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Pacific Northwest and California freshwater resources are key elements in the life history and ecology of Pacific salmon and steelhead listed as threatened or endangered under the Endangered Species Act. Risk to listed Pacific salmonid species can be assessed by evaluating the spatial and temporal co-occurrence of salmonid species at sensitive life stages and pesticide concentrations at levels that may elicit adverse effects. Understanding the potential for the co-occurrence requires knowledge of pesticide use patterns and application methods, pesticide properties that influence environmental fate, as well as landscape/land management, edaphic, and climatic factors that influence off-site movement into surface water. Reported here is the use of a passive sampling device to monitor selected current use pesticides in surface water on a continuous basis. Passive sampling devices (PSDs) were deployed continuously in 5 watersheds within the Pudding River subbasin, critical habitat for the Upper Willamette River Chinook and Steelhead ESUs, between June 2010 and October 2011 in order to characterize the temporal trends in surface water concentrations. PSDs were deployed in off-channel habitats preferred by juvenile salmonids. The majority of the monitoring results were well below EPA aquatic life benchmarks, as well as levels of concern for listed salmonids. Using the EPA ecoregion framework watershed sensitivity to pesticide surface water loading was characterized. The Soil and Water Assessment Tool (SWAT) was used to assess the relationship between land management practices and PSD monitoring data collected in the Zollner Creek watershed. SWAT was evaluated under different parameterization scenarios representing increasing levels of local knowledge of the system in order to evaluate model performance in relation to average daily stream flow. Using spatially distributed precipitation data and incorporating engineered drainage features into model parameterization resulted in a satisfactory fit of average daily stream flow indicating satisfactory characterization of the watershed hydrology. SWAT was then used to simulate the fate of chlorpyrifos and trifluralin, the two most commonly detected pesticides in the PSD monitoring. The pattern of simulated time-weighted average (TWA) pesticide concentrations was similar to measured values. However, simulated pesticide TWA concentrations consistently underestimated measured values. The most likely source of this bias is underrepresented pesticide use practices.

Continuous Monitoring and Modeling to Assess Pesticide Exposure in Critical Habitat for Pacific Salmonids

by
Philip K. Janney

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I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

Philip K. Janney, Author

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CONTRIBUTION OF AUTHORS

In all chapters, Dr. Jeffrey Jenkins contributed to intellectual formulation and manuscript preparation. In Chapter 2, Dr. Kim Anderson contributed to the field implementation of sampling and provided instrumentation, method development, and analysis.

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Chapter 1 - Introduction

Pesticides are chemicals that are used to prevent or limit the impacts of pests including insects, fungi, unwanted plants, bacteria, and rodents on human health, animal health, and agricultural production (Cheng 1990, Costa 2008). Beginning in the 1940s, synthetic pesticides were commercialized and have since become a major component of modern agricultural practices (Casida and Quistad 1998, Costa 2008, Cheng 1990). Though the use of synthetic pesticides has proven to be beneficial through increased agricultural productivity, pesticide use is not without risk of unintended adverse impacts (Wauchope 1978, Cheng 1990, Haque 1975, Casida and Quistad 1998). One of the main concerns regarding pesticides is the movement from the site of application leading to the potential for exposure of non-target organisms to pesticides and often unknown adverse effects (Wauchope1978, Cheng 1990, Haque 1975).

Recent examples in California and the Pacific Northwest of concern regarding non-target effects of pesticide use are the mandated consultations under the Endangered Species Act (ESA) between the US Environmental Protection Agency (EPA) and the NOAA National Marine Fisheries Service (NFMS). These consultations address the impact of pesticide use in the landscape surrounding critical freshwater habitats on the continued existence of 26 Pacific salmonid evolutionarily significant units (ESUs). The resulting Biological Opinions (BOs) represent a series of comprehensive risk assessments concerning exposure of ESA listed Pacific salmonids to pesticides. One of the challenges in completing these risk assessments was characterizing exposure of ESA listed Pacific salmonids to pesticides in fresh water environments. The exposure characterizations presented in the BOs rely primarily on large scale surface water monitoring programs designed to evaluate long term trends in pesticide surface water concentration and edge-of-field pesticide fate models based on standard parameterization scenarios (NMFS 2008-2012b). While the surface water monitoring data was useful in providing insight into potential real world exposures, NFMS did identify some areas of uncertainty associated with utilizing this data to characterize risk to listed Pacific salmonid species. First, the monitoring programs were designed to capture long term trends in pesticide surface water concentrations and not to capture peak exposure concentrations in sensitive habitats utilized by juvenile salmonids. Pesticide surface water data from monitoring programs such as the Nation Water Quality Assessment (NAWQA) program that was utilized in the NFMS assessments are designed to characterize trends in surface water quality by collecting samples at fixed intervals (Gilliom et al 2006). These fixed intervals are often not coordinated with known pesticide application periods which can result in underestimation of peak concentrations (NFMS 2008). Also, as monitoring programs were not designed specifically to assess exposure of Pacific salmonids, samples were not collected in off-channel habitats frequently utilized by juvenile salmonids (Beechie et al 2005, Roni 2002, Morley et al 2005). Due to the fact that these off-channel habitats are often shallow and with low flow, the dilution capacity of these habitats is lower than that of the main stream channel resulting in the potential for exposure to higher concentrations of pesticides. As juvenile salmonids utilize these habitats for extended durations, there is particular interest in characterizing exposure in these environments. NFMS relied on AgDrift model simulations to evaluate expected concentrations in these environments in the absence of monitoring data (NFMS 2008-2012b). Second, monitoring data and edge-of-field estimates have limited applicability to other locations within the geographic extent ESA listed Pacific salmonids due to the variability of site specific conditions that influence pesticide fate in the environment. Third, pesticide surface water monitoring data is representative of past pesticide use practices and conditions and are unlikely to be representative of current and future pesticide use practices. Finally, there is a lack of understanding of the relationship between surface water monitoring data and pesticide use practices in the surrounding landscape. This makes it difficult to establish a direct link between pesticide use and exposure of listed Pacific salmonid to pesticides in surface waters (NFMS 2008-2012b). The research presented here represent is focused on presenting methods to address these identified areas of uncertainty in evaluating exposure of ESA listed Pacific salmonids to pesticides.

Research presented in Chapter 2 on assessing pesticide exposure in off-channel habitats under current pesticide use practices. Due to the spatial and temporal variability in both the presence of Pacific salmonids based on life history strategies and the occurrence of pesticides in surface waters, continuous monitoring is necessary to evaluate the potential for co-occurrence pesticides and salmonids in off-channel habitats. Active sampling techniques such as grab sampling and automated samplers present a number of challenges when evaluating contaminant variability over the time frame necessary to characterize salmonid exposure including logistical difficulty in collecting the number of samples necessary as well as financial considerations (Vrana et al 2005, Stuer-Laurisdon 2005). Passive sampling devices (PSDs) offer many advantages compared to active sampling techniques. PSDs operate on the basis of free flow of contaminants in the sampled medium such as air, water, or pore water into the PSD collection medium based on differences in chemical potential in accordance with Fick's 1st law of diffusion (Namiesnik et al 2005, Kot-Wasik et al 2005). PSDs can be deployed over longer periods of time, allowing for the sequestration and concentration of trace contaminants that would require large samples volumes using traditional sampling techniques to quantify (Vrana et al 2005, Stuer-Laurisdon 2005). The extended deployment periods of PSDs also allow for the capture of episodic fluctuations in contaminant concentration resulting in time-weighted average concentrations (Namiesnik et al 2005, Kot-Walsik et al 2005, Huckins et al 2006). Additionally, PSDs sequester the freely dissolved ([C_{free}]) or bioavailable fraction of contaminants in the aquatic environment (Huckins et al 2006, Allan et al 2012). Based on these advantages, PSDs represent a potential means of characterizing pesticide concentrations in salmonid off-channel habitats. While a variety of PSDs have been developed to and demonstrated to assess pesticide concentrations in aquatic environments (Alvarez et al 2005, Tran et al 2007, Schäfer et al 2008, Shaw et al 2010, Harman et al 2012, O'Connell et al 2014), PSDs constructed of low-density polyethylene (LDPE) without a triolein sorbent medium (Anderson et al 2008) were utilized in this study. LDPE PSDs have also been demonstrated to sequester legacy and current use pesticides in aquatic systems (Anderson et al 2008, Anderson et al 2014). LDPE PSDs offer an additional advantage in that the physical characteristics of the polymer itself are similar to biological membranes and mimic passive biological uptake (Huckins et al 2006, Anderson et al 2008). LDPE PSDs were deployed sequentially in off-channel habitats within critical habitat of ESA listed Pacific salmonids in order to assess exposure in these habitats throughout the course of a year. Evaluating pesticide concentrations continuously allows for characterization of pesticide exposure at any time point when listed Pacific salmonid species may be utilizing the off-channel habitats.

In order to address uncertainty in the relationship between pesticide surface water monitoring data and pesticide use practices, a systems based approach is best to understand the complex processes that dictate pesticide fate. Pesticide fate is a function of site specific conditions including application timing, amount, placement, and formulation; physiochemical properties of the pesticide; soil properties and conditions; landscape topography; climate; and land management practices (Wauchope 1978, Grover 1988, Cheng

1990). Pesticide environmental fate models can provide a means of characterizing pesticide transport to surface waters in relation to spatial and temporal variability in site specific conditions (Cheng 1990). Watershed scale modeling is important in the integrated management of natural resources and environmental management as it provides a means of evaluating the overall impact of the complex interactions and processes of land management practices on water quality (Jakeman et al, 2003, Arnold et al 1998). Watershed scale hydrologic models were first introduced with development of the Stanford Watershed Model in 1966 (Crawford and Lindsay 1966). Soon after the introduction of the Stanford model, several other watershed scale hydrologic model were developed, however none incorporated the simulation of non-point source (NPS) pollution (Arnold et al 1998). Beginning in the 1970s, research within the USDA Agricultural Research Service (ARS) regarding the processes that influence NPS pollution including pesticides was integrated into a systems model known as CREAMS that simulated the impact of land management on edge of field hydrology and NPS pollution generation (Knisel 1980). Modifications to the CREAMS model to incorporate pesticide groundwater loading led to the development of the GLEAMS model (Leonard 1987). These models, in addition to the crop and erosion simulation model EPIC (Williams 1990), characterizing the complex field scale processes were integrated into a watershed scale framework that became the Soil and Water Assessment Tool (SWAT) (Arnold et al 1998). The SWAT model was developed to evaluate the effects of land management practices on watershed hydrology and water quality. SWAT has been widely utilized with more than 1800 peer-reviewed publications describing applications worldwide (Gassman 2014). SWAT offers many advantages including a geographic information system (GIS) interface that allows to model parameterization based on readily available GIS data sets (Olivera et al 2006), an online user support community, as well as open source code allowing for evaluation and modification of model processes.

Despite the widespread use of the SWAT model, there are less than 30 peer-reviewed applications of the model related to simulation of pesticide fate (Gassman 2014). Though the number of applications is limited, SWAT has been shown to accurately characterize pesticide fate at the watershed scale (Larose et al 2007, Luo et al 2009, Vazquez-Amabile et al 2006, Bothias et al 2011). One application has demonstrated the utility of the model in characterizing risk of atrazine levels exceeding water quality standards (Vazquez 2006). In this study, SWAT was utilized in conjunction with PSD monitoring to address the relationship between current pesticide use practices in the landscape surrounding listed Pacific salmonid habitat and pesticide surface water concentrations. PSDs provide a time-weighted average concentration over a period of weeks which is an optimal time step for evaluating model estimates. Pesticide transport in SWAT is dictated by mass transfer with water and as such an accurate characterization of the hydrology of the system is imperative. Chapter 3 describes use of the SWAT model to characterize the hydrology of an Oregon watershed containing ESA listed Pacific salmonid habitat that was monitored as part of the work presented in Chapter 2. The SWAT model parameterized to characterize watershed hydrology was then used in Chapter 4 to evaluate the relationship between pesticide use practices and PSD monitoring data.

The focus of the research presented in this dissertation is to demonstrate the use of PSDs and watershed scale environmental fate models to provide a systems level approach for evaluating pesticide exposure patterns. There can be a great deal of uncertainty associated with characterizing exposure using monitoring or modeling data alone. However, the combination of the tools can leverage the benefits of real-world data obtained through monitoring and the characterization of the complex processes captured in models in order to provide a better understanding of exposure.

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Chapter 2 - Continuous pesticide monitoring in the Pudding Subbasin, Oregon – Critical habitat for Pacific salmonids

2.1 Introduction

Pacific Northwest and California freshwater resources are key elements in the life history and ecology of Pacific salmon and steelhead (*Oncorhynchus sp*.). In addition to overfishing, critical habit degradation and loss has been identified as contributing to population decline, resulting in 26 evolutionarily significant units (ESUs) listed as threatened or endangered under the Endangered Species Act (ESA) (Good et al 2005). Water quality degradation is a major concern, including the impact of pesticide use practices in urban, rights of way, agricultural, and forestry landscapes within watersheds that comprise much of the Pacific salmonid freshwater habitat. Surface water monitoring studies (Gilliom et al 2006; Hladik et al 2014; Tuttle 2014) have reported seasonal concentrations of individual pesticides and mixtures that may adversely impact Pacific salmonid fitness and survival (Macneale et al 2010). Recent ESA mandated consultations between the US Environmental Protection Agency (EPA) and the NOAA National Marine Fisheries Service (NMFS) have resulted in a series of Biological Opinions (BOs) that provide a comprehensive assessment of the risks to listed Pacific salmonids that may result from registered uses of products containing 37 pesticide active ingredients (NMFS 2008, 2009, 2010, 2011, 2012a, 2012b).

Aquatic risk assessment is generally focused on the individual and requires information on an organism's susceptibility to a chemical stressor and behaviors that determines exposure, as well as the chemical(s) use or discharge pattern and environmental fate (Suter et al., 2005). However under Section 7(a)(2) of the ESA, the BOs produced by NMFS must assess the potential for the pesticide products to jeopardize the continued existence of listed Pacific salmonid ESUs or result in any destruction or adverse modification of critical habitat defined for each ESU on which they rely for continued existence (National Research Council 2013). Characterizing risks to Pacific salmonids necessary to assess population level impacts requires complex spatial and temporal information on life history and ecology, as well as pesticide use patterns and environmental fate (Macneale et al 2010). Salmonid behavior and life-stage specific susceptibility to pesticides is compared to patterns of exposure to estimate risk. Population models can then be used to estimate impacts of pesticide exposure on fitness and survival (Hanson et al 2012).

