassification into user specified classes; alternative computations of raster cell slope and aspect. The program RASFOR is a raster formatting utility. It reads the unformatted raster files produced by programs DEDNM and RASPRO, and reformats them into either ASCII or GIS (ARC/INFO) specific files.

The program AgFlow helps create grids of the watershed that contain cells with homogeneous characteristics (USDA, 2000). AgFlow uses eleven files from TopAGNPS as input and creates hydro-geomorphic grids with reach and cell attributes. The reach attributes include average elevation, reach length and slope; and cell attributes include cell area, average elevation, aspect, slope and length (sheet, shallow and concentrated) and RUSLE LS-factor. Average cell area is 12.77 ha. The forest and rangeland regions of the watershed have slopes of 0.2-0.4, while croplands are located in the flat valley floor at elevations of 66 to 20m.

The DEM-based TopAGNPS output was imported into the MapWinGIS interface. Figures 5 and 6 illustrate the subwatershed delineation and connectivity between the subwatersheds and the generated channel network.

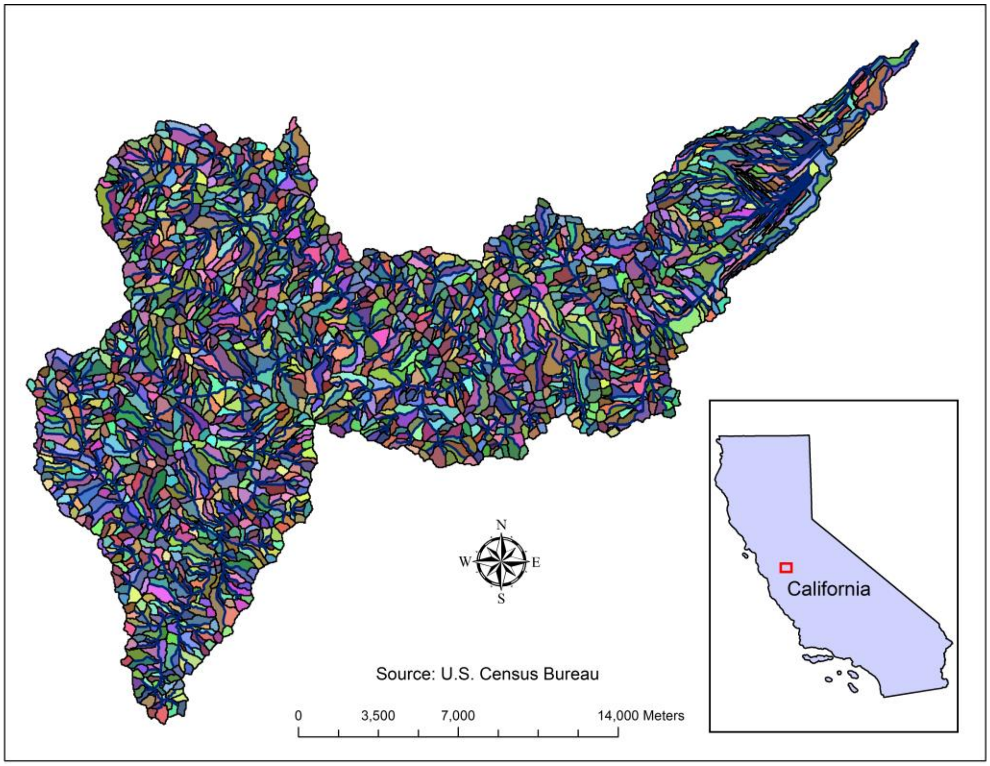

Figure 5: Orestimba Creek Sub-watershed delineation

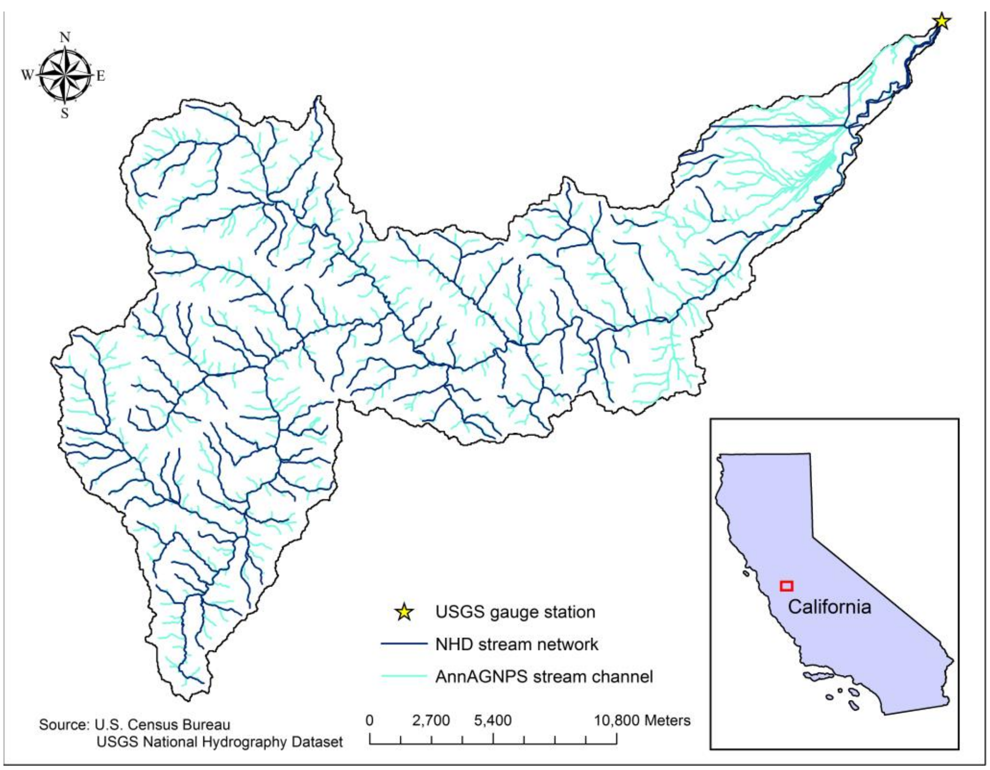

Figure 6: Generated stream network as compared to the USGS NHD stream network.

3.3.4 Soil data

AnnAGNPS requires that a dominant soil type, along with its characteristics, be selected for each subwatershed. Current soil information can be obtained through the USDA-Natural Resources Conservation Service (NRCS) or be created by the user. The USDA-NRCS established three soil geographic data bases representing kinds of soil maps: Soil Survey Geographic (SSURGO) database, the State Soil Geographic (STATSGO) database and the National Soil Geographic (NATSGO) database. The SSURGO database consists of county-level maps, metadata, and tables which define the proportionate extent of the component soils and their properties for each map unit. SSURGO database have been served as an excellent source for determining erodible areas and developing erosion control practices, reviewing site development proposals and land use potential, making land use assessments, and identifying potential wetlands and sand and gravel aquifer areas (USDA, 1995). At scales ranging from 1:12,000 to 1:63,360, the SSURGO database is at the finest level of digital soil mapping. Spatially distributed soil properties required by the AnnAGNPS simulation include soil texture, layer properties, pH value, RUSLE K-factor, bulk density, $CaCO_3$ concentration, organic matter ratio, wilting point, field capacity, hydraulic conductivity etc. Detailed spatial soil information for Orestimba Creek Watershed were extracted from 1:24000 scale 2003 SSURGO database for western part of Stanislaus County where Orestimba Creek watershed is located (USDA 2013b). AGNPS MapWinGIS interface was then used to intersect the subwatershed cells with the spatial soils data, using the field map unit symbol (MUSYM) as the unique soil identifier in the overlay. During this process, the predominant soils type were determined and assigned to each generated cell (Figure 7).

Forty soil SSURGO types were identified in the Orestimba Creek Watershed with clay loam and being dominant for croplands, followed by loam and clay. A single National Soil Information System (NASIS) soil file associated with SSURGO spatial data was downloaded as a text file (.txt) that contained all the related soil physical and chemical properties information. The file was selected for those forty soil types, and organized and text formatted into files soil_layer.csv and soil_dat.csv, and then imported into the AnnAGNPS Input Editor.