Pacific salmonid life history strategies are highly varied, including age at seaward migration, residence time in freshwater, estuarine, and ocean environments, ocean distribution and migratory patterns, and age and season of spawning migration (Croot and Marcolis 1991, Quinn 2005). Pacific salmonids exhibit at least one of two general freshwater rearing and migration life history strategies: ocean-type which migrate back to the ocean soon after emergence or stream-type which rear in freshwater habitats following emergence prior to migrating back to the ocean (Quinn 2005). While in freshwater environments, juvenile salmonids rely on variety of different habitat types during migration and rearing in both large rivers and low order natal and non-natal streams. Many of the freshwater habitat preferences displayed by juvenile salmonids are for shallow, slow moving waters which provide adequate cover, protection from high flow and diverse prey communities (Beechie & Bolton 1999, Beechie et al 2005, Roni 2002, Roni et al 2002, Teel et al 2009, Henning et al 2006, Morley et al 2005). There is particular concern regarding exposure of juvenile salmonids to pesticides in shallow water and off-channel habitats due to decreased dilution capacity of these habitat types (Poletika et al 2011). In addition, indirect effects to salmonids can occur due to disturbances to natural prey abundance and diversity in these environments following pesticide exposure (Liess 2005, Schulz 2004, Macneale et al 2014).

Risk to listed Pacific salmonid species is determined by evaluating the spatial and temporal co-occurrence of salmonid species at sensitive life stages and pesticide concentrations at levels that may elicit adverse effects (Macneale et al 2010). Understanding the potential for the co-occurrence requires knowledge of pesticide use patterns and application methods, pesticide properties that influence environmental fate, as well as landscape/land management, edaphic, and climatic factors that influence off-site movement into surface water (Wauchoupe 1978, Leonard 1988, van der Werf 1996). Pesticide concentrations in aquatic environments have been shown to fluctuate on temporal scales ranging from hourly to seasonally (Leu et al 2004, Gilliom et al 2006, Johnson et al 2011). This leads to the need to characterize aquatic pesticide concentrations on a continuous basis in order to evaluate the co-occurrence of pesticides and listed Pacific salmonid species. In addition, the interface between pesticide application sites and surface water should be evaluated over the range of salmonid freshwater habitat, including edge-of-field, watershed, subbasin, and regional scales.

This study was conducted in the Pudding River subbasin, Oregon, which contains critical habitat designated for the Upper Willamette River (UWR) Chinook and Steelhead ESUs. This 136,870 hectare subbasin originates in the western slope of the Cascades and flows northwestward into the Willamette Valley. The Willamette Valley is one of the most diverse agricultural regions in the world, producing more than 170 varieties of crops. The agricultural areas within the Pudding subbasin are characteristic of this diversity, consisting of a wide variety of field, vegetable, fruit, orchard and nursery crops, with equally diverse pest management and concomitant pesticide use strategies. The diversity of pesticide use raises concern for surface water loading of multiple pesticides which may result in complex patterns of exposure to salmonids and their food web.

Pesticides in the surface waters of the Pudding River subbasin have been documented through federal and state agency monitoring campaigns dating back to the early 1990s. The US Geological Survey (USGS) has collected samples from Zollner Creek watershed, located in the Pudding River subbasin, from 1993 to the present, as a part of the National Water Quality Assessment (NAWQA) program (USGS 2013). In addition, samples have been collected less frequently at four additional locations within the watershed. Grab samples were collected using a combination of fixed-frequency and extreme-flow (often high flow conditions) sampling. Fixed-frequency sampling generally occurred in two phases with 2-4 samples collected per month during high pesticide use periods that ranged from 3-9 months and 1-2 samples collected per month for the remaining months (Gilliom et al 2006). Beginning in 2005, the Oregon Department of Environmental Quality Pesticide Stewardship Program (ODEQ PSP) collected samples annually at 6 sites within the Pudding River subbasin including the Zoller Creek watershed, focusing mainly on high pesticide use periods (ODEQ 2013). USGS NAWQA grab samples were streamflow-weighted, depth- and width-integrated composites (Gilliom et al 2006). ODEQ PSP grab samples were collected from a single location near the center of the stream channel (Masterson et al 2012).

Grab samples provide an instantaneous measurement of concentration, and depending on sampling frequency, critical events may be missed; many samples may be required to adequately characterize the variability in pesticide surface water concentration over weeks and months, particularly during pesticide use seasons. Passive sampling devices (PSDs) can capture episodic fluctuations of contaminants as time-weighted average (TWA) concentrations over the deployment period. In addition, it is practical to deploy PSDs sequentially to characterize contaminant fluctuations on a continuous basis. Deployment on the order of a few weeks allows the PSDs to accumulate and concentrate low levels of contaminants with detection limits often significantly lower than grab samples (Namiesnik et al 2005, Kot-Wasik et al 2007). In addition, PSDs have been shown to sequester the freely dissolved fraction of contaminants in aquatic systems in a manner that simulates passive uptake by biological organisms (Huckins et al 2006, Allan et al 2012).

Historically, USGS and others have employed grab sample surface water monitoring, on a weekly, bi-weekly, or monthly basis primarily during the pesticide use season, to establish long-term water quality trends. While these monitoring results are an important resource for identifying areas of concern that may focus future research, the sampling design may not be adequate to sufficiently characterize the pattern of pesticide exposure to aquatic life, and the likelihood of harm to listed salmonids and their food web. While daily grab sampling may address this concern, it is resource intensive and often not practical. A practical alternative is surface water monitoring employing PSDs, which can be deployed sequentially on a continuous basis. Sequential TWA concentrations over a period of a few weeks are useful in characterizing chronic exposure. In addition, to address the potential for fluctuating pesticide concentrations during the sampling period, TWA concentrations can be "compressed" to estimate exposure levels if the measured TWA actually occurred as a much shorter pulse, such as 96 hours, a typical exposure period used for acute aquatic life benchmarks. In this study, low-density polyethylene PSDs were deployed to continuously measure selected current use pesticides in freshwater environments characterized as off-channel habitats or shallow water environments, preferred by juvenile salmonids – a sensitive life stage, and where pesticide concentrations are likely to be higher due to a limited capacity for dilution and slower dissipation rates compared to the main stream flow (Poletika et al 2011).

2.2 Materials and Methods

2.2.1 Study Site

The study area chosen for this project was the Pudding River subbasin, a portion of the Molalla-Pudding Subbasin (HUC8:17090009) located in the Willamette Valley to the south-east of Portland, OR and the north-east of Salem, OR (Figure 2.1). The Pudding River subbasin drains an area of 1369 km^2 (USGS 2013) that contains a wide variety of land uses that including 54% agricultural, 38% forested and 8% urban lands (NASS 2011). Urban and agricultural areas are predominantly located on the Willamette Valley floor while forested areas are located primarily in the foothills of the Cascades in the eastern portion of the subbasin. PSDs were deployed at five locations within the Pudding River subbasin representing the cumulative impacts of upstream activities in four unique watersheds within the Pudding River subbasin and the Pudding River subbasin as a whole. Watershed and subbasin locations are shown in Figure 2.1 and watershed and subbasin characteristics are given in Table 2.1.

2.2.2 PSD Fabrication

Passive sampling devices utilized in this study were constructed of low-density polyethylene tubing using methods described in Sower et al 2008. In brief, commercially available low-density polyethylene (LDPE) tubing was pre-cleaned with hexanes to remove any potential chemical interference. The cleaned tubing was then heat sealed at one end, fortified with a performance reference compound (PRC) solution containing a combination of PCB-77 (*d6*), PCB-100, PCB-180 and pentachloronitrobenzene in order to determine *in-situ* chemical uptake rates and finally heat sealed on the remaining end to produce a 2.7 x 100 cm two-layer membrane strip. PCB-77 (*d6*), PCB-100, PCB-180 and pentachloronitrobenzene obtained from Cambridge Isotope Laboratories (Andover, MA) were used as PRCs.

2.2.3 Sample Collection

During the course of this study – June 2010 to October 2011 – PSDs were deployed at the 5 locations within the Pudding subbasin also used in USGS and ODEQ monitoring (Figure 2.1). Samplers were deployed in stainless steel cages, 5 PSDs per cage, at each sampling location. Cages were anchored to a fixed point on shore and a weight was attached 0.5m from the bottom of the cages in shallow water environments, i.e., off-channel habitat environments, or habitats closely resembling off-channel habitat environments, as described in the NMFS BO (NMFS 2008). PSDs were deployed for 21-28 day periods except for two sampling events which lasted longer due to high water conditions rendering sampling sites inaccessible. From October 2010 to October 2011, HOBO water level loggers were attached to stainless steel cages to monitor temperature and head pressure to ensure that cages remained submerged. Following each sampler deployment, PSDs were retrieved and replaced with new samplers. PSDs were transported to Oregon State University and processed as described in Anderson et al 2008. PSDs were spiked with tetrachloro-m-xylene (TCMX) and PCB-209 as surrogate recovery standards prior to extraction. Solvents utilized in the pre-cleaning, cleaning, extraction and sample preparation processes were Optima® grade or better (Fisher Scientific, Pittsburgh, PA). Surrogate compounds were from AccuStandard (New Haven, CT).

2.2.4 Chemical Analysis

Samples were analyzed using the method described in Anderson et al 2014. Briefly, sample extracts were injected with 4,4'-dibromooctafluorobiphenyl as an internal standard. Samples were then analyzed using an Agilent 6890N Gas Chromatograph (GC) equipped with dual electron capture detectors (ECD) and dual Agilent 7683 injector towers. Additionally, 30% of field samples were analyzed by GC/MS retention time locking Automated Mass Deconvolution Identification Software (AMDIS) and reference library to confirm positive GC-ECD findings. The analyte list, which contains both current use and legacy pesticides, is given in Anderson et al 2014; 4,4'-dibromooctafluorobiphenyl was used as an internal standard. Native pesticides and internal standards were obtained from AccuStandard (New Haven, CT).

A total of 80 field samples, 32 field quality control samples and 116 laboratory generated quality control samples were analyzed, such that over 60% of the samples analyzed were quality control samples. Quality control samples included field and trip blanks for each PSD deployment/retrieval event, laboratory preparation blanks, instrument blanks, continuing calibration verification (CCV) and matrix overspikes. Recoveries of CCVs and matrix overspikes were within data quality objectives of ±20% and ±50% respectively. Levels of all target analytes were below levels of quantitation in all blank quality control standards. Water concentrations were calculated from PSD extract data using an empirical uptake model based on PRC-derived sampling rates (Huckins et al 2002). The use of PRCs allows for calculation of site-specific *in-situ* sampling rates accounting for variable exposure conditions such as temperature, flow and fouling (Huckins et al 2002, Anderson et al 2008). This model is generally applied in instances where PRC recovery is between 20-80%, which was the case in this study. In instances where the PRC recoveries were outside of this range, sampling rates were determined using an improved nonlinear least-squares method (Booij et al 2010, Allan et al 2012).

The LDPE PSDs utilized in this study have been shown to sequester non-polar and many semi-polar contaminants including many pesticides (Petty et al 2004, Adams et al 2007, Lohmann 2012, Sethajintanin and Anderson 2006, Anderson et al 2008). Partitioning of these chemicals into LDPE is driven by the hydrophobicity of the chemical and has been found to be positively correlated with log K_{ow} and negatively correlated with water solubility (Adams et al 2007, Lohmann 2012). During the time that PSDs were deployed in the Pudding River subbasin, there were nearly 500 pesticide active ingredients registered for use in the state of Oregon (Daniels and Boyer 2013) demonstrating a wide range of physiochemical properties (University of Hertfordshire 2013); for example, reported log K_{ow} values range from -6.19 – 12.3 and water solubilities range from $1x10^{-6}$ – $2.5x10^{6}$ mg/L (20^{o}C). However, nearly 200 of these pesticide active ingredients have a combination of log K_{ow} values greater than 3 and water solubilities generally less than 100 mg/L (20^{o}C) that favor LDPE PSD sequestration. This study focused on demonstrating the utility of LDPE PSDs for continuous monitoring using a subset of these current use pesticides – alachlor, chlorothalonil, chlorpyrifos, dacthal (DCPA), endosulfan, endosulfan sulfate, metolachlor, permethrin, terrazole, and trifluralin. Physiochemical properties of these pesticides, as well as rank compared to all pesticides registered in Oregon, are shown in Table 2.2. Additional criteria for selecting these pesticides were: 1) labeled for use on crops/sites likely to be found in the Pudding River subbasin, 2) chlorothalonil, chlorpyrifos, DCPA, metolachlor and trifluralin are characterized as Pesticides of Interest (POI) or Pesticides of Concern (POC) by the Oregon interagency Water Quality Pesticide Management Team due to frequency of detection and/or measured concentrations relative to aquatic life benchmarks (Riley et al 2011), 3) chlorothalonil, chlorpyrifos, metolachlor, and trifluralin are included in NMFS BOs.

2.3 Results

PSDs were continuously deployed in the Pudding River subbasin from June 2010 to October 2011 to monitor for selected current use pesticides in order to characterize the spatial and temporal variability of freely dissolved surface water concentrations in off-channel habitats favored by UWR Chinook and Steelhead ESUs during sensitive life stages. Figure 2.1 shows the sampling points at the outlet of 5 watersheds within the Pudding River subbasin. The Pudding River watershed sampling location is the most downstream and therefore is influenced by the discharge from the 4 upgradient watersheds designated Little Pudding River, Silver Creek, Abiqua Creek, and Zollner Creek. The subbasin contains over 170 and 235 river kilometers of critical habitat designated for the UWR Chinook and Steelhead ESUs respectively (Figure 2.1).

Results of surface water monitoring for the current use pesticides alachlor, chlorothalonil, chlorpyrifos, dacthal, endosulfan, endosulfan sulfate, metolachlor, permethrin, and trifluralin are shown in Table 2.3; chloroneb and terrazole were analyzed for but not detected. Data are presented as minimum, median, maximum concentrations in ng/L, and frequency of detection above the limit of quantitation (LOQ). Figure 2.2 shows box plots of median, 25th and 75th percentile concentrations, with whiskers from the minimum to maximum.

Chlorpyrifos was the most commonly detected current use pesticide, present in greater than 80% of the samples. The chlorpyrifos highest maximum concentrations were measured at the Little Pudding River, 15.9 ng/L, and Zollner Creek, 12.5 ng/L. Median chlorpyrifos concentrations ranged from 0.18 to 4.02 ng/L, with the highest median concentrations measured at the Little Pudding River and Zollner Creek. Trifluralin was detected at a frequency near 80% for all sampling locations except Silver Creek. The trifluralin highest maximum concentration, 15.4 ng/L, was measured at Zollner Creek. Median trifluralin concentrations for all sites ranged from 0.009 to 0.93 ng/L, with the highest median trifluralin concentrations measured at Zollner Creek and the Little Pudding River. Endosulfan (sum of endosulfan I and endosulfan II) was detected in at least 50% of samples. The highest maximum endosulfan concentration, 17.1 ng/L, was measured at the Little Pudding River. Median endosulfan concentrations for all sites ranged from 0.69 to 3.40 ng/L. The detection frequency of endosulfan sulfate, a degradate of endosulfan, was 100% at Zollner Creek, 85% at the Little Pudding River, 67% at the Pudding River, 31% at Silver Creek, and 27% at Abiqua Creek. The endosulfan sulfate highest maximum concentration, 28.3 ng/L, and highest median concentration, 4.99 ng/L, were measured at Zollner Creek. Median endosulfan sulfate concentrations for all sites ranged from 0.42 to 4.99 ng/L. Dacthal was detected at all of the sampling locations except for the Pudding River(LOQ 0.016 ng/L). Dacthal was measured in 77% of the Little Pudding River samples, including the highest maximum concentration, 0.47 ng/L, and the highest median concentration detected, 0.29 ng/L. Dacthal was detected much less frequently at Zollner Creek, Abiqua Creek, and Silver Creek. Chlorothalonil was measured in at least two samples collected from each site and most frequently detected (46%) in the Little Pudding River. The highest maximum chlorothalonil concentration, 9.34 ng/L, was measured in the Little Pudding River. Chlorothalonil median concentrations for all sites ranged from 1.68 to 3.18 ng/L. Metolachlor was measured in 2 samples collected from the Pudding River, 3 samples in Abiqua Creek, 3 samples in Zollner Creek, and most frequently detected (46%) in the Little

Pudding River. Metolachlor was not detected in Silver Creek (LOQ 0.67 ng/L). The highest maximum concentration, 327.7 ng/L, and the highest median concentration, 176.0 ng/L, were measured in Zollner Creek. Metolachlor median concentrations for the remaining sites were 61.2, 6.40, and 4.65 ng/L for Little Pudding River, Abiqua Creek, and the Pudding River, respectfully. Permethrin, sum of *cis*- and *trans*-permethrin, detection frequency ranged from 31% at Silver Creek to 8% in the Pudding River. The permethrin highest maximum concentration, 0.703 ng/L, and highest median concentration, 0.050 ng/L, were measured in Silver Creek. Permethrin median concentrations for all sites ranged from 0.013 to 0.050 ng/L. Alachlor was detected once in Silver Creek, 32.9 ng/L, and once in Zollner Creek, 1.36 ng/L.

2.4 Discussion

The Pudding River subbasin was chosen for this study as monitoring studies conducted over the past 20 years have shown the presence of pesticides in surface water. Both USGS and ODEQ monitoring programs are designed to assess trends in pesticide levels in surface water using grab samples collected at fixed frequencies (USGS 2013, ODEQ 2013). The most frequently sampled site – Zollner Creek – has been sampled annually since 1993. USGS suspended sampling in the Pudding subbasin in 2008, but ODEQ began pesticide sampling in 2006, collecting most samples between March and July. From 2006 to 2009, ODEQ sampling was focused on assessing trends of 10 organophosphate insecticides, including chlorpyrifos, as well as triazine herbicides atrazine and simazine. In 2009, the sampling program was expanded to include nearly 100 pesticides. The combination of USGS and ODEQ sampling data provides a nearly 20 year record of chlorpyrifos monitoring data at the Zollner Creek sampling site. For the remaining sampling sites, the ODEQ sampling provides a 6 year history of chlorpyrifos concentrations and a 3 year history for the other pesticides detected in the PSD samples reported here.

ODEQ detected only two of the pesticides found in the PSD samples, chlorpyrifos and metolachlor, which were detected at the Zollner Creek, Little Pudding River, and Pudding River monitoring sites (Table 2.4). The detection frequency of chlorpyrifos at these sites was 30%, 22%, and 5% respectively. Chlorpyrifos was not detected at the Zollner Creek and Pudding River monitoring sites from January 2008 through 2011, and at the Little Pudding River monitoring from May 2009 through 2011. The detection frequency of metolachlor at the Zollner Creek, Little Pudding River, and Pudding River monitoring sites was 78%, 82%, and 31% respectively. Metolachlor was detected at these sites through 2011. The lack of any pesticide detections in Abiqua Creek and Silver Creeks resulted in decreased sampling frequency in 2009. Between 2009 and 2011 ODEQ sampled for, but did not detect, the remaining pesticides detected in the PSD samples at the Zollner Creek, Little Pudding River, and Pudding River monitoring sites. This can be attributed to PSD LOQs, generally an order of magnitude lower than grab sampling techniques. During the current study period – June 2010 to October 2011 – USGS did not collect grab samples in the Pudding River subassin. However, historically (1993 to 2008) USGS reports detections in the Zollner Creek watershed of the same current use pesticides detected in this study (Table 2.4).

In addition to facilitating continuous monitoring, PSDs are generally capable of detecting lower levels of freely dissolved pesticides compared to grab sampling techniques. For example, in this study the PSD LOQ for chlorpyrifos is approximately 1500 times lower than the DEQ LOQ employing grab samples during the same time frame. PSDs in this study were also used to characterize concentrations found in shallow water and off-channel habitats preferentially utilized by juvenile salmonids. Typical grab sampling methods require that samples are collected from the center of the stream channel or integrate samples collected from across the entire stream channel in order to produce a sample that is representative of the entire stream rather than focusing on the habitats that are ecologically significant to threatened and endangered Pacific salmonid ESUs. This is partially due to the purpose of many sampling studies which are designed to evaluate trends in contaminant levels as is the case for USGS and ODEQ sampling. Sampling in this manner provides a representative concentration found in the stream channel. The need to sample the main channel or integrate samples across the stream channel is also partially necessary in order to collect a sample large enough to meet the analytical requirements to detect trace level contaminants such as pesticides. The ability of PSDs to remain stationary in shallow water and off-channel habitats and concentrate trace levels of contaminants over time make them uniquely suited to evaluate pesticide exposure in these types of environments. When compared with grab sampling data collected during the same time frame was the PSD sampling took place, PSD samples provided measurements of pesticide concentration in shallow water and off-channel habitats while grab sampling data indicated that pesticide exposure did not occur.

Table 2.5 shows the EPA Office of Pesticide Programs acute and chronic aquatic life Benchmarks for current use pesticides detected by continuous PSD surface water monitoring in Pudding River subbasin watersheds, June 2010-October 2011. The aquatic life benchmarks, expressed in ng/L, are not enforceable standards but represent a level of concern for the protection of aquatic life. Comparing the maximum pesticide concentrations measured (21 day TWA) to these benchmarks shows that surface water concentrations for all but 3 pesticides are at least an order of magnitude below the most sensitive chronic aquatic life benchmark. For 2 of the pesticides (chlorpyrifos and metolachlor) the maximum concentrations were within an order of magnitude of the most sensitive chronic aquatic life benchmarks. In addition, chlorpyrifos and metolachlor were the most frequently detected pesticides. Only the endosulfan maximum concentration of 17.1ng/L exceeded an aquatic life benchmark, the chronic benchmark for invertebrates – 10 ng/L (Table 2.5). Figure 2.3 shows the chlorpyrifos 21 day TWA PSD surface water concentrations by watershed for continuous monitoring from June 2010 to October 2011. Figure 2.4 also shows chlorpyrifos PSD concentrations relative to the ODEQ chlorpyrifos grab sample LOQ of 25 ng/L, and the most sensitive chlorpyrifos aquatic life benchmark. During this period ODEQ collected 8 grab samples, primarily collected in the spring, reporting no detections above a LOQ.

One challenge of using PSD data for exposure characterization in aquatic risk assessment is that PSDs provide a time-weighted average concentration of freely dissolved pesticides measured over the duration of deployment, usually a few weeks. While this measurement may be useful in assessing chronic exposure, the TWA concentration does not account for fluctuation in pesticide concentration during deployment. However, to assess the potential for acute exposure, the TWA concentration can be compressed to represent a scenario when PSD pesticide sequestration occurs as single pulse over a shorter time period. For example, Table 2.5 shows the maximum 21 day TWA pesticide concentrations for all watersheds in the Pudding River subbasin, as well as the compressed 96 hour concentration estimate, a typical exposure period in toxicity tests used to derive the acute aquatic life benchmarks in Table 2.5. These data show that even if the 21 day TWA concentrations are compressed to 96 hours, only two pesticides exceed acute aquatic life benchmarks. The chlorpyrifos 96 hour concentration estimate of 83.5 ng/L exceeds the acute aquatic life benchmark for invertebrates (50 ng/L), and the endosulfan 96 hour concentration estimate of 89.8 ng/L exceeds the acute aquatic life benchmark for fish 50 ng/L).

2.4.1 Spatial Analysis

Based on historic monitoring data and the present study, pesticides have been detected at higher concentrations and more frequently at the Zollner Creek and Little Pudding River sampling sites compared to Abiqua Creek and Silver Creek sampling sites. Using spatial analysis, pesticide surface water loading can be characterized as a function of landscape/land management, edaphic conditions, and climate. One method of evaluating the combination of these variables is the US EPA's Ecoregion framework (USEPA 2013). Ecoregions are geographic areas that contain relatively homogeneous abiotic and biotic ecosystem components including the spatially explicit variables climate, soils, geology, vegetation, land cover/land management, topography and hydrology (Omerick 1987). Ecoregions are defined in a hierarchical fashion based on the scale of the assessment with the detail increasing with ecoregion level. Level I and II ecoregions are defined at the continental scale for North America, level III ecoregions are defined at the national scale for the US, and level IV ecoregions are defined at the state level (Bryce et al 1999). Ecoregions can be utilized to compare geographic differences in interactions between the terrestrial and aquatic environments as well as tailor water quality standards and management suggestions to regional needs in order to achieve realistically attainable goals (Griffith et al 1999, Omerick 1987). Trends in water quality have been found to be similar within defined ecoregions (Griffith et al 1999).

The Pudding River subbasin contains 5 Level IV ecoregions: Willamette River and tributaries gallery forest (3b), Prairie terraces (3c), Valley foothills (3d), Western Cascades lowlands and valleys (4a), and Western Cascades mountaine highlands (4b) (Figure 2.4) (Table 2.1). Of particular interest are land use and hydrologic differences between these ecoregions that may influence pesticide surface water concentrations. Over 90% of the Little

Pudding River and Zollner Creek watersheds are located within ecoregion 3c. While the Abiqua Creek and Silver Creek watersheds lie within numerous ecoregions, over 71% of both watersheds lie within ecoregion 4a. Level IV ecoregions 3c and 4a are located within different level I, II, and III ecoregions, indicating large scale differences in the ecosystems represented. Attributes of the two ecoregions that represent the majority of the HUC 10 to HUC 12 watersheds monitored in this study can be used to evaluate the differences in the sensitivity to pesticide surface water concentrations at the watershed scale.

Ecoregion hydrologic attributes are of particular interest in evaluating the potential for pesticide surface water loading and the sensitivity of surface waters to pesticide loading. For example, streams in ecoregion 3c are typically characterized as low gradient, often entrenched or channelized due to anthropogenic activity, with peak flows occurring during winter months in response to rainfall events. Streams in ecoregion 3d, 4a, and 4b are typically characterized as moderate to high gradient channels flowing through canyon features, with peak flows occurring the winter months in response to rainfall events as well as higher flow events during the spring snow melt (OWEB 1999). These ecoregion hyrdrologic attributes – stream morphology and flow pattern – can be used to differentiate stream discharge that influences pesticide surface water concentrations. As Abiqua Creek, Pudding River, Silver Creek, and Zollner Creek watersheds are gauged; hydrologic data was available to compare stream flow during the course of the study. Average daily stream flow for water years 2010 and 2011 were obtained for each of the watersheds. Stream flow data for the Pudding River and Zollner Creek watersheds were obtained from USGS gages, station IDs 14202000 and 14201300, respectively. Stream flow data for the Abiqua and Silver Creek watersheds was obtained from the Marion Soil and Water Conservation District’s Water Quantity Program.

One method for comparison of stream flow between watersheds is the stream flow duration curve (Vogel 1995). Stream flow duration curves provide a graphical representation of the relationship between the magnitude of flow and the frequency of flow events over a given period of time. Stream flow duration curves for average daily stream flow for water years 2010 and 2011 combined are shown in Figure 2.4, and represents stream flow over the duration of the study except for the last 7 days of deployment in October of 2011.

Figure 2.5 shows that flow duration curves for Abiqua Creek, Pudding River, Silver Creek, and Zollner Creek over water years 2010 and 2011. The cumulative distribution of flows in the Abiqua Creek and Silver Creek watersheds were nearly identical with minimum, median, and maximum flows all within the same order of magnitude. This demonstrates not only a similar magnitude of flow between the two watersheds but also that there is a similar response to hydrologic loading and low flow periods. The flow duration curve for the Zollner Creek watershed is an order of magnitude lower than those for the Abiqua Creek and Silver Creek watersheds. A major determinant of this difference is that Abiqua Creek and Silver Creeks, predominately located in the 4a ecoregion, originate in the Cascades resulting in greater flow compared to streams, such as Zollner Creek, originating in the 3c ecoregion.

The ecoregion framework is most useful in evaluating differences in sensitivity to pesticide surface water loading at the watershed scale. To evaluate watershed features that influence pesticide occurrence in off-channel habitats requires further refinement. Off-channel habitats are unique to channel morphology that is ultimately determined by watershed scale and beyond hydrologic influences. Little Pudding River and Zollner Creek watersheds are characterized as being located in the in the Pudding River subbasin main flow channel with highly incised stream banks as the result of long term intensive agricultural land use. Highly incised stream banks cut off the stream channel from natural flood plain environments as well as lead to diminished stream habitat complexity and reduced availability of off-channel habitats (Constantinescu et al 2009). Additionally, due to the very low average daily flow compared to other USGS NAWQA sampling sites (Johnson et al 2011), Zollner Creek in total has been characterized as a surrogate for off-channel habitat (Poletika et al 2011, Teply et al 2011). Samples collected in the Abiqua Creek, Pudding River, and Silver Creek watersheds were collected in in-stream features separated from the thalweg such as alcoves, channel edge sloughs, and off-channel pools found throughout the year opposed to seasonal features such as floodplains and ephemeral streams. These in-stream geomorphological features are important refugia for aquatic organisms (Lancaster & Hildrew 1993) as well as hydrologic sinks and sources for nutrients and contaminants (Constantinescu et al 2009). Contaminants move between the main stream and off-channel habitats by dispersion across the boundary layer, which is influenced by the geometry of the off-channel habitat and the velocity of the main stream flow (Uijttewaal et al 2001). Occurrence of pesticides in these off-channel habitats is a result of either direct input from land management practices adjacent to the feature via run-off, spray drift, or subsurface flow or mass transport from the main stream. In both cases, flow of the main channel influences the concentration of pesticides found in the off-channel habitat. For pesticides input directly into off-channel habitats, the rate of exchange increases with increased stream velocity. As such, streams with higher flow velocities such as the Abiqua Creek and Silver Creek sites can clear pesticides in off-channel habitats faster than slower streams such as Zollner Creek. In the case of pesticides that enter off-channel habitats from the main stream, streams with higher flow have a higher dilution capacity. As such, the amount of pesticides that may be transferred into an off-channel habitat would be less than in a lower flow stream with a diminished dilution capacity. While hydrologic characteristics can be useful in evaluating the potential dilution capacity, hydrology is insufficient to assess potential sensitivity to pesticide loading. Pesticide use practices in the surrounding watershed landscape must also be considered.

When evaluating exposure of ESA listed Pacific salmonid species or non-point source pollution related to pesticides, there is a great deal of uncertainty surrounding the spatial and temporal aspects of pesticide use. Measuring pesticides in surface water at the outflow integrates spatially all land use and associated pesticide use practices upstream within the watershed. The ecoregion framework, designed primarily to evaluate wildlife habitat, can also be used to investigate the relative differences in pesticide use and expected pesticide surface water concentrations at the watershed outflow.