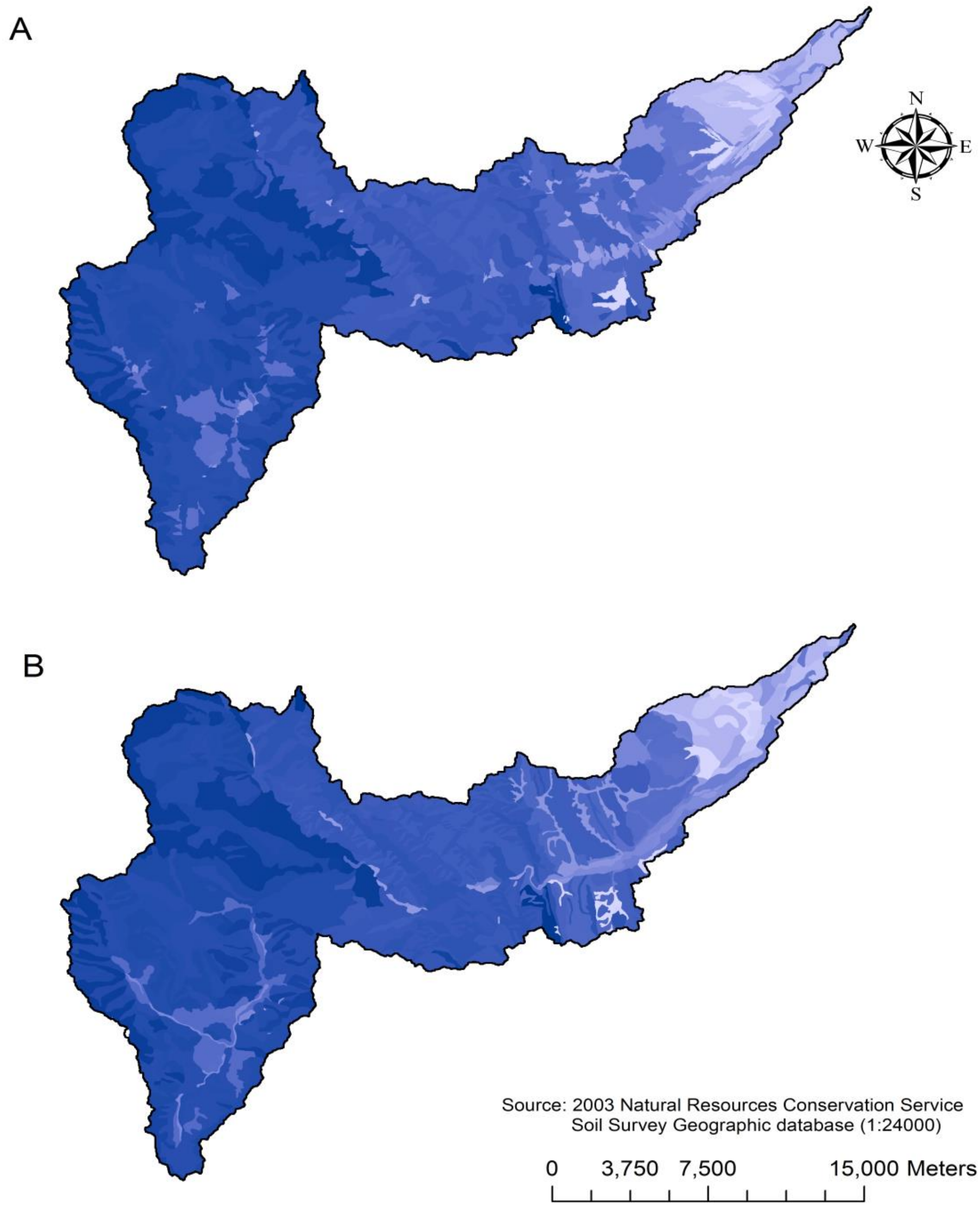

Figure 7: SSURGO soil types as assigned to sub-watershed cells (A) and throughout the delineated watershed (B)

3.3.5 Land use data

Contemporary land use, cropping management and operation information in Orestimba Creek watershed during simulation period are critical in providing estimates of the pesticide runoff. AnnAGNPS has the capability of simulating watershed conditions with changing land use and crop management over simulation period. To evaluate the impact of different land cover types on pesticide runoff, the 2004 Stanislaus county land use map obtained from California Department of Water Resources (CDWR) was used in this study as a base year land use layer information (CDWR, 2004). The land use survey conducted for this map was in 1998 through 2004. Since single year land cover map might not be sufficient to represent land cover change during the entire simulation period as it does not provide detailed crop rotation information (Luo and Zhang 2009), land cover maps from USDA National Agriculture Statistical Survey (NASS) Cropland Data Layer (CDL) for the years of 2007-2010 were used to expend multiple cropping types and rotational information. The USDA-NASS CDL is a LANDSAT mosaic image of georeferenced Landsat 5–TM and Landsat 7–ETM scenes. It is in ERDAS Imagine .tif file format and has a spatial resolution of 30 m^2.

The AnnAGNPS MapWinGIS interface requires that the land cover information be in a shapefile format, so the .tif file must be converted to a shapefile. The detailed steps of converting .tif CDL to shapefile can be referred to

Tagert dissertation (Tagert 2004). For each CDL, a ‘Neighborhood Functions’ process was first performed on the original tif image in ERDAS Imagine 2011 using a 3x3 kernel and majority function. The Neighborhood Functions process has a smoothing effect on the classified image subset by eliminating island pixels, or pixels of one class that are completely surrounded by pixels of another class. Eliminating island pixels prevents single-pixel island polygons and speeds the model processing. The smoothed image output was reprojected to the correct coordinate system and converted to a polygon shapefile in ArcGIS using the raster to polygon option in Conversion extension. Finally, a dissolve process was performed on the land cover shapefile to combine any adjacent polygons. The dissolve process resulted in multipart features being created, each of which represents a single discontiguous land cover type in the attribute table. The attributes of the newly dissolved shapefile were updated to reflect the new combined land cover class. CDWR and CDL land cover shapefile layers were intersected with the sub-watershed cells in AGNPS MapWinGIS interface, using the land cover attribute field ‘Class Name’ as the field identifier in the overlay. After the overlay process, each sub-watershed cell was assigned with one land cover class, which was based on the dominant land cover class within that subwatershed cell. Validation of land cover assigned to the AnnAGNPS subwatershed was conducted to determine how well the land cover information from the original file was reflected in the delineated subwatershed land cover designations. This process was achieved by using original land cover layer as reference image, and calculating and comparing the percentage of each land cover class in both the original land cover layer and in the subwatershed file. The heterogeneity of some land cover classes, especially almonds and tomatoes were overrepresented in the subwatershed file, while shrub land and mixed forest were underrepresented. These particular classes were adjusted and assigned to fewer or more subwatershed cells using the AnnAGNPS input editor, to more accurately reflect the class percentages in the reference land cover layer (table 3). A total of fifteen land cover types were defined for Orestime Creek watershed. Because only five types of land use identifier (cropland, pasture, forest, rangeland, and urban) are accepted by AnnAGNPS input, the fifteen types of land cover in subwatershed were reclassified accordingly. Each land use type was assigned to a land use identifier. Mixed forests and rangelands (Grassland/Herbaceous and shrub/scrub) dominate the Coastal Range area of the watershed, while walnuts (28%), tomato (23.3%), almonds (21.7%), dry beans (10.5%), and citrus (6.5%) are top five groups of crop in lower Orestimba Creek sub-basin where cropping area is mainly located. Changes in cropping type have been detected before and after 2007 for certain fields. Almond to walnut and walnut to almond are two dominant Figures represents the land cover layer and the land cover classes from 2000 to 2006 as assigned to AnnAGNPS delineated subwatershed cells layers respectively.