Due to the limited availability of pesticide use data in the state of Oregon, land use/land cover information was used as a proxy for pesticide use based on labeled chemical uses. Differences in the land cover/land use associated with the level IV ecoregions found within the Pudding River subbasin are evident. For example, in ecoregion 3c land cover consists of forested riparian areas and upland vegetable, fruit, and field crops. Land cover associated with ecoregion 3d includes orchards, vineyards, pasture and a higher proportion of forested areas compared to ecoregion 3c. In ecoregions 4a and 4b, land covers consist primarily of forestry and recreation with some pasture lands being found in ecoregion 4a.

In the absence of more specific land use data, such as cropping practices, general descriptions of upland landuse and vegetation can be used evaluate expected landuse and the relative intensity of pesticide use. For the Pudding subbasin watersheds monitored in this study, the landuse patterns are consistent with the ecoregion descriptions. The Little Pudding and Zollner Creek watersheds which are located nearly entirely in ecoregion 3c, consist of 72% and 90% of watershed area defined as agricultural landuses respectively

(NASS 2011). These agricultural landuses represent a variety of vegetable, fruit and field crops. The Abiqua Creek and Silver Creek watersheds located predominantly in ecoregion 4a consist of 21% and 14% of watershed areas defined as agricultural landuses respectively. In conjunction with the lower percentages of agricultural areas within the Abiqua Creek and Silver Creek watersheds, 75% and 80% of the watershed areas are defined as forested compared to 5% and 4% of the Little Pudding and Zollner Creek watersheds.

Using an ecoregion-based approach, differences in landscape, vegetation, hydrology, and land use were used to assess the relative sensitivity of the Pudding River subbasin watersheds to pesticide surface water contamination. Our evaluation suggests that watersheds whose headwaters originate in ecoregion 3c appear to be more sensitive to pesticide contamination. This is likely due to higher pesticide inputs associated with the predominately agricultural landscape and lower stream flow associated with the low gradient. Consequently, the low order streams found in this ecoregion, including Zollner Creek and the Little Pudding River, have diminished dilution capacity. They also had the highest median and maximum pesticide concentrations. The upland Abiqua Creek and Silver Creek watersheds that are predominately located in ecoregions 3d, 4a, and 4b appear to be less sensitive to pesticide contamination. This is likely due to large portions of the watershed containing upland vegetation and land uses that do not receive significant pesticide inputs, as well as the majority of the surface waters in the Abiqua Creek and Silver Creek watersheds are located in ecoregions 3d, 4a, and 4b which are associated low order streams with higher flow due to a higher gradient of the stream channels as well as higher hydrologic input from increased precipitation (including snowmelt) at the higher elevations associated with these ecoregions. This higher level of hydrologic loading throughout the upper portions of the Abiqua Creek and Silver Creek watersheds lead to higher flows at the sampling locations and in areas draining agricultural lands leading to a higher dilution capacity of surface waters in these watersheds compared to the Little Pudding and Zollner Creek watersheds.

While intensity of pesticide use is a major determinant of pesticide surface water loading, in the absence of pesticide use data the ecoregion framework can provide means to quickly evaluate watersheds with regards to the potential for pesticide use and the sensitivity or receiving water to pesticide surface water loading. More detailed evaluation of landscape and hydrologic characteristics can further demonstrate the differences in the environmental setting of the monitoring locations and provide insight into the sensitivity of surface waters to pesticide surface water loading. For example, Johnson et al 2011 evaluated temporal trends in pesticide surface water concentrations in 15 surface waters draining HUC4 to HUC12 size watersheds located in California, Idaho, Oregon, and Washington that are located within the geographical extent of critical habitat defined for several ESUs of threatened and endangered Pacific salmonid species. While this study did not utilize the ecoregion framework to characterize the differences in the watersheds, the attributes evaluated by Johnson et al were consistent with those chosen for our assessment. Utilizing data obtained from the USGS NAWQA online database, we evaluated landscape characteristics, including drainage area and percentage of agricultural land uses within the drainage area, and the hydrologic parameters average daily flow and average stream width. These metrics were compared to median chlorpyrifos concentrations between 1992 and 2014 (USGS 2013). Chlorpyrifos was chosen as an example for this analysis due to the high detection frequency in the Pudding River subbasin and the long sampling record amongst the NAWQA sampling sites in addition to known risks to salmonid species and aquatic macroinvertebrates that comprise their food web. The NAWQA sampling sites were ranked in ascending order in terms of drainage area, percent agricultural area, average stream width, and median concentration of chlorpyrifos detections. Radioplots of ranked parameters (Figure 2.6) show the relationship between the landscape and hydrologic characteristics and median chlorpyrifos concentrations. NAWQA sampling sites representing larger drainages areas had greater average daily stream flows and greater average stream widths while sites with smaller drainage areas had lower average daily flows and lower average stream widths. The highest median chlorpyrifos concentrations were associated with sampling sites with lower flows and smaller stream widths. This could be, in part, due to the diminished dilution capacity of these streams compared to larger streams due to the differences volume of water associated with the sampling sites. Additionally, the highest median chlorpyrifos concentrations were associated with the sampling sites with the greatest percentage of agricultural area. This may be due, in part, to voluntary cancellation of all chlorpyrifos residential uses and stop sale in December 2001. The plots show that the highest median concentrations of chlorpyrifos are associated with the smaller streams and the larger streams with the highest percentages of agricultural land use areas within the watershed. The Thorton Creek NAWQA site is an exception in this evaluation. Thorton Creek had the lowest percentage of agricultural land use in the drainage area however it had the highest median concentration of chlorpyrifos detected. Closer examination of the Thorton Creek records show that detection frequency of chlorpyrifos at this site was 2.3% (n= 130) and all detections occurred prior to the halt of retail sale for residential use in December 2001. Similar patterns can also be seen in the ODEQ PSP monitoring in the Pudding River subbasin. The highest median chlorpyrifos concentrations have been found in the Little Pudding and Zollner Creek watershed which have greater percentages of agricultural areas and lower flows than the Abiqua Creek and Silver Creek watersheds.

In addition to characterizing watershed sensitivity to pesticide surface water loading, the ecoregion framework is also useful in characterizing salmonid habitat, including influences on life histories that, in turn determine life-stage specific spatial and temporal co-occurrence and exposure to pesticides. For example, fish assemblages within the Willamette Basin have been shown to be correlated with ecoregions (Waite and Carpenter 2000). Analysis of 24 streams within the Willamette Basin, including Abiqua Creek, Little Pudding River, and Zollner Creek, found that the abundance of salmonid species were greater in stream reaches typically found in Cascade ecoregions such as 4a and 4b. Based on this analysis, there is a greater likelihood that ESA listed salmonids found in the Pudding River subbasin would be found in surface waters of the Abiqua Creek and Silver Creek watersheds, predominately located in these ecoregions.

2.4.2 Pesticide and Salmonid Co-occurrence

Listed salmonid life history, as influenced by ecoregions, in conjunction watershed scale continuous pesticide surface water monitoring data should allow further refinement to evaluating the likelihood of co-occurrence, life-stage specific pesticide exposure patterns, and the potential harm to listed salmonids, and their food web.

The Pudding River subbasin contains critical habitat defined for the UWR Chinook and Steelhead ESUs. Additionally, each of the PSDs deployed in this study were located in stream reaches defined as critical habitat for at least one of the ESUs. The ESUs found in the Pudding River subbasin represent an interesting case. In the case of UWR Steelhead, spawning occurs between March and June and fry emerge between June and August. UWR Steelhead juveniles demonstrate a stream type life history pattern rearing in the headwater tributaries and upper portions of the subbasins in which they emerged for 1-4 years before migrating back to the ocean (NMFS 2011). In the Pudding River subbasin, spawning habitat is found in the Abiqua and Silver Creek watersheds making these more likely locations for juvenile steelhead rearing. As demonstrated by the PSD sampling data, pesticide concentrations found in these watersheds remained well below levels of concern throughout the course of the year. Portions of the Little Pudding River and Zollner Creek watersheds also contain stream reaches designated as critical habitat for the UWR Steelhead characterized rearing and migration habitats. While it is less likely that juvenile steelhead would spend prolonged periods of time in these reaches due to habitat quality, pesticide concentrations in these stream reaches while higher than those found in the Abiqua and Silver Creek watersheds remained below levels of concern throughout the year. The life history strategies of the UWR Chinook present a more complex scenario in evaluating the co-occurrence of salmonids and pesticides. UWR Chinook spawning occurs between August and October with fry emerging between December and March of the following year. UWR Chinook juveniles demonstrate a wide variety of life history strategies based on the timing of seaward migration following emergence (Schroeder et al 2007). Three life history strategies are defined by fry migrating to the upper reaches of the mainstem of the Willamette River and lower reaches of tributaries joining the mainstem to rear shortly following emergence. Juveniles employing these life history strategies rear in the upper reaches of the mainstem of the Willamette until starting migration toward the ocean in June, September or February within the year following emergence. Juvenile Chinook employing these life history strategies spend little time in the surface waters such as the Pudding River tributary watersheds monitored in this study and more time in habitats more like the Pudding River site. In these larger water bodies, pesticide concentrations were well below levels of concern throughout the course of the year. There are two other life history strategies employed by juvenile UWR Chinook which rely on rearing in the subbasins of the Upper Willamette River that contain the natal reaches. Juveniles that rear in the lower reaches of the watersheds from which they emerged begin their seaward migration in October of the year following emergence or March of the second year following emergence. For juvenile UWR Chinook in the Pudding River subbasin, spawning habitats can be found in the Abiqua Creek watershed, with rearing and migratory habitat found in the Pudding River as well as the Little Pudding River and Zollner Creek watersheds. For UWR Chinook juveniles that rear in spawning reaches during this time, pesticide concentrations remained orders of magnitude below levels of concern. While some juveniles might utilize critical habitat in the Little Pudding and Zollner Creek watersheds, the pesticide concentrations experienced may be higher than those found in the Abiqua Creek watershed but still fall below levels of concern throughout the time periods they may be found in these habitats.

2.5 Conclusions

Knowledge of the co-occurrence of pesticides, salmonids, and their food web, on or approaching a continuous basis, is necessary to adequately assess the likelihood of harm to listed salmonid ESUs. Continuous pesticide monitoring using PSDs provides a practical alternative characterizing patterns of pesticide exposure. Pesticide TWA concentrations, derived from PSD deployment over a period of a few weeks, provides useful information for the assessment of potential chronic effects. If pesticide concentrations are expected to fluctuate over the PSD deployment period, compressed TWA data can also be used to estimate acute effects of short term pulse, such as 96 hours. The LDPE PSDs employed in this study sequester semipolar and nonpolar pesticides representing a subset of the pesticides that are labeled for use in the Pudding River subbasin. Other PSD substrates have also been developed that sample more hydrophilic pesticides (Alvarez et al 2005, Tran et al 2007, Schäfer et al 2008, Harman et al 2012, O'Connell et al 2014).

Pudding River subbasin continuous monitoring results for chlorothalonil, metolachlor and trifluralin, identified as Pesticides of Interest (POI), and chlorpyrifos identified as a Pesticide of Concern (POC) by the Oregon interagency Water Quality Pesticide Management Team (WQPMT) (Riley et al 2011), show that chorpyrifos and trifluralin are most frequently detected, and all were found at levels significantly below the most sensitive aquatic life benchmark. These pesticides are also included in NMFS listed salmonid ESU Biological Opinions.

Historically, the Zollner Creek sampling site within the Pudding River subbasin has consistently reported some of the highest pesticide concentrations in the Pacific Northwest. This data has been used to raise water quality concerns associated with pesticide use in general without regard for hydrologic setting and other watershed characteristics that contribute to the sensitivity of Zollner Creek to pesticide loading. In addition, the Zollner Creek watershed is located in one of the most intensely farmed regions in the world. This 39 km^2 watershed contains more than 500 fields producing more than 40 different crops and is estimated to use ~100 pesticides. Using an ecoregion approach, the Zollner Creek watershed is characterized as a low gradient small stream with a high percentage of agricultural area. The low flow volume and low dilution capacity, along with high potential for pesticide use results in a greater sensitivity for pesticide surface water contamination. By contrast, Abiqua and Silver Creeks demonstrated low levels of pesticide contamination for both PSD and traditional grab sampling methods. Both watersheds contain a relatively small proportion of agricultural area, and Abiqua and Silver Creeks have much higher dilution capacity. This analysis demonstrates that the ecoregion framework may be useful in screening Willamette River Basin watersheds for sensitivity to pesticide surface water loading.

UWR Chinook and Steelhead life histories show the greatest life-stage specific opportunities for co-occurrence with pesticides in surface water based on the time spent rearing in freshwater habitats. While Zollner Creek shows some of highest pesticide concentrations, it contains less than 3.5% and 1.6% of the total critical habitat in the Pudding River subbasin for UWR Chinook and Steelhead, respectively. The Zollner Creek portion of the critical habitat defined for these ESUs is predominantly used for migration and rearing. Based on the varied life history strategies of the UWR Chinook, only a portion of juvenile salmonids spawned in the subbasin remain to rear, and do so primarily in the larger tributaries to the Willamette River such as the Pudding River. Consequently, the potential for a juvenile UWR Chinook ESU cohort to be exposed to the pesticides monitored in this study above a level of concern is low, with a very small proportion likely to co-occur with the highest pesticide concentrations measured in Zollner Creek. While juveniles of the UWR Steelhead ESU rear in freshwater environments for up to a year before outward migration, rearing generally occurs in headwater streams more closely associated with natal reaches, resulting in a low potential to be exposed to the pesticides monitored in this study above a level of concern. Zollner Creek, which contained the highest pesticide concentrations reported in this study, can be best classified as off-channel habitat for UWR Chinook or Steelhead juveniles rearing in the mainstem of the Pudding River during high flow periods generally occurring between October and April. During this period measured pesticide levels remained well below aquatic life benchmarks, as well as levels of concern for sublethal effects deemed protective of juvenile salmonids.

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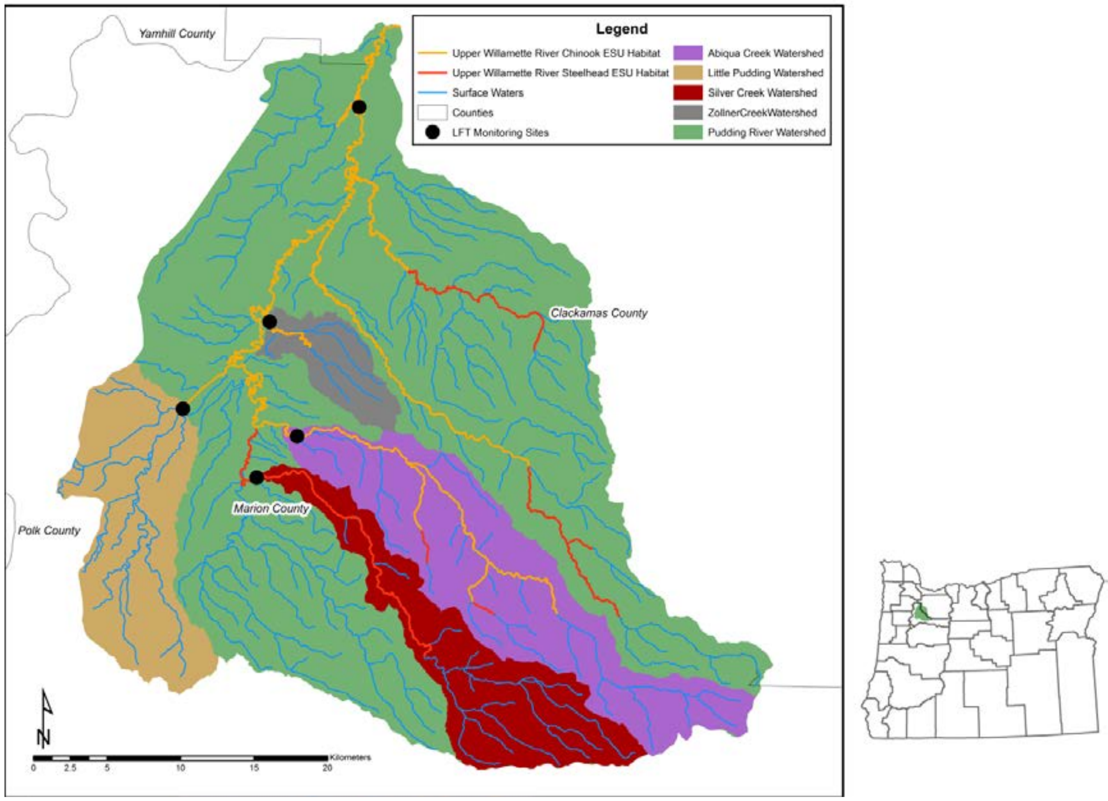


Figure 2.1. PSD sampling locations in the Pudding River subbasin and the watersheds draining to each sampling location. Black circles represent the PSD sampling locations. The surface water network is represented by blue lines and NMFS designated Critical Habitat for Upper Willamette River Chinook and Upper Willamette River Steelhead ESUs are shown in orange and red respectively.

Table 2.1. Pudding River subbasin watershed and stream flow characteristics.

Watershed	Watershed Area[a] (km^2)	Oregon Level IV Ecoregion[b] (% watershed area)					Land Use/Land Cover[c]			Stream Flow[d,e] (m^3/s)				
		3b	*3c*	*3d*	*4a*	*4b*	*% Ag*	*% Forest*	*% Developed*	*Mean*	*Min*	*10th Percentile*	*90th Percentile*	*Max*
Abiqua Creek	198	0	6.3	14.4	71.3	8	21	4	75	9.07	0.068	0.456	19.9	86.9
Little Pudding River	228	0	97	3	0	0	72	23	5	-	-	-	-	-
Pudding River	1369	4	47.8	17.6	28.5	2.1	53	9	38	38.7	0.878	1.64	95.9	221
Silver Creek	128	0	1.4	22.1	74.6	1.9	14	6	80	6.39	0.048	0.510	15.2	64.3
Zollner Creek	39.1	0.3	99.7	0	0	0	90	6	4	0.698	0.003	0.017	2.01	9.01

[a]Watershed areas obtained from NHDPlus catchment geospatial data layers (http://www.horizon-systems.com/NHDPlus/NHDPlusV2_data.php).
[b]Percentage of watershed area classified as given Oregon Level IV Ecoregion (USEPA 2013).
[c]Percentage of watershed area classified as land use/land cover type in USDA NASS 2011 Oregon Cropland Datalayer (NASS 2011).
[d]Average daily stream flow data for Abiqua Creek and Silver Creek derived from Marion Soil and Water Conservation District stream flow measurements (http://www.marionswcd.net/programs/water-programs/stream-flow-program/).
[e]Average daily stream flow data for Pudding River (Station ID: 14202000) and Zollner Creek (Station ID: 14201300) derived from USGS stream flow measurements (USGS 2013a).

Table 2.2. Physiochemical properties of current use pesticides detected by continuous PSD surface water monitoring in the Pudding River subbasin, June 2010-October 2011, and percent rank relative to all pesticides registered in Oregon.

Chemical	Molecular Weight[a] (g/mol)	% Rank MW[b]	log K_{ow}[a]	% Rank log K_{ow}[b]	Water Solubility[a] (mg/L)	% Rank Water Solubility[b]	K_{OC}[a] (mL/g)	Soil Degradation DT50[a] (days)	Vapor Pressure[a] (mPa)
Alachlor	269.77	0.352	2.89	0.521	240	0.622	335	14	2.9
Chlorothalonil	265.91	0.344	2.92	0.495	0.81	0.248	850	22	0.076
Chlorpyrifos	350.89	0.647	4.96	0.82	1.05	0.269	8151	50	1.43
Dacthal	331.96	0.577	4.3	0.747	0.21	0.21	2963	59	0.21
Endosulfan	406.93	0.806	3.62	0.825	0.32	0.184	11500	50	0.83
Endosulfan sulfate	422.92	-	3.66	-	0.48		5194	-	-
Metolachlor	283.8	0.389	2.9	0.611	120	0.672	530	90	1.7
Permethrin	391.3	0.775	6.1	0.936	0.2	0.168	100000	13	0.007
Trifluralin	335.28	0.59	5.34	0.883	0.221	0.179	15800	181	9.5

[a]Physiochemical properties from IUPAC Footprint database (University of Hertfordshire 2013)
[b]Percent rank represent the percentage of pesticides registered in the state of Oregon from the PICOL online database (Daniels and Boyer 2013) with physiochemical property values less than that of the pesticide.

Table 2.3. Current use pesticides detected (ng/L) by continuous PSD surface water monitoring in Pudding River subbasin watersheds, June 2010-October 2011.

Water-shed		Pesticide								
		Alachlor	Chlorothalonil	Chlorpyrifos	Dacthal	Endosulfan	Endosulfan Sulfate	Metolachlor	Permethrin	Trifluralin
	LOQ (ng/L)	0.69	0.68	0.0046	0.016	0.005	0.15	0.67	0.0023	0.0028
Abiqua Creek	# Detect (samples)	0 (15)	4 (15)	12 (15)	2 (15)	8 (15)	4 (15)	3 (15)	3 (15)	13 (15)
	Detect Freq (%)	0	27	80	13	53	27	20	20	87
	Minimum (ng/L)	-	0.97	0.0084	0.057	0.0058	0.59	5.25	0.016	0.02
	Median (ng/L)	-	2.16	0.20	0.073	0.69	0.83	6.40	0.025	0.06
	Maximum (ng/L)	-	5.04	0.78	0.090	4.26	1.05	10.6	0.109	0.72
Little Pudding River	# Detect (samples)	0 (13)	6 (13)	13 (13)	10 (13)	7 (13)	11 (13)	6 (13)	1 (13)	11 (13)
	Detect Freq (%)	0	46	100	77	54	85	46	8	85
	Minimum (ng/L)	-	1.78	0.18	0.050	0.074	0.41	53.2	-	0.04
	Median (ng/L)	-	2.10	4.02	0.29	2.44	1.12	61.2	-	0.23
	Maximum (ng/L)	-	9.34	15.9	0.47	17.1	3.17	89.0	0.017	1.2
Pudding River	# Detect (samples)	0 (18)	6 (18)	18 (18)	0 (18)	10 (18)	12 (18)	2 (18)	3 (18)	14 (18)
	Detect Freq (%)	0	33	100	0	56	67	11	17	78
	Minimum (ng/L)	-	1.19	0.23	-	0.22	0.30	3.01	0.003	0.012
	Median (ng/L)	-	1.82	0.94	-	1.56	0.74	4.65	0.013	0.11
	Maximum (ng/L)	-	3.01	7.62	-	5.86	2.30	6.29	0.033	0.48
Silver Creek	# Detect (samples)	1 (16)	2 (16)	15 (16)	2 (16)	7(16)	5 (16)	0 (16)	5 (16)	6 (16)
	Detect Freq (%)	6.3	12	94	13	44	31	0	31	38
	Minimum (ng/L)	-	2.19	0.087	0.14	0.026	0.33	-	0.021	0.006
	Median (ng/L)	-	3.18	0.18	0.16	1.27	0.42	-	0.050	0.009
	Maximum (ng/L)	32.9	4.17	0.92	0.19	2.31	0.63	-	0.703	0.016
Zollner Creek	# Detect (samples)	1 (17)	3 (17)	17 (17)	4 (17)	9 (17)	17 (17)	3 (17)	2 (17)	17 (17)
	Detect Freq (%)	5.9	18	100	24	53	100	18	12	100
	Minimum (ng/L)	-	1.23	0.69	0.046	0.32	2.75	167.5	0.013	0.21
	Median (ng/L)	-	1.68	3.82	0.13	3.40	4.99	176.0	0.026	0.93
	Maximum (ng/L)	1.36	6.72	12.5	0.32	6.56	28.3	327.7	0.038	15.4

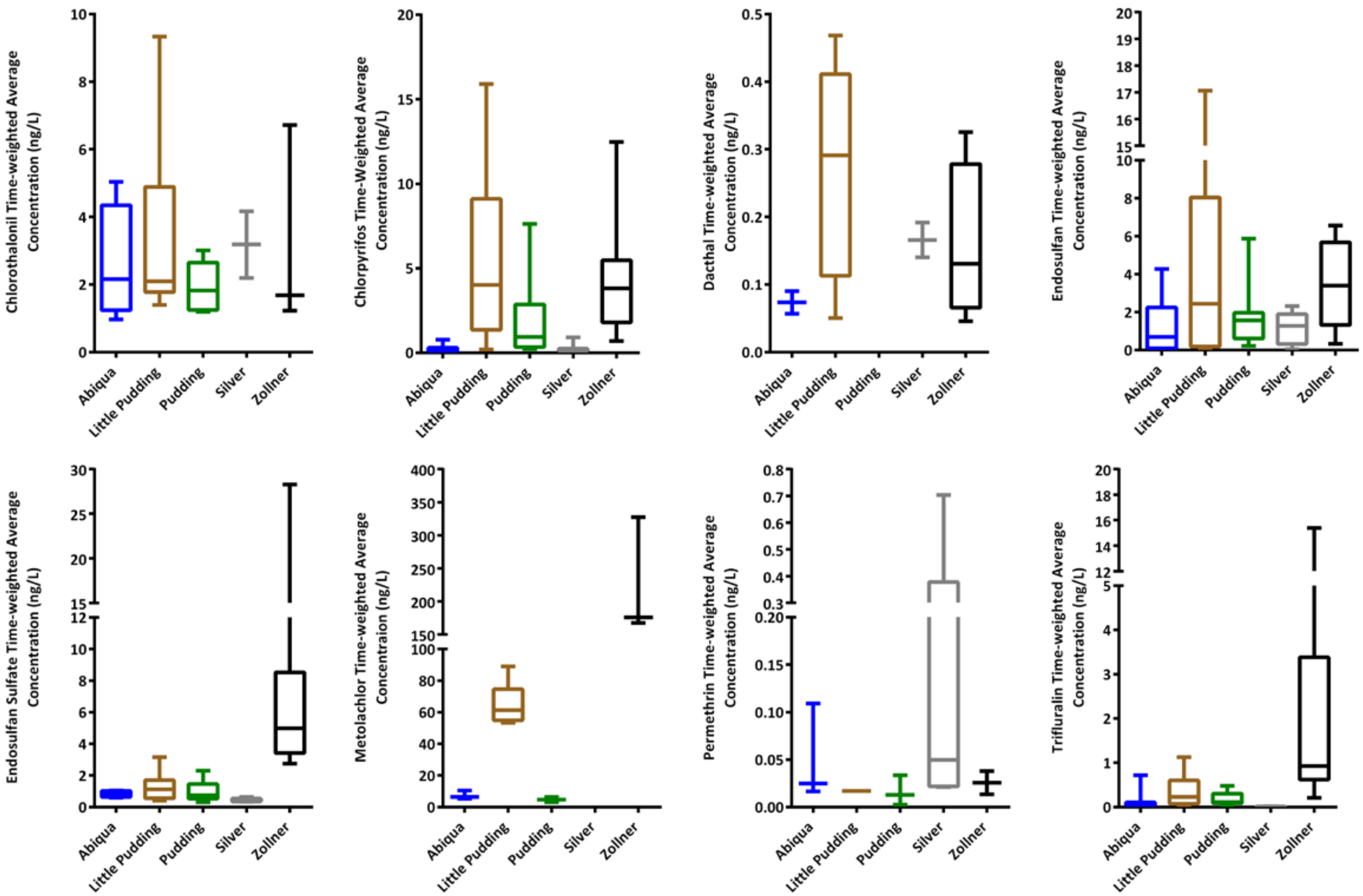


Figure 2.2. Box plots of median, 25th and 75th percentile TWA concentrations, with whiskers from the minimum to maximum, of current use pesticides detected by continuous PSD surface water monitoring in Pudding River subbasin watersheds, June 2010-October 2011.

Table 2.4. Historic record of grab sample surface water monitoring for pesticides detected (ng/L) by continuous PSD surface water monitoring in the current study; Oregon Department of Environmental Quality (ODEQ) 2006-2011, and United States Geological Survey (USGS) 1993-2008 and 2010-2012.

		Alachlor	Chlorothalonil	Chlorpyrifos	Dacthal	Endosulfan	Endosulfan Sulfate	Metolachlor	Permethrin	Trifluralin
		Pesticide								
ODEQ	LOQ (ng/L)	10	25	25	20	25	25	10	40	20
USGS	LOQ (ng/L)	2	35	5	2	4.7	16	13	5	2
Little Pudding (ODEQ)[a]	# Detect (samples)	0(24)	0(11)	10(41)	0(15)	0(20)	0(17)	27(32)	0(21)	0(17)
	Detect Freq (%)	0	0	24	0	0	0	82	0	0
	Minimum (ng/L)	-	-	12	-	-	-	15.4	-	-
	Median (ng/L)	-	-	32.5	-	-	-	26.7	-	-
	Maximum (ng/L)	-	-	58	-	-	-	231	-	-
Pudding (ODEQ)[a]	# Detect (samples)	0(21)	0(9)	2(40)	0(16)	0(17)	0(14)	10(21)	0(19)	0(16)
	Detect Freq (%)	0	0	5	0	0	0	47.6	0	0
	Minimum (ng/L)	-	-	19	-	-	-	9.6	-	-
	Median (ng/L)	-	-	34.5	-	-	-	17	-	-
	Maximum (ng/L)	-	-	50	-	-	-	33.8	-	-
Zollner (ODEQ)[a]	# Detect (samples)	0(24)	0(7)	8(40)	0(14)	0(15)	0(12)	23(23)	0(17)	0(13)
	Detect Freq (%)	0	0	20	0	0	0	100	-	-
	Minimum (ng/L)	-	-	23	-	-	-	17.1	-	-
	Median (ng/L)	-	-	44.5	-	-	-	73.4	-	-
	Maximum (ng/L)	-	-	177	-	-	-	1670	-	-
Zollner (USGS)[b]	# Detect (samples)	37(168)	0(52)	135(168)	27(168)	6(63)	62(63)	168(168)	0(168)	94(168)
	Detect Freq (%)	22	0	80	16	9.5	98	100	0	56
	Minimum (ng/L)	2.96	-	2.98	0.6	2.4	6.8	8	-	0.7
	Median (ng/L)	10.6	-	9.6	3.9	11.9	17.1	62.3	-	5.85
	Maximum (ng/L)	360	-	401	39	29.1	184	1780	-	22.1

[a]Results of ODEQ Pesticide Stewardship Partnership pesticide sampling conducted between 2006-2011 (ODEQ 2013).
[b]Results of USGS NAWQA sampling conducted between 1993-2008 and 2010-2012 (USGS 2013b).
Results for Abiqua Creek and Silver Creek sites are not included as all results were below limits of quantitation.