Table 3*: Land use percentages (%) for the delineated Orestimba Creek watershed 2000-2006*

Land Use Class	Percentage of total area (%) in original land cover layer	Percentage of total area (%) as determined by AnnAGNPS	Percentage of total area (%) used in Final Adjusted land cover layer
Barren Land	0.221	0.344	0.242
Cultivated Crops	6.927	17.083	14.765
Deciduous Forest	0.008	0.000	0.000
Developed/High Intensity	0.002	0.000	0.000
Developed/Low Intensity	0.156	0.002	0.000
Developed/Medium Intensity	0.027	0.000	0.000
Developed/Open Space	1.059	0.049	0.172
Emergent Herbaceous Wetlands	0.012	0.000	0.000
Evergreen Forest	0.010	0.000	0.000
Grassland/Herbaceous	26.707	25.488	26.471
Mixed Forest	20.325	16.461	17.525
Open Water	0.126	0.000	0.000
Pasture/Hay	0.177	0.151	0.157
Shrub/Scrub	44.109	40.182	40.435
Woody Wetlands	0.134	0.238	0.233

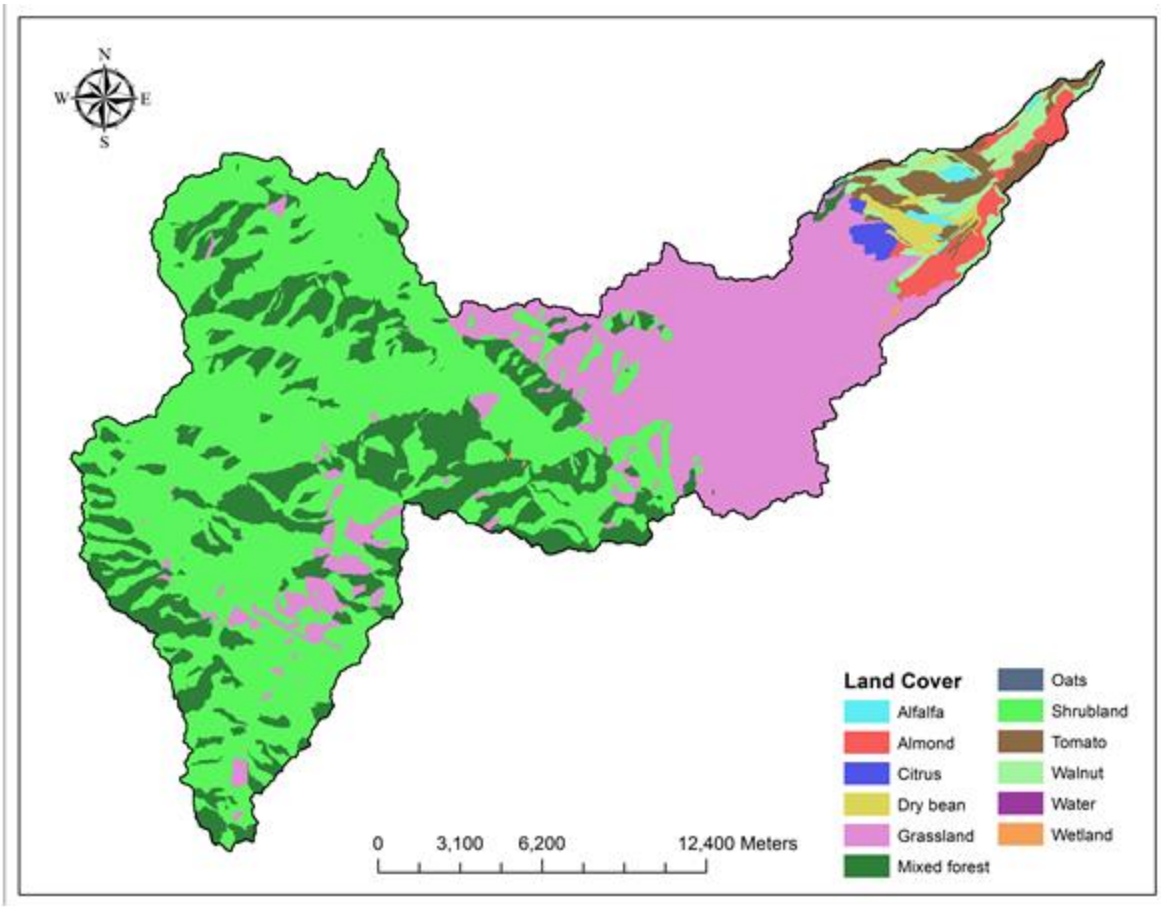

Figure 8: Cropland data land use/land cover as assigned to subwatershed cells (2000-2006).

3.3.6 Field Management data

In AnnAGNPS the field related data section consists of management field data, management operations data, management schedule data, crop data, non-crop data, irrigation application data, fertilizer application data, and pesticide application data. Management field data contain the field land use type, the management schedule implemented for a management field and the first year of a rotation. The management schedule data contain crop planting progress and are required for the scheduling of events for both cropland and non-cropland. Cropland management schedule and operation data can be retrieved from RUSLE (1 and 2) database provided by AnnAGNPS. The RUSLE2 was developed jointly by the USDA-Agricultural Research Service (ARS), the USDA-Natural Resources Conservation Service (NRCS), and the University of Tennessee. RUSLE2 is an upgrade of the text-based RUSLE DOS version 1. It is a computer model containing both empirical and process-based science in a Windows environment that predicts rill and inter-rill erosion by rainfall and runoff. Crop cover management entries in the NRCS RUSLE2 database are keyed to NRCS cropping-management zones (CMZ). CMZ 34 where Orestimba Creek Watershed was located from NRCS national RUSLE2 guideline was applied to obtain management schedule and operation data including residue cover remaining, area disturbed, initial random roughness, final random roughness, operation tillage depth, and information regarding pesticide applications. RUSLE 2 was also utilized to import crop growth parameters and non-cropland use data. Soil Conservation Service curve number (CN) is a major factor in creating management schedule input. CN describes the potential maximum retention of a surface after runoff begins. It varies by storm type for a given soil type and is affected by many factors, such as vegetation cover, vegetation growth state, and antecedent soil moisture. CN is important in accurately predicting runoff and sediment yields, so appropriate CN needed to be assigned to each land use and land cover type (Table 4). In this study, CN Manning's n coefficient for each land cover was determined based on NRCS TR-55 reference (USDA-NRCS, 1986).

Table 4: *Initial CN values for each AnnAGNPS cells (AMC-II)*

Crop description	Initial curve numbers (CN) for hydrologic soil groups			
	A	B	C	D
Row crops straight	67	78	85	89
Small grain straight	63	75	83	87
Close-seeded straight	58	72	81	85
Forest	36	60	73	79
Herbaceous	30	62	73	85
Desert shrub	49	68	79	84
Wetlands	30	30	30	30

3.3.7 Pesticides

One widely used OP pesticide Chlorpyrifos (O,O-diethyl O-3,5,6-trichloropyridin-2-yl phosphorothioate, CAS 2921-88-2) was selected in the risk assessment. Selecting chlorpyrifos as test agent in this study was justified by its high ranks in the list for both usage and toxicity. This pesticide is on the list of 28 pesticides with “high overall relative-risk level” identified by the Central Valley Regional Water Quality Board (CEPA 2007). Chlorpyrifos is the primary utilized for insect control on almond, walnut and stone fruit in the watershed, with the majority applied before and after herbicide spray during irrigation season (Cryer et al., 2001). There is a general increasing trend for the uses of chlorpyrifos 2005, while the amounts dropped from 2005 to 2010 (Table 7). Annual average use of those pesticides in the Stanislaus County was about 79000 pounds for chlorpyrifos during 2000-2010. Table 5 shows the physiochemical properties of Chlorpyrifos applied in its transport and fate simulation. Most of the pesticide properties were obtained from published databases for instance chemical property database for the CalTOX4.0 model (USDA-ARS 2001 and McKone et al., 2003). CalTOX4.0 model is a model developed by environmental scientists at University of California to assist health-risk assessments that address multimedia pollutants. This model includes a dynamic multimedia transport and transformation model that can be used to assess time-varying concentrations of contaminants that are placed in soil layers. Pesticide annual application rate during 2000 through 2010 can be retrieved from California's pesticide use reporting program (CDPR) Pesticide Use Report (PUR) database. CDPR-PUR data is organized following Meridian, Township, Range, and Section (MTRS) geographic units. California township shapfile was intersected with OCW watershed using AnnAGNPS MapWinGIS to determine MTRS units for each cell. Annual pesticide's application rates obtained for each MTRS units from Agricultural Pesticide Use Web Mapping Service of CDPR were directly linked with the corresponding subwatershed defined for the AnnAGNPS simulation. Pesticide application was set as 50% for foliage fraction and 50% for soil fraction and fraction of pesticide wash off foliage was set to 0.65.

For this study, because of lacking actual cumulative crop plant area, chlorpyrifos application was divided into multiple applications with stable rates toward the crop harvest time. The number of pesticide applications was based on the field operation information provided by RUSLE2. The 2000-2010 seasonal progress for almond planted in OCW and the subsequent application rates can be found in Table 6.

Table 5: *Physical and chemical properties of Chlorpyrifos*

Parameter and description	Unit	Chlorpyrifos
Henry's law constant	Pa-m^3/mol	0.001
Octanol-water partition coefficient (K_{ow})		83176
Organic carbon partition coefficient (K_{oc})	L/kg	6025.6
Solubility	mg/L	0.4
Half-life in air	day	0.26
Half-life in canopy	day	3.3
Half-life in sediment	day	52.5
Half-life in soil	day	30.0
Half-life in Surface water	day	53.0
Half-life in Ground water	day	21.0

Table 6: *Almond planting progress with subsequent chloropyrifos application in Orestimba Creek Watershed for 2000 in township section M06S08E26.*

Crop Schedule	Operation	Pesticide Incremental Change from Previous Application (%)	Pesticide Application (lb acre $^{-1}$)
Feb. 15	Sprayer insecticide	20	1.3813
Mar.1	Begin growth		
Mar. 15	Sprayer insecticide	20	1.3813
Mar. 31	Sprayer insecticide	20	1.3813
April 1	Sprayer herbicides post-emergence		
April 10	Disk, inter row strips		
May 1	Sprayer insecticide	20	1.3813
May 10	Disk, inter row strips		
June 1	Sprayer herbicides post-emergence		
June 10	Disk, inter row strips		
June 15	Land plane		
July 1	Sprayer insecticide	20	1.3813
Aug. 10	Harvest		
Nov. 1	Pruning		

Table 7: *Chlorpyrifos application information for Stanislaus County from 2000 – 2010*

Year applied	Summed pounds	Treated acres	Rate (lbs/acre)
2000	67179	49996	1.3437
2001	74449	49389	1.5074
2002	64518	43722	1.4756
2003	90864	58089	1.5642
2004	97714	62176	1.5716
2005	98519	65268	1.5095
2006	91044	63133	1.4421
2007	79597	53878	1.4774
2008	72365	51908	1.3941
2009	69311	46494	1.4908
2010	64607	41925	1.5410

3.3.8 Simulation period data

Rainfall-runoﬀ erosivity factors (R) were calculated by using equation recommended by Renard and Freimund (1994) and 279.4 mm as mean annual precipitation which was calculated from agGEM execution. Ten Year frequency storm energy intensity (EI) number was calculatedby using the R-factor from the equation recommended by Renard and Freimund (1994). Specific rainfall distribution for watershed needs to be assigned to AnnAGNPS for calculating peak discharges and runoff volumes for drainage areas. NRCS developed four synthetic 24-hour rainfall distributions (I, IA, II, and III) from available National Weather Service (NWS) duration-frequency data (Hershfield 1961; Frederick et al., 1977) or local storm data. Types I which represents the Pacific maritime climate with wet winters and dry summers was chosen for model calibration and validation (USDA-NCRS, 1986).

3.3.9 Model calibration and validation procedure

All watershed datasets were created and modified in CSV format using Excel and used as input directly imported into AnnAGNPS Input Editor version 5.40 (Bingner and Theurer, 2013). Calibration and validation of the AnnAGNPS model for both the hydrological and pesticide components of AnnAGNPS were on a monthly basis for OCW. Model calibration for stream discharge was carried out by comparing observed values from USGS with baseflow-added runoff produced by AnnAGNPS simulations. The calibration of stream discharge was adjusted with two sensitive AnnAGNPS parameters for runoff volume (SCS RCN and interception evaporation values) until coefficient of determination r^2 and coefficient of efficiency NSE exceeded certain values, the simulation results were reasonably close to the observed values and no more change can be made to improve model's performance. Both parameters were reported as key factors in obtaining accurate prediction of runoff and sediment yield (Yuan et al., 2001; Shrestha et al., 2006; and Licciardello et al., 2007).

Chlorpyrifos concentration calibration for the Orestimba Creek Watershed was performed after the stream discharge had been calibrated. Predicted pesticide loading was summarized at watershed outlet and compared to the reported in-stream pesticide loads at watershed USGS gaging station. Because of limited research on the sensitivity of model's pesticide parameters, there was limited information in selecting the calibration parameters. For this study, pesticide calibration was accomplished by adjusting the percentage of pesticides applied to the soil and foliage and the percentage wash-off from foliage. According to Zuercher (Zuercher et. al., 2011) these parameters were independent from the stream discharge calibration and can be adjustable under different management and field conditions. Similar to stream discharge calibrations, calibration of pesticide concentrations was completed when the NSE and r^2 values reached stable values and no more improvement could be made to model's performance by changing corresponding calibration parameters. To allow the model to adjust the initial soil water storage terms, the first three years (January 1997 to December 1999) were used as the model initialization years. The calibration period for both the OCW stream flow was from January, 2000 to December, 2002 and validation period was conducted from January, 2003 to

December, 2010. Pesticide concentrations were calibrated from January 2000 to December 2002 and validated from January 2003 to December 2006.

Model performance was quantitatively evaluated at monthly scale by examination of the mean, standard deviation (SD), coefficient of determination (r^2), root mean square error (RMSE) and the Nash and Sutcliffe coefficient of efficiency (NSE) (Nash and Sutcliffe, 1970). Summary of coefficients and difference measures for model evaluation and their range of variability is listed in Table 8.

Table 8: *Coefficients for model evaluation and their range of variability.*

Coefficient	Equation	Range of Variability
Coefficient of determination	$r^2 = \left[\frac{\sum_{i=1}^{n}(O_i-\bar{O})(P_i-\bar{P})}{\sqrt{\sum_{i=1}^{n}(O_i-\bar{O})^2}\sqrt{\sum_{i=1}^{n}(P_i-\bar{P})^2}}\right]^2$	0 to 1
Coefficient of efficiency	$NSE = 1-\frac{\sum_{i=1}^{n}(O_i-P)^2}{\sum_{i=1}^{n}(O_i-\bar{O})^2}$	$-\infty$ to 1
Root mean square error	$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(P_i-O_i)^2}{n}}$	0 to ∞

n = number of observations

O_i, P_i = observed and predicted values at the time step i.

$\bar{O}$ = mean of observed values

Mean and standard deviation describes how similar the frequency distribution of the model results to the measured frequency distribution. The r^2

emphasis on the linear relationship between the observed and predicted values and indicates how much the observed values is explained by the prediction. r^2 itself is insufficient and often misleading evaluation criterion, so the coefficient of efficiency (NSE) was included to assess model efficiency (Nash and Sutcliffe, 1970). NSE simulation indicates how well the plot of observed versus simulated values fits the 1:1 line. NSE is integrated with the root mean square error (RMSE), which describes the difference between the observed values and the model predictions.

The range of variability for these criteria are 0 to 1 for r^2, $-\infty$ to 1 for NSE, and 0 to ∞ for RMSE. 1 was considered as optimal value for r^2 and NSE and 0 for RMSE. According to common practice, simulation results in this study were considered to be unsatisfactory if NSE < 0.36, satisfactory if $0.36 <$ NSE < 0.75 and good if NSE > 0.75 (Van Liew and Garbrecht, 2003).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Stream flow calibration and validation

The observed stream discharge in the calibration period of January 1, 2000 to December 31, 2002 indicated the yearly rainfall was between 213.6 and 308.6 mm (mostly concentrated from November to March). The corresponding annual stream discharge was from 193.2 $m^3 s^{-1}$ to 422.07 $m^3 s^{-1}$. Actual total stream flow includes direct runoff and base flow. Because AnnAGNPS model does not compute base flow contribution to stream flow, in order to compare observed and simulated stream flow, base flow had to be separated from the measured total stream flow data and added to the simulated runoff data. Web-based Hydrograph Analysis Tool (WHAT) was applied in this study to determine base flow from stream flow. WHAT is a Web-based hydrograph separation system that automatically separate base flow from stream flow using USGS daily stream flow database at USGS web server. User can choose his preferred base flow separation method. In this study, a digital filter (BFLOW) base flow separation method (Lyne and Hollick, 1979) was applied in WHAT to separate historical base flow from stream flow at USGS gaging station 11274538. BFLOW filter (Arnold et al., 1995; Arnold and Allen 1999) has been widely applied in various hydrological models such as The Long-Term Hydrologic Assessment Tool (L-THIA) (Harbor, 1994; Bhaduri et al., 2001; Lim et al., 2001; Lim et al., 2006), SWAT (Arnold et al., 1995), and HSPF (Bicknell, 1997). The daily base flow output was downloaded in csv format and added to the predicted runoff volume to calculate total stream flow discharge.