Table 2.5. EPA Office of Pesticide Programs Aquatic Life Benchmarks reported in (ng/L) for current use pesticides detected by continuous PSD surface water monitoring in Pudding River subbasin watersheds, June 2010-October 2011, for comparison to the maximum time weighted average (TWA) concentration and the maximum TWA concentration compressed to 96 hours, the typical acute benchmark exposure period.

Pesticides detected in the Pudding River Subbasin	EPA Office of Pesticide Programs Aquatic Life Benchmarks						PSD Monitoring Results	
	Fish		Invertebrate		Nonvascular Plants	Vascular Plants	Maximum TWA concentration (ng/L)	TWA concentration compressed to 96 hr (ng/L)
	Acute (ng/L)	Chronic (ng/L)	Acute (ng/L)	Chronic (ng/L)	Acute (ng/L)	Acute (ng/L)		
Alachlor	900000	187000	1250000	110000	1640	2300	32.9	172.7
Chlorpyrifos	900	570	50	40	140000	-	15.9	83.5
Chlorthalonil	5250	3000	1800	600	6800	630000	9.34	49.0
Dacthal	15000000	-	13500000	-	>11,000,000	>11,000,000	0.47	2.47
Endosulfan	50	110	300	10	428000	-	17.1	89.8
Endosulfan sulfate	1900	-	150000	-	-	-	28.3	148.6
Metolachlor	1600000	1000000	550000	1000	8000	21000	327.7	1720
Permethrin	395	51.5	10	1.4	68000	-	0.703	3.69
Trifluralin	20500	1140	280000	2400	7250	43500	15.4	80.8

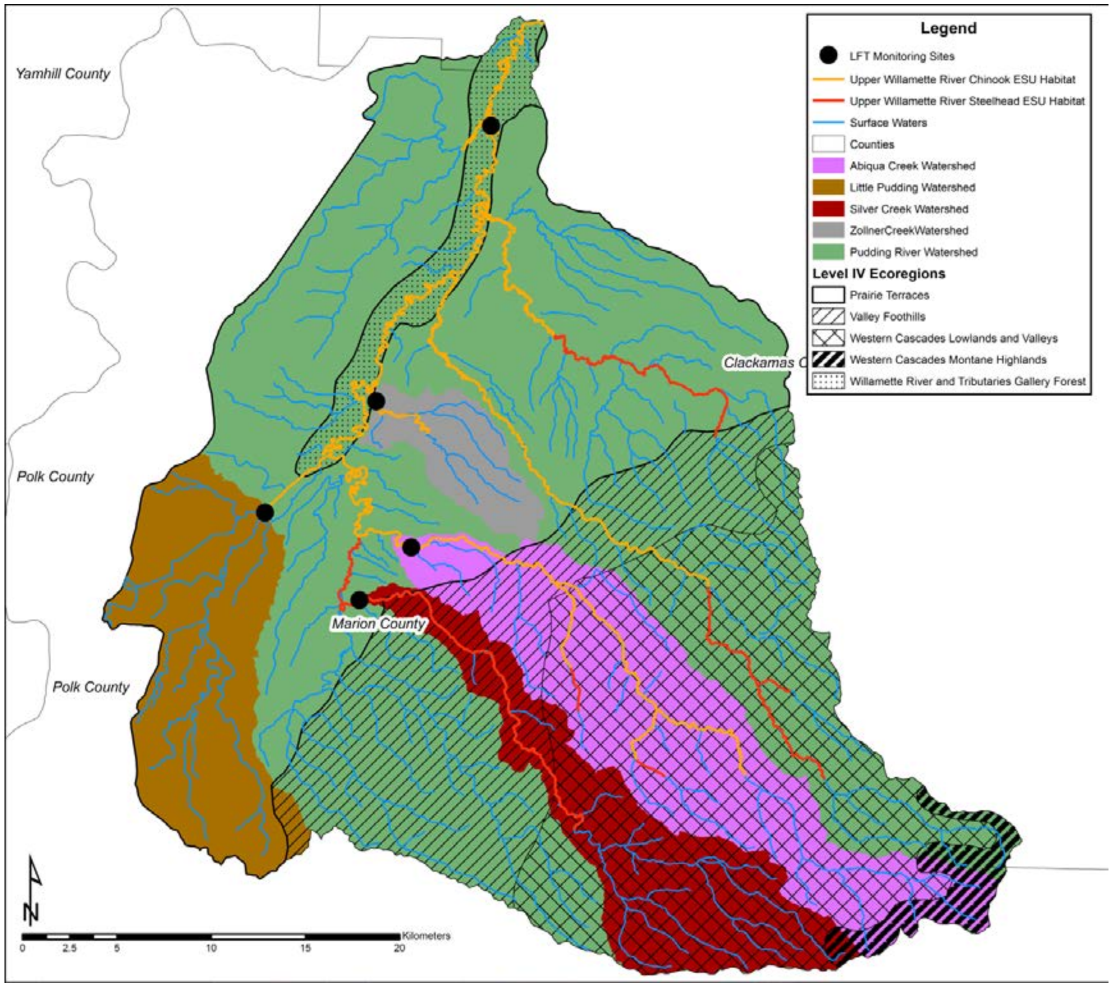
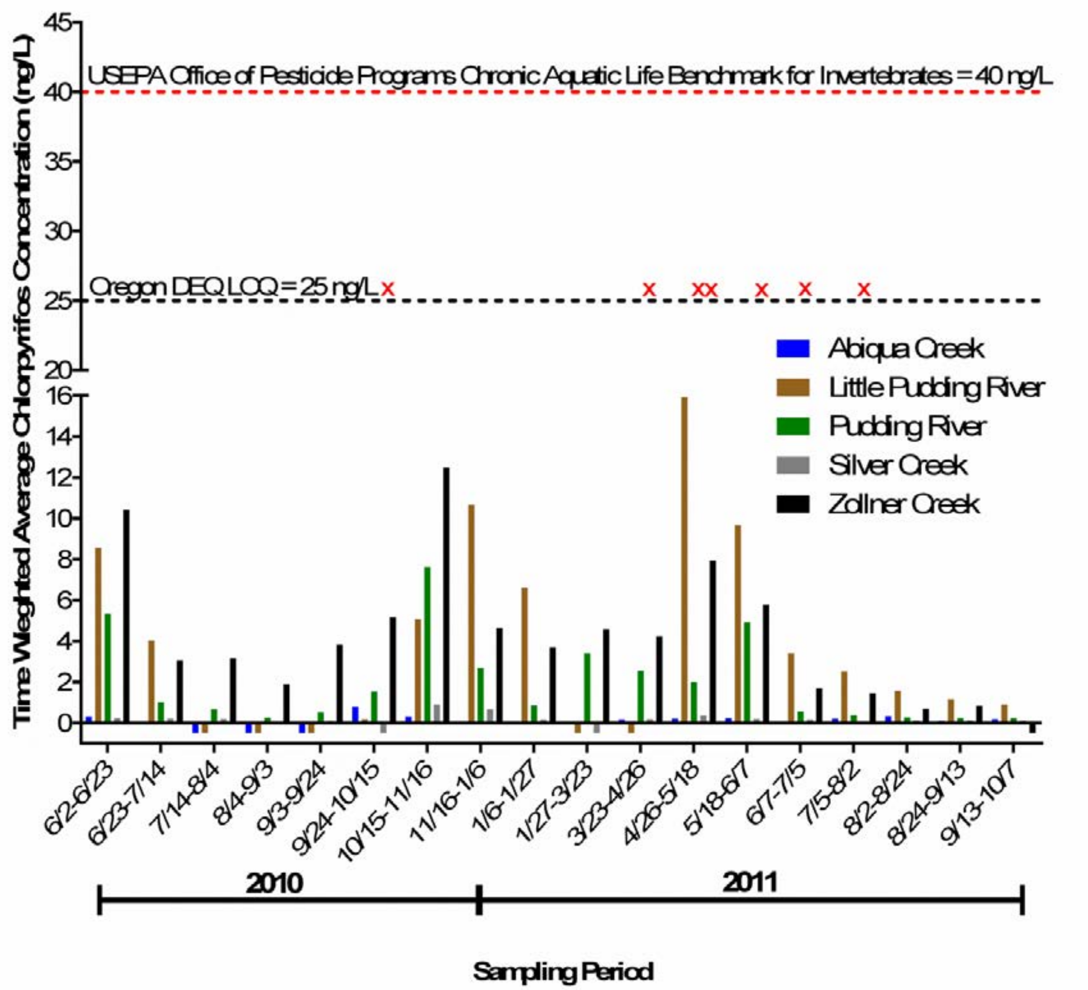


Figure 2.3. Map of the EPA defined Level IV Ecoregions located in the Pudding River subbasin.



USEPA Office of Pesticide Programs Chronic Aquatic Life Benchmark for Invertebrates = 40 ng/L
Oregon DEQ LOQ = 25 ng/L
Time Weighted Average Chlorpyrifos Concentration (ng/L)
Abiqua Creek
Little Pudding River
Pudding River
Silver Creek
Zollner Creek
6/2-6/23
6/23-7/14
7/14-8/4
8/4-9/3
9/3-9/24
9/24-10/15
10/15-11/16
11/16-1/6
1/6-1/27
1/27-3/23
3/23-4/26
4/26-5/18
5/18-6/7
6/7-7/5
7/5-8/2
8/2-8/24
8/24-9/13
9/13-10/7
2010
2011
Sampling Period

Figure 2.4. Plot of chlorpyrifos monitoring results in the Pudding River subbasin between June 2010 and October 2011. Concentrations are shown on the vertical axis in ng/L. Values below the horizontal axis show sampling periods were samples were not collected due to the disappearance of sampling devices. The black dotted line represents the LOQ (25 ng/L) of Oregon DEQ sampling conducted during the same time period as PSD samples were collected. A total of 6 Oregon DEQ sampling events occurred during the PSD monitoring campaign with levels below the limit of detection reported for each of these events. The red line represents the lowest EPA OPP Aquatic Life Benchmark (Chronic Invertebrate = 40 ng/L) established for chlorpyrifos in surface waters.

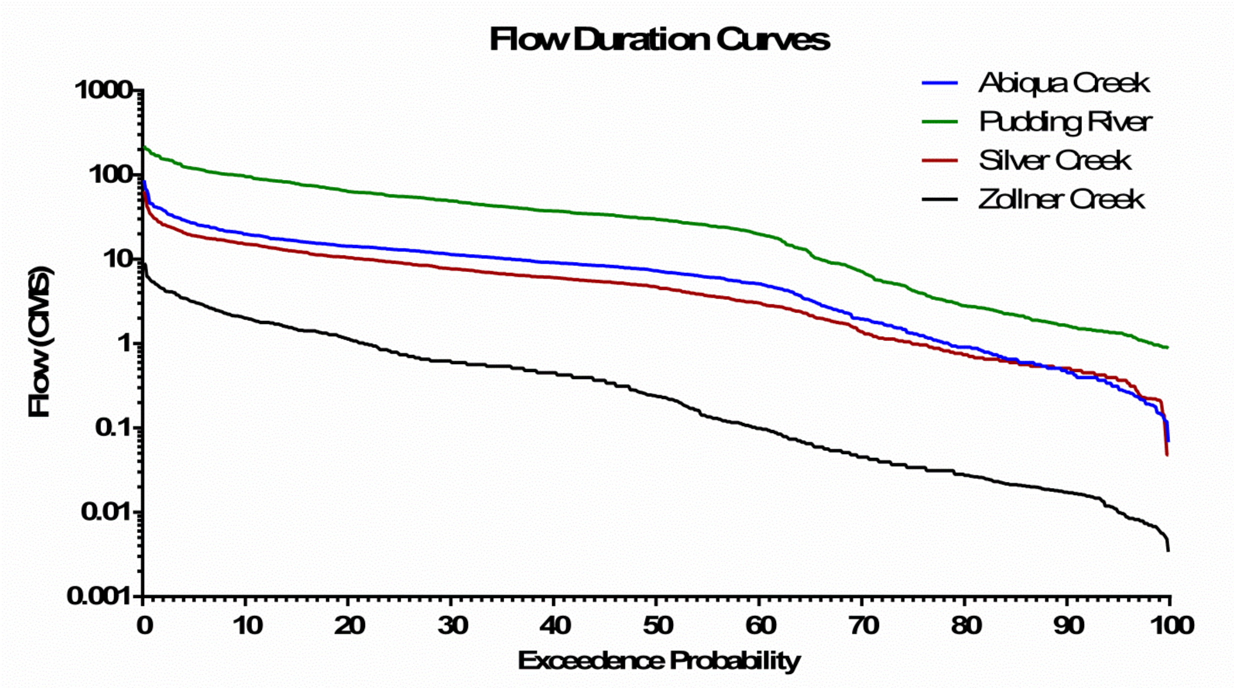
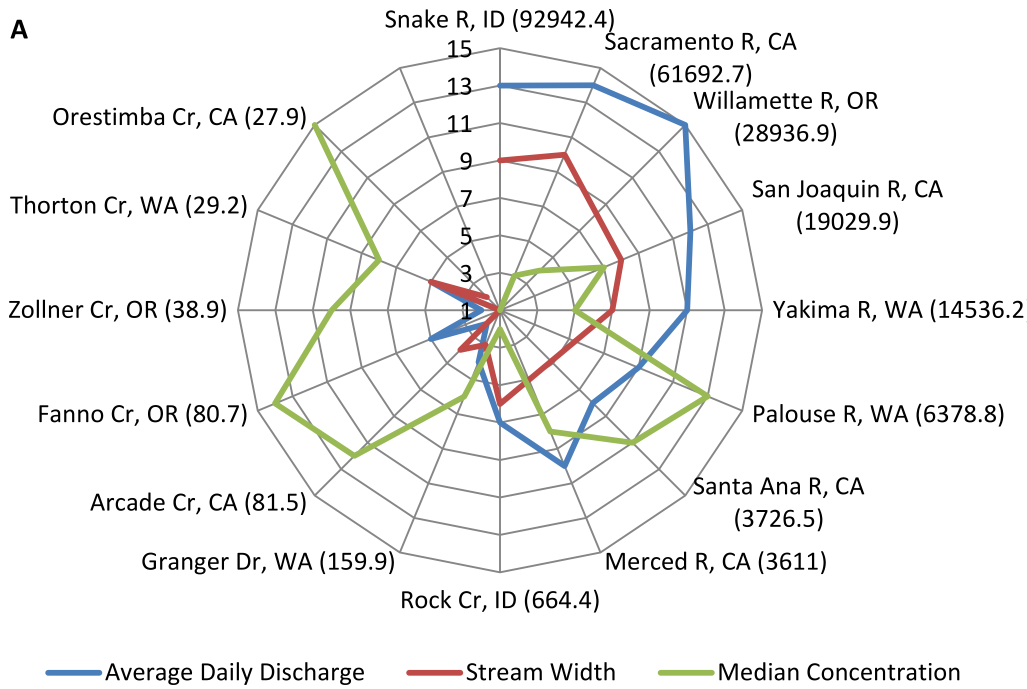


Figure 2.5. Flow duration curves of average daily stream flow for Abiqua Creek, Pudding River, Silver Creek, and Zollner Creek for water years 2010 and 2011. The flow duration curves represent the frequency distribution of flow magnitudes during the defined period.