AnnAGNPS simulation results for Orestimba Creek watershed, prior to calibration, after calibration and validation are shown in table 9. Calibration of stream flow in the Orestimba Creek watershed was accomplished on a monthly basis for January, 2000, to December, 2002. The simulated stream flow prior to calibration indicated satisfactory performance before calibration based on r^2 and NSE statistics ($r^2 = 0.54$ and NSE = 0.37), however, the time series data showed an under-prediction in overall runoff, and over-prediction during extreme hydrological months.

The SCS curve number has been recognized as the most important factor for accurate prediction of runoff and sediment yields. Initial CN values for different hydrological soil groups were decreased by 10% for corresponding land cover types. The model was then recalibrated. However, the results were still not close enough to the observed levels. Changing rainfall distributions from type I to type IA didn't make much difference either. Rainfall interception is generally defined as the difference between gross precipitation and net precipitation and is the portion of precipitation that is retained on exposed surface where it can evaporate (Crockford and Richardson 2000, Binger and Theurer 2005). Rainfall interception occurs with every precipitation event and can significantly affect the amount of surface runoff. The default values of maximum and minimum interception evaporation values are 2.5 mm and 0.2 mm. AnnAGNPS allows the user to specify the minimum and maximum interception. At this point, minimum and maximum interception values were increased in pairs until the mean predicted stream flow values were close enough to the mean observed values. The final values for minimum and maximum rainfall interception were 1.78 mm and 5.33 mm respectively. My selection of values is within the range of values reported in literature. Savabi and Stott (1994) have reported minimum and maximum rainfall interception for various crop residue, and average rainfall interception values for winter wheat, soybeans and corn residue value were 2.3, 2.0 and 1.8 mm. Brye et al. (2000) reported the average rainfall interception value for prairie residue of 12.3 mm. Conventional tillage and more than 70% of forest and rangeland in OCW are probably also accounted for the increased rainfall interception values. After adjusting interception values and calibration of stream flow for OCW was considered complete.

After calibration, simulations in steam flow discharge showed some improvement, with r^2 and NSE between measured and predicted monthly stream flow increased to 0.58 and 0.40 respectively, showing a satisfactory prediction (Figure 9). The time series data of post-calibration simulations also appeared more reasonable with smaller over-predictions at rainfall event, less amount of scatter indicating a higher accuracy.

The performance of the calibrated model was validated for the period of January 2003 to December 2010 in terms of stream flow discharge. In general, the time series plot of observed and predicted stream flow indicated monthly stream flow predicted matches the observed record quite well except for some differences (Figures 10 and 11). Validation results of stream discharge from the calibrated model (Table 9) indicated good model performance at the monthly scale and were better than those obtained in the calibration period (ENS increased by 0.77, and r^2 increased by 0.78). Overall, the simulated monthly stream flow values were about 10.98% less than the mean observed stream flow.

According to Chiew et al. (1993), the flow estimates can be classified as acceptable if they have NSE greater than 0.6 and mean simulated flow is always within 15% of mean recorded flow. However, similar to the calibration results, time series stream flow discharge data indicated a few over-predictions and under-predictions at significant rainfall season, which occurred through December to March. The predicted values were generally less than observed value during irrigation season from April to November. There were two occasions when the model predicted considerable runoff, however no runoff record has been observed.

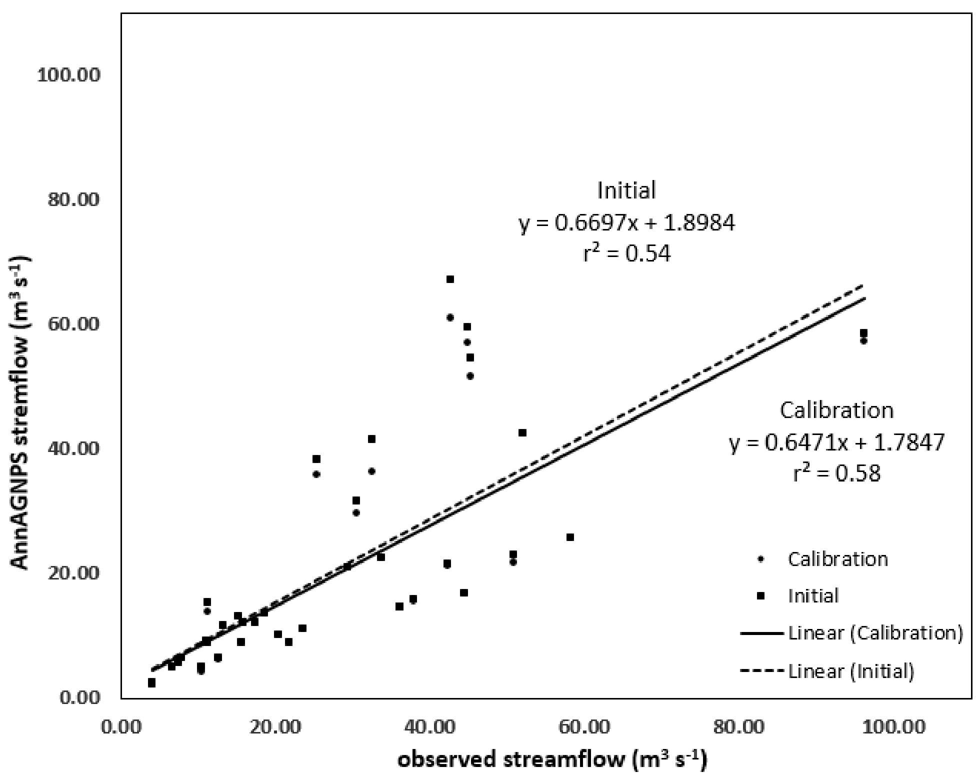

Figure 9: Comparison between prediction and observed monthly stream discharge before and after calibration

Table 9: *AnnAGNPS performance for Orestimba Creek Watershed monthly stream flow*

Modeling phase	Time period	Mean (m^3 s^{-1}) Simulated	Mean (m^3 s^{-1}) Observed	SD (m^3 s^{-1}) Simulated	SD (m^3 s^{-1}) Observed	r^2	NSE	RMSE (m^3 s^{-1})
Initial	2000-2002	20.33	27.53	17.43	19.70	0.54	0.37	4.98
Calibration	2000-2002	19.60	27.53	16.34	19.70	0.58	0.40	4.69
Validation	2003-2010	16.67	18.73	29.58	30.89	0.78	0.77	4.72

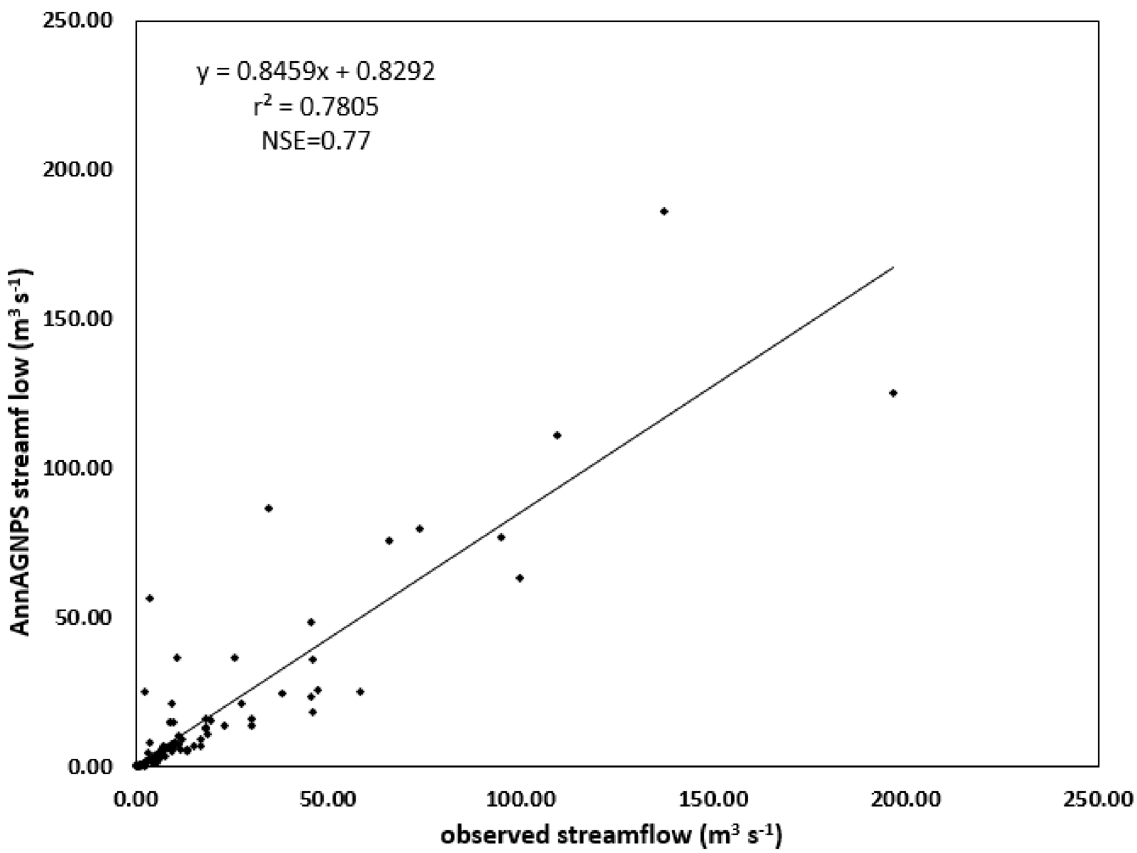

Figure 10: Comparison between predicted and observed monthly stream discharge at validation period

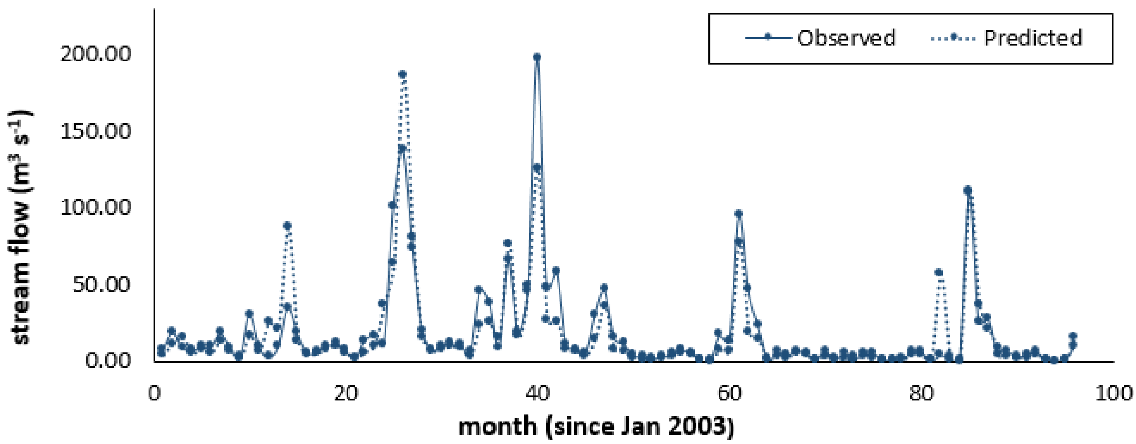

Figure 11: Observed and predicted monthly stream discharge versus time at validation period

Similar to the under-predictions of stream flow during irrigation season from April to November, Yuan et al., (2001) and Das et al., (2008) have reported the model simulation of less stream flow from May to September. Yuan et al. (2001) explained that the runoff generation is less from the fields due to high evapotranspiration (ET) demands during growing season. Under or overestimate ET could affect the overall balance, particularly during the summer months when ET demand is higher. This is also true for OCW, where the growing season generally expands from March to October. It is suggested that measured ET data are needed in the future to validate simulated ET results. The under-predictions might also be associated with lack of irrigation data, as irrigation along with rainfall and snowmelt are three water inputs considered in model's runoff prediction. The availability of climate data also plays an important role in model performance and accuracy. Spatial variability of precipitation data has been identified as one of the major limitations in large scale hydrologic modeling (Arnold et al., 1998). The Patterson weather station is located near the outlet of the watershed (Figure 3), using one rainfall station's data to represent the entire watershed neglects the spatial distribution of rainfall and thus would impact stream flow prediction. When further examining the monthly stream flow series plot and daily rainfall records for the Patterson weather station, stream flow spikes appeared at month 13 and 82, December 2003 and October 2009 (Figure 10) (due to a recorded rainfall event), however no response was observed in the USGS discharge data at the watershed outlet. It is possible these were localized rainfall events not significantly contributing to total measured watershed stream flow. Under this circumstance, rainfall values at the station are distributed over the entire watershed in AnnnAGNPS, resulting in higher stream flow predictions. The stream flow simulation results for AnnAGNPS almost certainly would improve if additional stream gauge and weather station data were available (Heathman et al., 2008). Over-prediction at extreme hydrological events by AnnAGNPS has been reported in a number of published articles (Polakov et al., 2007; Das et al., 2008; Heathman et al., 2008; Zuercher et al., 2011). One possible reason for this over-prediction is that AnnAGNPS calculates daily and sub-daily water balance using SCS TR-55 method rather than using conservation-based continuity equation. SCS TR-55 calculates and updates daily SCS CN values using antecedent moisture condition based on soil wilting point, soil and field hydrologic group CN and field capacity. Daily heavy rainfalls caused unrealistically high CN values and as a result, led to over prediction in runoff.

4.2 Chlorpyrifos calibration and validation

Calibration of chlorpyrifos concentrations was conducted for the time period January 1, 2000 through December 2002. Observed chlorpyrifos data was obtained from USGS National Water Information System at gauge station #11274538. Preliminary data analysis indicated pesticide sampling was conducted biweekly or monthly since 1997. About 66% samples during rainfall season were taken within 3 days after rainfall events. After the initial run the calibrated stream flow model, only small portion of pesticides were picked up by the model at rainfall events. No pesticides have been detected by the model through May to September for the entire three years. Besides, predicted pesticide concentrations were extremely low compared with observed data. After carefully evaluating the inputs to the model, it is confirmed that there was no mistake regarding pesticides related inputs and no adjustment of parameters can be made to improve model's performance.

One major reason that no pesticides were predicted during irrigation season is lack of actual irrigation data. Irrigation application data is not required in AnnAGNPS, but it can be manually input if referenced. Some of the irrigation parameters in the model include irrigation application date, application cycle, application method, application amount, and application rate etc. In previous stream discharge validation process, lacking irrigation data has been identified as one factor contributing to the under-prediction during irrigation season. Irrigation tailwater and spillwater are the main sources of stream flow and carrying media of pesticide residues in the lower reaches of the creek (Luo and Zhang 2008). Irrigation water as one water input in daily water balance calculation in AnnAGNPS directly affects the fate and transport of pesticides dissolved in runoff and attached in sediment. Since AnnAGNPS does not compute base flow and there has been little rainfall and no irrigation water input during May through October, it was not unexpected that the model estimated an absence of pesticides. The irrigation application data for OCW were not included in this study because they were not available. Previous studies assessing pesticides concentration prediction at OCW (Luo and Zhang 2009a,b) did not encounter such problem. In both studies, irrigation data were also not included in the model evaluation input (PRZM and SWAT), however both models contain a built-in module of automatic irrigation that simulates the irrigation water application. This module calculates average daily soil moisture, and irrigation is activated if soil moisture falls below a threshold value defined by the users as a fraction of the available water capacity (PCDEPL). The amount of soil moisture deficit is then added per unit area to the system as irrigated water by the model. Because of AnnAGNPS's discrepancy in handling irrigation data, seven-month period of data failed to be simulated.

The available event-based predicted pesticide concentration during rainfall season (December to March) was used to calculate average monthly concentration and then compared with observed monthly data in series plot and 1:1 linear plot. The AnnAGNPS model greatly under-predicted all the monthly chlorpyrifos concentration, and the simulated values were approximately 1/1000 of measured values. Both series plot and statistical values indicated that AnnAGNPS was inadequate to simulate chlorpyrifos concentration. When examining series plot, it was noticed that AnnAGNPS was able to capture the trend of peak chlorpyrifos concentration if not the magnitude. During calibration period, chlorpyrifos concentrations were generally the lowest in December, and concentration spikes were observed at March.