A
Snake R, ID (92942.4)
Sacramento R, CA (61692.7)
Willamette R, OR (28936.9)
San Joaquin R, CA (19029.9)
Yakima R, WA (14536.2)
Palouse R, WA (6378.8)
Santa Ana R, CA (3726.5)
Merced R, CA (3611)
Rock Cr, ID (664.4)
Granger Dr, WA (159.9)
Arcade Cr, CA (81.5)
Fanno Cr, OR (80.7)
Zollner Cr, OR (38.9)
Thorton Cr, WA (29.2)
Orestimba Cr, CA (27.9)
15
13
11
9
7
5
3
1
Average Daily Discharge
Stream Width
Median Concentration

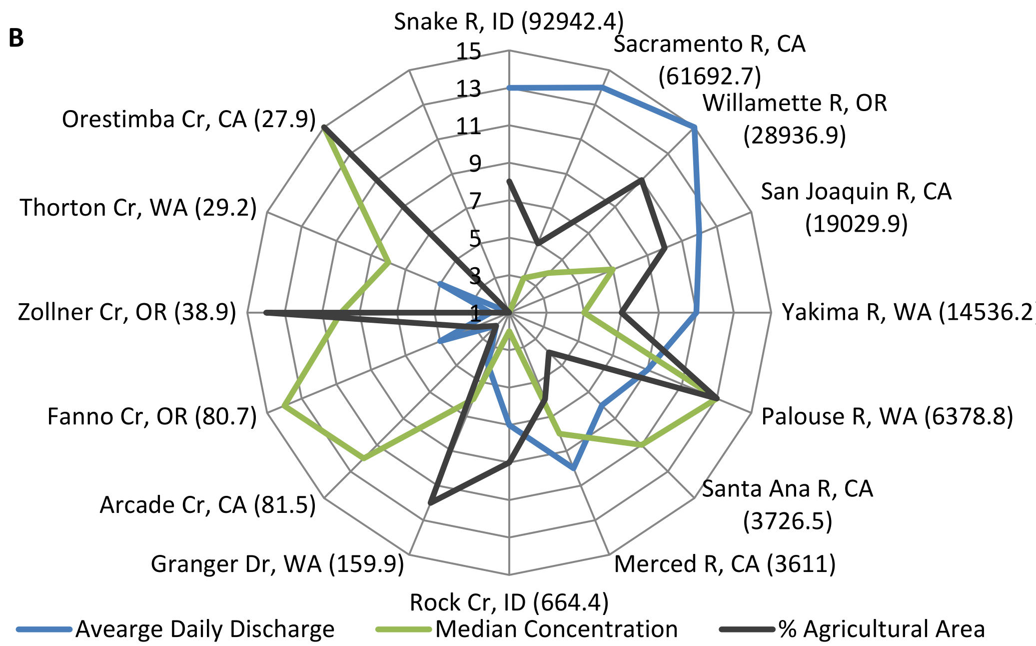

B
Snake R, ID (92942.4)
Sacramento R, CA (61692.7)
Willamette R, OR (28936.9)
San Joaquin R, CA (19029.9)
Yakima R, WA (14536.2)
Palouse R, WA (6378.8)
Santa Ana R, CA (3726.5)
Merced R, CA (3611)
Rock Cr, ID (664.4)
Granger Dr, WA (159.9)
Arcade Cr, CA (81.5)
Fanno Cr, OR (80.7)
Zollner Cr, OR (38.9)
Thorton Cr, WA (29.2)
Orestimba Cr, CA (27.9)
15
13
11
9
7
5
3
1
Avearge Daily Discharge
Median Concentration
% Agricultural Area

Figure 2.6. Radio plots of rank of median concentrations of chlorpyrifos detected in USGS NAWQA sampling in western US subbasins (Figures 2.6a and 2.6b). The median concentrations are ranked in ascending order with higher median concentrations appearing towards the outer ring of the plots. The sampling sites are arranged around the outside of the plot in descending order or drainage area contributing to the sampling site with the drainage area in km^2 in parentheses. Figure 5a shows the ranked median concentrations detected at NAWQA sampling sites in relation to average stream width ranked in ascending order and average daily flow ranked in ascending order. Figure 5b shows the ranked median concentrations detected at NAWQA sampling sites in relation to average daily flow ranked in ascending order and ranked percentage of the drainage area that is classified as agricultural.

Chapter 3- Hydrologic Assessment of the Zollner Creek Watershed using the Soil and Water Assessment Tool

3.1 Introduction

Nonpoint source (NPS) pollution, including sediment, nutrients and pesticides from agricultural lands and its impact on surface water quality is a major concern. Section 303(d) of the Clean Water Act requires states, territories and tribes to evaluate waterways in order to determine if waters meet established water quality standards. Recent integrated assessments of data reported to the US EPA indicate that 52% of the assessed rivers and streams nationally are considered threatened or impaired. Of these impaired rivers and streams, the probable cause of impairment was most commonly identified as agriculture. The states, territories or tribes are required to develop Total Maximum Daily Loads (TMDLs) which specify a level of pollutant that the listed water can receive without exceeding the established water quality standard. In the case of NPS pollution from agricultural landscapes, the sources, timing, and level of pollutants entering a receiving water can be highly variable due to climatic variables, physical landscape characteristics, and agricultural management practices. As such, dynamic ecohydrological models have become useful tools in developing an understanding of the link between agricultural landscape practices and impacts on surface water quality. Many models have been developed to evaluate the effects of NPS pollution at the watershed scale and have been reviewed by Borah and Bera (2004).

In addition to the use in the development of TMDLs, watershed scale ecohydrologic models have been shown to be useful tools in assessing the effects of conservation and mitigations measures on water quality. In 2003, the USDA began the Conservation Effects Assessment Program (CEAP), a national program implemented to develop a mechanistic understanding of the effects of conservation practices on water quality. Due to the variability to NPS pollution and the limited availability of monitoring data, models have become useful tools in evaluating the effects of conservation practices. Additionally, the implementation of conservation practices can be costly. Models provide means to evaluate the potential impacts of conservation practices based on site specific conditions prior to implementation in order to identify efficacious methods and placement.

The Soil and Water Assessment Tool (SWAT) is a watershed scale ecohydrologic model developed by the USDA ARS to evaluate the impact of land management practices on water yield and quality. SWAT has been applied to assess water balance and NPS pollution issues at the watershed scale both nationally and internationally as shown in two extensive reviews of SWAT applications and developments (Gassman et al 2007, Douglas-Mankin et al 2010). The SWAT model has been utilized in TMDL development studies (Horn et al 2004) and has been incorporated in the US EPA TMDL development tool BASINS (Di Luzio et al 2002). SWAT is also one of two models accepted for use in the USDA Conservation Effects Assessment Project (CEAP), a national program implemented to develop a mechanistic understanding of the effects of conservation practices on water quality (Heathman et al 2008). Studies comparing the models accepted in CEAP studies have identified SWAT as the preferable model based on model performance in simulating streamflow and atrazine loss (Heathman et al 2008) and streamflow, sediment loss and nutrient loss (Parajuli et al 2008). SWAT has been shown to be a beneficial tool is the evaluation of mitigation measures to reduce the impacts of NPS pollution on water quality. Several studies have utilized GIS technology and NPS pollution indices to identify the spatial distribution of potential source areas and possible mitigation strategies (Polyakov et al 2005, Tomer et al 2003, Tomer et al 2009, Qui 2009). While these methods have been successful, they only provide a static evaluation of potential NPS loading based on empirical relationships between landscape characteristics and loading. Models such as SWAT simulate the processes that dictate NPS loading and provide a dynamic characterization of NPS loading in a spatial and temporal context (Krysanova et al 2008). Moving beyond the static evaluation to a more dynamic characterization based on processes rather than indices can provide a more refined evaluation of optimal mitigation strategies. The implementation of mitigation measures, often referred to as best management practices (BMPs) can be costly, and the overall impact on water quality is often dependent on the placement of BMPs at the watershed scale (Maas et al 1985, Jha et al 2009, Gitau et al 2004, Arabi et al 2008). As such models such as SWAT are useful in the evaluation of potential mitigation measures for two main reasons. First, due to their ability to characterize the spatial and temporal variability in factors contributing to NPS loading including landscape characteristics, weather patterns and land management practices models can be used to identify sensitive areas that are more susceptible to NPS loading (Gitau et al 2004, Tripathi et al 2003, Jha et al 2009). This can be beneficial in the placement of mitigation measures in order to achieve the greatest impact on water quality at the watershed scale (Maas et al 1985, Tripathi et al 2003). Second, models can be used to identify the mechanistic processes contributing to NPS loading and evaluate different BMP strategies to determine optimum strategy. This allows stakeholders to identify conservation practices with the greatest impact prior to making the financial commitments necessary to implement a BMP strategy (Arabi et al 2008, Gitau et al 2004).

SWAT has been utilized to evaluate critical source areas and BMP placement at the watershed scale, focusing mainly on sensitive subbasins within the watershed studied. These studies mainly evaluated BMP strategies to mitigate sediment (Zhang and Zhang 2011, Tripathi et al 2005, Bracmort et al 2006) and nutrient (Tripathi et al 2005, Santhi et al

2001, Jha et al 2009, Bracmort et al 2006) loading within the critical subbasins. Limited studies have focused on BMP strategies to mitigate pesticide loading at the watershed scale (Zhang and Zhang 2011, Holvoet et al 2007). SWAT has also been shown to be successful in the evaluation of the effects of BMP strategies at the field scale (Gitau et al 2008, Gitau et al 2004, Daggupatti et al 2011). These studies focused on optimization of BMP strategies to reduce sediment and nutrient loading from individual farms as well as the cost of implementation. In all of these studies, SWAT was utilized to evaluate the relative change in contaminant load at the measurement point between different management and BMP strategies. Due to the inherent uncertainties associated with watershed scale modeling, it is unreasonable to assume that modeling can predict exact changes in contaminant loading (Jakeman and Letcher 2001). However as the simulations are based on the mechanistic processes that dictate contaminant loading which are influenced by the physical and chemical characteristics of the landscape, they can provide evidence of the potential efficacy of actually implementing the BMP strategies in real settings.

For this study, SWAT was applied to the Zollner Creek watershed, a small agricultural watershed in the Willamette Valley, OR. SWAT was chosen to model the hydrology of the watershed based on the widespread application of the model both nationally and internationally (Gassman et al 2007), the availability of a GIS model interface for model parameterization (Olivera et al 2006) and the existence of a SWAT user community. The Zollner Creek watershed was chosen for this study based on known NPS pollution of surface waters in the watershed. In 2008, the Oregon Department of Environmental Quality (ODEQ) developed a TMDL for the Molalla-Pudding River basin which includes the Zollner Creek watershed. TMDLs for Zollner Creek were established for temperature, sediment, nutrients, metals and the two legacy pesticides dieldrin and chlordane. While TMDLs were only developed for dieldrin and chlordane, monitoring conducted to develop the TMDLs found many current use pesticides as well.

Zollner Creek was monitored for pesticides from 1993-2008 by the USGS as part of the National Water Quality Assessment Program (NAWQA), with a monitoring station located near the confluence with the Pudding River serving as a long term trend site. USGS monitoring during this time found high detection frequencies of a wide variety of pesticides and high levels of pesticides in surface waters of the watershed. Starting in 2005, the ODEQ performed water quality monitoring the Pudding River basin including monitoring sites in the Zollner Creek watershed as part of the Pesticide Stewardship Partnership (PSP). The goal of the PSP is to monitor pesticides in surface waters in the state of Oregon in order to establish an understanding of the long term trends of pesticide levels in surface waters. ODEQ then presents this data to stakeholders in the areas monitored in order to encourage voluntary measures to reduce surface water contamination. ODEQ PSP monitoring, like USGS NAWQA monitoring found high frequency of detections of current use pesticides in the Zollner Creek watershed as well as detection levels higher than those found in other surface waters monitored in the PSP program. Additionally, the USGS has established a stream gauge at the monitoring location near the mouth of Zollner Creek providing stream flow data necessary for SWAT performance evaluation and calibration.

The goal of this study is to characterize the hydrology of the Zollner Creek watershed using the SWAT model. In order to most accurately characterize the watershed hydrology, several model parameterizations were evaluated in order to assess the applicability of commonly utilized input datasets to a small, diverse agricultural watershed and the impact of more detailed model input data derived from local knowledge of the system. Using the most accurate representation of the watershed, we evaluated the water yields of the individual subbasins within the watershed to identify areas that exhibited a strong hydrologic connection to surface waters within the Zollner Creek watershed and potential characteristics that lead to NPS loading.

3.2 Methods and Materials

3.2.1 Study Area

The Zollner Creek watershed is located in Marion County, OR and is part of the Molalla-Pudding Watershed (HUC8: 17090009) (Figure 3.1). The watershed is 3885 ha of which approximately 91% is utilized for agriculture. Examination of the USDA National Agricultural Statistics Service (NASS) 2011 Oregon Cropland Data Layer indicates the heterogeneous nature of cropping practices in the watershed as there are 43 different agricultural land uses designated in the area. Seed/sod grass are the predominant commodities grown in the watershed (30.4% of watershed area) with a variety of vegetable crops (20.3% of watershed area) and grain crops (13.4% watershed area) accounting for much of the remaining watershed area. The Zollner Creek watershed is a fairly flat area located predominately on the floor of the Willamette Valley with its headwaters located in the higher elevations in the eastern portion of the watershed approaching the foothills of the Cascade Mountains. The elevation in the watershed ranges from 37 to 149 m above sea level with the average elevation being 69 m above sea level. Weather in the Willamette Valley is characterized by cool, wet winters followed by warm, dry summers (Ulrich & Wentz 1999). The Zollner Creek watershed receives on average 966 mm of rainfall annually.