For the only two pesticide studies published in the literature using AnnAGNPS, low predicted pesticide concentration were observed in both studies (Healthman et al., 2008 and Zuercher et al., 2011). Healthman et al. (2008) observed atrazine concentrations were extremely under-predicted (approximately 1/100) in the non-calibration process. Zuercher et al. (2011) later pointed out that the GLEAMS code sequence in the model for defining pesticide routine was incorrect and they confirmed it was the reason that their and Healthman's atrazine predictions were low. Zuercher et al. (2011) also mentioned that latest version (AnnAGNPS 5.00) with corrected code was released in 2010.

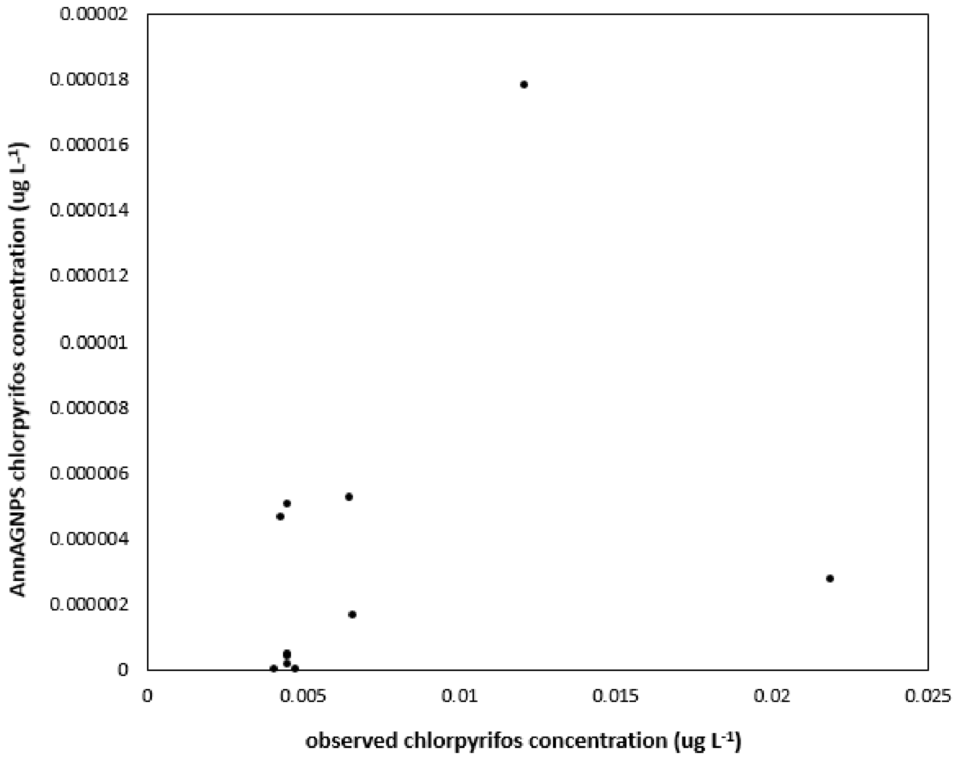

Figure 12: Comparison of predicted and observed monthly chlorpyrifos loading at rainfall season calibration period

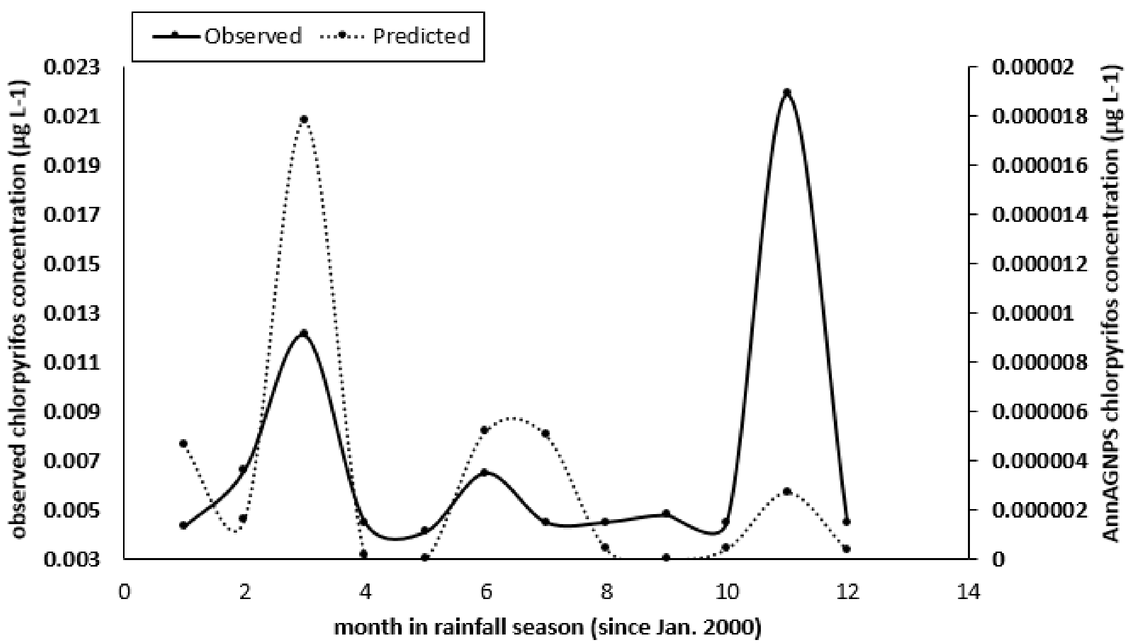

Figure 13: Observed and predicted monthly chlorpyrifos loading versus time at calibration period rainfall season (note the difference in Y axis units)

Since there was only one calibration study for pesticide using AnnAGNPS (Zuercher et al., 2011), only limited information could be referred to on the sensitivity of the model for pesticide parameters. In this study, three parameters were considered for adjusting chlorpyrifos concentration: fraction of chlorpyrifos applied to the foliage and soil, and also pesticide washoff fraction. In order to increase chlorpyrifos concentrations at watershed outlet, more fraction of chlorpyrifos should be assigned to soil, and less fraction needed to be assigned to the foliage, as pesticides caught on canopy degrade or volatilize rapidly. This does make sense, in fact, in San Joaquin Valley region where OCW is located, majority of chlorpyrifos is applied on crops, almond, and walnut via ground spray, while on alfalfa and cotton, via aerial spray (Zhang et al., 2012). Because chlorpyrifos concentrations were extremely low in pre-calibration, and were still very low even when soil fraction increased to 90%, final fraction of chlorpyrifos applied to the soil was increased to 100%, leaving no chlopyrifos applied to the foliage. As no chlorpyrifos was applied to foliage, there was no need to adjust chlorpyrifos washoff fraction. No parameters can be adjusted at this point, and the model was rerun for calibration.

The statistical results indicated that calibrated model had slightly better performance than pre-calibration (Table 10). It should be mentioned that the detection limit for chlorpyrifos concentrations is 0.005 µg/L, 0.0045 µg/L was used for chlorpyrifos concentration that was below detection limit. The r^2 was bad (0.17), and the NSE value was negative (-1.92), indicating model is poor in predicting chlorpyrifos concentrations for the rainfall event (Figure 11 and 12). It was also noticed that adjusting the portion of chlorpyrifos applied to the soil increased chlorpyrifos concentrations at cells and watershed outlet, but did not increase the number of events that chlorpyrifos being detected by the model.

Validation was conducted for monthly chlorpyrifos concentrations in rainfall season (December to March) from December 2003 to February 2006 with calibrated AnnAGNPS model. The reason for choosing this time period is that these were the only complete and continuous months of observed pesticide. Results from examining observed data showed that majority of monthly concentration (eight out of eleven) were below detection limit (Figure 13). The poor performance of the model in calibration period was confirmed in validation period. The model greatly under-predicted monthly chlorpyrifos concentration and had $r^2 = 0.078$. The NSE was extremely low (-36.4). All the results suggested that OCW may not be possible to use AnnAGNPS for prediction of chlorpyrifos concentrations.

Table 10: *AnnAGNPS performance for Orestimba Creek Watershed monthly chlorpyrifos loading at rainfall season*

Modeling phase	Time period	Mean (µg L^{-1}) Simulated	Mean (µg L^{-1}) Observed	SD (µg L^{-1}) Simulated	SD (µg L^{-1}) Observed	r^2	NSE	RMSE (µg L^{-1})
Initial	2000-2002	2.29E-06	0.0069	3.50E-06	0.0052	0.15	-1.92	0.0085
Calibration	2000-2002	2.87E-06	0.0069	5.06E-06	0.0052	0.17	-1.92	0.0085
Validation	2003-2006	3.83E-06	0.005	3.07E-06	0.00086	0.078	-36.4	0.005

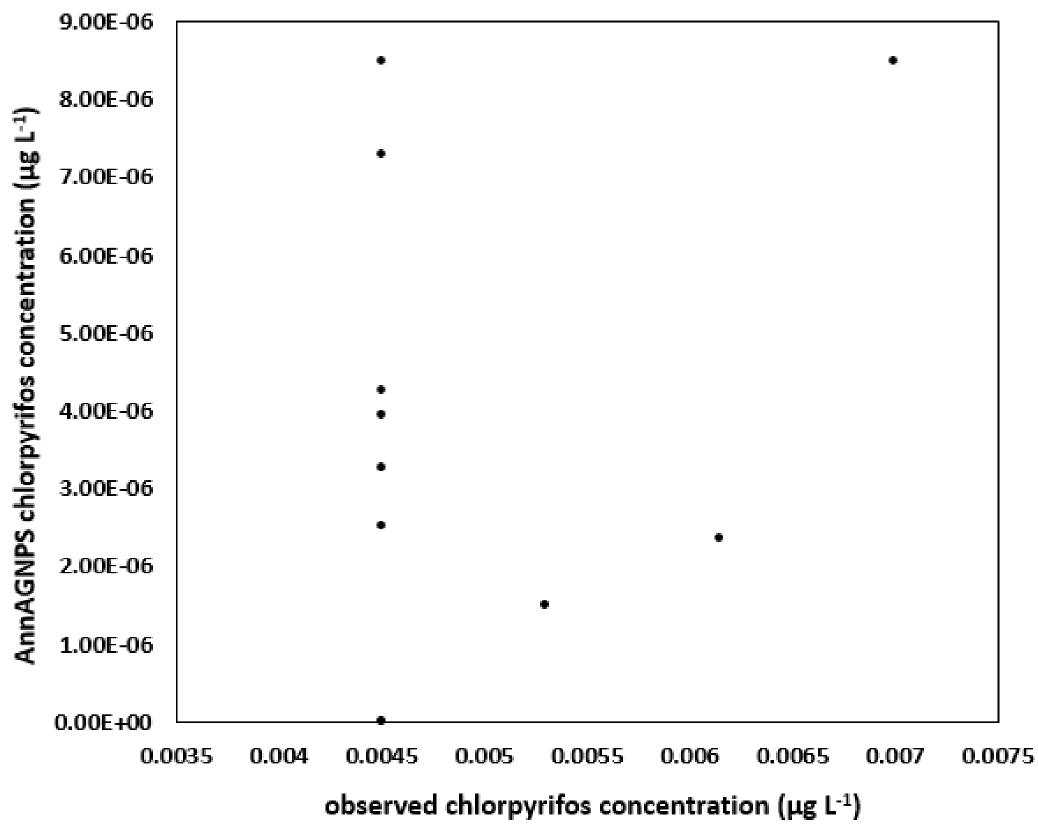

Figure 14: Comparison of predicted and observed monthly chlorpyrifos loading at rainfall season validation period

Besides lacking of irrigation data, model's poor validation results could have been caused by coarse resolution of sampling data utilized for calibration and validation. In-stream pesticide concentrations are highly variable both spatially and temporally, and associated with field sampling uncertainty. The measured data being compared with model prediction is from single grab samples taken during storm runoff events. This is a fairly coarse measurement, and therefore, the statistics based on the measured data in this study was considered only as representative indications of the actual contamination levels. There was also a high uncertainty on measured chlopyrifos concentrations when they were below detection limit. Signing a rough value to an unknown concentration may have even added more error to the model's prediction. Moreover, the AnnAGNPS model has inherent limitations. The biggest limitation is that all of the runoff and associated sediment, nutrient and pesticide loads for a single day are routed to the watershed outlet before the next time step simulation. This limitation proved to be the main factor limiting the model's validity for OCW with respect to runoff and pesticide loading.

Table 11: *Summary of AnnAGNPS performance of Orestimba Creek Watershed monthly stream flow and pesticide loading prediction in validation period*

Modeling phase	Period	r^2	NSE	Model performance
Stream flow validation	Jan.2003 – Dec. 2010	0.78	0.77	Good
Pesticide loading validation	Jan. 2003 – Dec. 2006	0.078	-36.4	Unsatisfactory

CHAPTER 5

SUMMARY AND CONCLUSION

In this study, the AnnAGNPS model hydrologic and pesticide routines were evaluated for their performance at predicting stream discharge and chlorpyrifos concentration in stream water in 40733.1 ha Orestimba Creek Watershed. The modeling system accounted for spatial variability on the parameters of land cover, cropping management, soil properties, and pesticide application. A USGS 1 arc-second NED DEM and Orestimba creek stream network from NHD was used to delineate the OCW into 4377 cells with average 12.79 ha in size. 2004 Land use data provided by California Department of Water Resources was used to obtain land use information between 2000 and 2006. USDA National Agriculture Statistical Survey (NASS) cropland Data Layer (CDL) was used to update land use and crop rotation information from 2007 through 2010. Spatial soil data was obtained from Soil Survey Geographic database (SSURGO), and soil physical properties were updated from NASIS soil database. Dominant land use and soil type was determined by intersecting delineated watershed cells with land use and soil shapefiles. Crop and non-crop information, cropping management schedule and operation were obtained from URSLE 2 database provided by AnnAGNPS. Annual pesticide application rate for each MTRS was acquired from California PUR and was utilized to assign proper amount of chlorpyrifos to each cell. Climate data at Patterson Weather Station from 2000 to 2010 were retrieved from CIMS.

The model was calibrated and validated for hydrologic performance from 2000 to 2002 and 2003 to 2010. Both series plot and 1:1 plot and statistical analysis were conducted. Calibration results were satisfactory with r^2 of 0.58 and NSE of 0.40. The model was modified by adjusting curve number and rainfall interception values. Validation of monthly predicted stream discharge to the observed values with modified model indicated good performance, with r^2 and NSE of 0.78 and 0.77 respectively. Overall, the satisfactory statistical results and evaluations of stream flow discharge series graph indicated the model's runoff prediction was reasonable.

Calibration of AnnAGNPS for chlorpyrifos concentrations in OCW were conducted from 2000 through 2002 using calibrated hydrology model. The results of initial calibration showed no pesticide concentration was detected during irrigation season and the detected concentrations at rainfall season were significantly under-predicted. The model was the adjusted by increasing fraction of the chlorpyrifos to soil to 100%. The statistical results was unsatisfactory with r^2 of 0.128 and NSE of -1.9 .Validation of the model from 2003 to 2006 at rainfall season also produced unsatisfactory results, with r^2 of 0.078 and NSE of -36.4. The poor validation results may be due to, apart from lacking of irrigation data, coarse sampling resolution of the observed chlorpyrifos concentrations; uncertainty with observed concentration and inherent limitations of the AnnAGNPS model.

Overall, this study found that calibrated AnnAGNPS model produced satisfactory calibration and validation for stream discharge in OCW. The chlorpyrifos concentrations were poorly simulated for both calibration and validation period. Future recommendations to improve the performance of the AnnAGNPS for runoff and chlorpyrifos loading simulation in OCW would be: 1) increase the density of rain gages are used, so that a better spatial variation of precipitation can be captured. 2) Obtain actual irrigation application data to better predict the runoff and especially pesticides in irrigation tailwater and spillwater during irrigation season. Further study is also needed to determine the cause of the under-prediction of chlorpyrifos in runoff. A sensitivity analysis is also needed to determine the key parameters in AnnAGNPS pesticide routine in predicting pesticide concentration in runoff and sediment.

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