3.2.2 SWAT Model Description

SWAT is a watershed scale model developed by the USDA Agricultural Research Service to evaluate the impacts of land management practices on water, sediment and chemical yields. SWAT is a direct outgrowth of development of the Simulator for Water Resources in Rural Basins (SWRRB) model and includes features of several USDA ARS field scale models including Chemicals, Runoff and Erosion from Agricultural Management Systems (CREAMS) (Knisel 1980), Groundwater Loading Effects on Agricultural Management Systems (GLEAMS) (Leonard et al 1987) and Erosion Productivity Impact Calculator (EPIC) (Williams 1990). SWAT is a physically based continuous model that operates on a daily time step. SWAT includes eight major components including weather, hydrology, soils, plant growth, nutrients, pesticides, pathogens, and land management (Arnold et al 1998, Neitsch et al 2005). Model development and applications of SWAT have been reviewed by Gassman et al (2007) and more recent applications and developments of SWAT have been reviewed by Douglas-Mankin et al (2010).

For any application of SWAT, it is imperative to accurately simulate the hydrologic cycle of the watershed being studied as the hydrologic component of the model is the driving force behind all watershed processes simulated by the model. Hydrologic processes simulated by SWAT include precipitation, evapotranspiration, surface run-off, infiltration, percolation, channel transmission losses, channel routing, subsurface lateral flow and groundwater flow (Neitsch et al 2005). In order to simulate these processes, SWAT partitions the watershed into subbasins based on landscape topography and flow accumulation. The subbasins are further divided into hydrologic response units (HRUs), which are lumped land areas that are unique combinations of land use/land cover, soil type and slope. SWAT defines HRU distribution by layering the land use/land cover, soils and elevation data sets required as model inputs and using a threshold defined by the model user to determine the percentage of watershed area of land use/land cover, soils or slope that is necessary to define a HRU. For this study, the HRU definition thresholds were set to 0% in order to account for the heterogeneous cropping practices in the Zollner Creek watershed. Terrestrial hydrologic processes are simulated in the HRUs and water yield from each HRU are routed to channelized flow in the subbasin and SWAT routes the channelized flow to the watershed outlet.

For this study, ArcSWAT version 2009.93.7b was used to simulate the hydrology of the Zollner Creek watershed. ArcSWAT is an ArcGIS interface for the SWAT model that has been developed to derive SWAT input variables from readily available GIS data sources (Olivera et al 2006). ArcSWAT is available for download from the USDA Agricultural Research Service at the Grassland, Soil and Water Research Laboratory in Temple, Texas (http://swatmodel.tamu.edu/).

3.2.3 Model Parameterization

SWAT requires topographic, land use/land cover, soil and climatic data to simulate watershed processes. Climatic data can be simulated by the weather generator built into the model, however real data can be used to more accurately simulate the system. The topographic, land use/land cover and soils data required by the model can be found as free, readily available GIS data sets. The ArcSWAT user interface was used to organize the GIS datasets and populate model inputs using the information contained in GIS datasets. For this study several model parameterization scenarios were evaluated in which several input data sets were varied with increasing levels of local knowledge while the topography, soils and climatic parameters other than precipitation were held constant. The data sets that were held constant are described below followed by the description of the variations in each of the parameterization scenarios.

Topographic data in the form of a digital elevation model (DEM) is required by the model in order to delineate watershed and subbasin boundaries, stream routing and other physical watershed parameters including slope. For this study, a 10 m resolution DEM for the Zollner Creek watershed was obtained from the USGS Seamless Data Warehouse. In addition to utilizing the DEM to delineate stream routing, the USGS National Hydrographic Data Set for the Molalla-Pudding River Basin (HUC8:17090009) was used to identify the stream channels in the Zollner Creek watershed during the watershed delineation process. The Zollner Creek watershed contains one significant impoundment located on the main channel of Zollner Creek upstream of the confluence with its major tributary Bochsler Creek. The dam is 6m high creating a reservoir covering nearly 7.5 ha when filled. Due to the fact that detailed reservoir release rates were not available, the reservoir was modeled using the Average Annual Release method within the SWAT model with minimum daily outflow for all months set to 0.03 m^3/s per Oregon Department of Fish and Wildlife requirements for the construction of the dam.

Soils data for the Zollner Creek watershed were derived from the USDA Natural Resource Conservation Service Soil Survey Geographic database (SSURGO) data set for Marion County, OR. The SSURGO data set provides a geospatially referenced database of soil horizons identified in county level soil surveys. Data included in the SSURGO data set utilized by SWAT are the soil profile depth, moist bulk density, available water capacity of each horizon layer, saturated hydraulic conductivity and soil texture.

SWAT requires daily weather inputs including precipitation, maximum and minimum temperature, wind speed, solar irradiation, and relative humidity. Daily values of wind speed, solar irradiation and relative humidity measurements were obtained from an AgriMet weather station located in Aurora, OR located approximately 15 miles north of the centroid of the Zollner Creek watershed. Daily maximum and minimum temperature data were obtained from the NOAA National Climatic Data Center (NCDC) for a weather station located in Silverton, OR (COOPID: 357823) located approximately 5 miles southwest of the centroid of the Zollner Creek watershed.

For the different SWAT simulation scenarios evaluated, the SWAT model was parameterized with increasing degrees of local knowledge obtained through survey of the watershed and interaction with local growers, agronomists and agency personnel. Refinement of model inputs focused on accurately characterization of land use/land cover data, localized precipitation data, stream channel dimensions, and understanding of engineered features found in the watershed including tile drainage and reservoirs. The scenarios evaluated were parameterized as follows (summarized in Table 3.1):

Scenario A: In this scenario, the SWAT model was parameterized using commonly used land use/land cover and precipitation datasets. The land use/land cover data used for this scenario was the Zollner Creek watershed extracted from the 2011 Oregon Cropland Data Layer produced by the USDA National Agriculture Statistics Service. The data layer is 56 m resolution, georeferenced raster data set that categorizes land use/land cover using imagery from the Thematic Mapper instrument on the Landsat 5, the Enhanced Thematic Mapper on the Landsat 7 and Advanced Wide Field Sensor on the Indian Remote sensing RESOURCESAT-1. Imagery used to develop the data set was collected between October 2008 and August 2009. Land management practices for crops identified in the NASS data layer were scheduled using the heat unit approach in SWAT. Planting and harvesting dates for vegetable crops were estimated using Oregon State University Extension Service production guides when guides were available for crops (http://groups.hort.oregonstate.edu/content/vegetable-production-guides-0), otherwise SWAT default parameters were used. For seed/sod grass land uses, planting and harvesting dates were obtained from a degree day crop development model (Griffith & Nelson 2001). All other management operations were defined by SWAT default values.

Precipitation data is one of the most important input variables for hydrologic models. Precipitation can be highly variable in space and time and as such it is important in hydrologic modeling to use input data that can most accurately represent this variability across the watershed being modeled. One source of precipitation data is rain gauge data obtained from rain gauge networks located in or near the watershed being modeled (Sexton et al 2010). A widely used source of rain gauge data is the NCDC rain gauge network and many SWAT simulations utilize these precipitation measurements from the NCDC weather stations located in or near the study area (Olivera et al 2006, Tong & Naramngam 2007, Heathman et al 2009, Peschel et al 2006, Rossi et al 2008). For this scenario, daily precipitation measurements obtained from the NCDC for the Silverton, OR station (COOPID: 357823).

Scenario B: This scenario was designed to evaluate the effect of daily precipitation inputs on SWAT stream flow simulations. In watersheds where there is not a dense rain gauge network or few NCDC rain gauges within the watershed boundaries, such as the Zollner Creek watershed, next-generation radar (NEXRAD) estimations of precipitation can be useful model inputs. NEXRAD provides spatially continuous estimations of precipitation at 4x4 km^2 resolution which can help account for the spatial variability in precipitation in the absence of adequate rain gauge measurements (Sexton et al 2010). Several researchers have evaluated the use of NEXRAD precipitation data in SWAT applications (Sexton et al 2010, Tuppad et al 2010, Kalin et al 2006). The use of NEXRAD data may help to account for spatial variability, however the input of NEXRAD data into SWAT requires more time and effort than using rain gauge measurements. Daily gridded precipitation data based on radar and precipitation measurements was obtained from the National Weather Service Advanced Hydrologic Prediction Service (AHPS). The daily precipitation obtained was in the form of shapefiles identifying the centroids of the 4x4 km^2 grids in the Hydrologic Rainfall Analysis Project (HARP) coordinate system. The AHPS shapefiles contained the total daily precipitation measured in each HARP grid. AHPS daily precipitation data was available from 2005 to present. A total of 2555 shapefiles were downloaded from the AHPS and the daily precipitation data was extracted for points located within the Zollner Creek watershed boundary delineated by SWAT and formatted for input into the SWAT model. Since AHPS data prior to 2005 were not available, daily precipitation data from the Silverton NCDC station was used to amend the data set for the model warm up period. All other model parameters were set as described in Scenario A.

Scenario C: In this scenario, the effect of incorporating local stream channel dimension measurements on SWAT estimated flow. The SWAT model utilizes Manning's equation for unified flow which calculates flow based on the cross sectional area and hydraulic radius of the stream channel at a given water depth. The SWAT model assumes that the stream channel is a trapezoidal shape with the channel side slopes being 0.5 with the channel bottom width calculated from the required input parameters of bank full width and depth. In the previously described parameterization scenarios, the channel bank full width and depth parameters were calculated from the 10m resolution DEM during the ArcSWAT watershed delineation process. A stream survey was conducted in conjunction with the Marion Soil and Water Conservation District in the Zollner Creek watershed during which the bank full width and depth were measured at 44 points within the watershed. During the watershed delineation process, subbasin outlets were added to define the measured channel dimensions for the given portions of stream reaches in the watershed. This resulted in the delineation of 36 subbasins within the watershed of which the bank full width and depth were defined for 28 based on the stream channel survey and the remaining 8 subbasins retained the DEM derived width and depth parameters. All other parameters were the same as described for Scenario B.

Scenario D: This scenario was designed to evaluate the influence of land use/land cover data refined with the input of local growers and agronomists. Further evaluation of the NASS CDL revealed that some of the crops identified within the Zollner Creek watershed by the data set were not grown in the watershed. In order to refine the land use/land cover data input for the model, aerial imagery of the basin was obtained from the FSA National Agriculture Imagery Program (NAIP) for the 2009 and 2011 growing seasons. Field shapes displayed a high degree of fidelity between the 2009 and 2011 aerial images. The boundaries of individual fields were digitized using ArcGIS software. In order to accurately characterize the land use/land cover found in the watershed during the model evaluation period, local growers and agronomists that advised growers in the Zollner Creek watershed were consulted to identify the land use/land covers for each of the fields delineated from the NAIP aerial imagery. Through collaboration with local sources, nearly the land use/land cover was defined for nearly 70% of the watershed area. For fields which collaboration with local sources did not result in identification of the land use/land cover data, the land use/land cover within each field was defined as the land use/land cover identified by the NASS CDL if the majority of the field area was classified as the same crop type. Of the remaining 30% of the watershed area, land use/land cover data for 22% of the watershed area was defined by these methods. For the remaining 8% of the watershed area the land use/land cover data was unable to be determined by these means and were modeled as generic agricultural areas. All other SWAT model parameters were the same as described in Scenario C.

Scenario E: In this scenario, the effect of tile drainage on watershed hydrology was evaluated. Based on interaction and collaboration with local resources in the watershed, tile drainage was identified as a prevalent engineered feature in the watershed. The extent of tile drainage installed in the watershed however is unknown. In order to evaluate the impact of tile drain features on watershed hydrology, a probabilistic analysis was performed by randomly applying tile drains to HRUs accounting for varying percentages of the watershed area ranging from 10% to 70%. In an attempt to ensure the application of tile drainage features on a mechanistic basis to HRUs where engineered drainage would most likely be installed, criteria were defined for HRU selection. Following criteria outlined in the Simiplified SWAT approach (Peranginangin et al 2013), tile drainage features were applied to HRUs with soil classes described as “poorly drained” in the SSURGO database with HRU slope between 0-1%. HRUs that met these criteria however only accounted for 20% of the watershed area, so the criteria were expanded in order to evaluate scenarios applying tile drainage to more of the watershed area. To select HRUs that accounted for up to 40% of the watershed area, the criteria were altered to include HRUs of all soil classes with slopes between 0-2%. HRUs meeting these expanded criteria accounted for 54% of the watershed area. In order to select HRUs for the 60% and 70% scenarios, the criteria were expanded to include “poorly drained” soils of 0-5% and all other soil classes with slopes from 0-2%. HRUs meeting these criteria accounted for 72% of the watershed area. Tile drain parameters were edited to reflect general values outlined in the Simplified SWAT approach due to the lack of knowledge of the specifications of tile drainage systems installed in the Zollner Creek watershed. All other SWAT model parameters were the same as described in Scenario D.

SWAT was used to simulate the hydrology of the Zollner Creek watershed from 2003 to 2011 on a daily time step. Surface run-off was simulated using the Daily SCS Curve Number method, evapotranspiration was simulated using the Penman-Monteith method and channel routing was simulated using the variable storage method. The simulations for the years of 2003 and 2005 were considered a “warm up” period to establish the state of the system. SWAT flow estimations for the years of 2006 through 2008 were used to perform a sensitivity analysis in order to identify parameters and processes that effect surface water flow. Simulations for the years of 2006 through 2008 were also used in the calibration process in order to optimize hydrologic parameters for the Zollner Creek watershed for the scenario that most accurately characterized the Zollner Creek watershed hydrology. The performance of SWAT simulations of the Zollner Creek watershed based on the different parameterization scenarios was evaluated using daily simulated stream flow for the years of 2006 through 2008. The simulation period of 2009 through 2011 for the most accurate model parameterization scenario was used to evaluate the areas of the watershed that demonstrated a stronger influence on surface water flow in the watershed.

3.2.4 Model Performance Evaluation

The ability of SWAT to accurately simulate the hydrology of the Zollner Creek watershed was evaluated by comparing average daily stream flow simulated by the SWAT model to that observed by the USGS at a stream gauge located near the confluence of Zollner Creek with the Pudding River (USGS Station ID: 14201300). Average daily stream flow estimated by SWAT model simulations were compared to USGS observed data from between the years 2006 and 2008. Simulated average daily stream flow was visually compared to observed stream flow by comparison of daily hydrographs (SI) for the 2006 to 2008 periods as well as using flow duration curves. Flow duration curves represent the cumulative frequency of stream flow events during a given period of time (Vogel et al 1995) and are used in this study to evaluate the ability of the model to reproduce the observed cumulative distribution of flows as well as evaluate the magnitude of estimated flows over key ranges. SWAT performance was statistically evaluated using the Nash-Suttcliffe Modeling Efficiency Coefficient (NSE) (Nash & Suttcliff 1970), Percent Bias (PBIAS) (Gupta et al 1999), and the Root Mean Square Error-Observations Standard Deviation Ration (RSR) (Singh et al 2004). SWAT model performance was evaluated based on stream flow guidelines developed by Moriasi et al 2007, summarized in Table 3.2. The guidelines presented are for evaluation of models operating on a monthly time step. While evaluation criteria can be modified to account for the greater variability at the daily time step, this study adhered to the guidelines as presented.

3.2.5 Sensitivity Analysis

Sensitivity analysis was conducted to identify parameters that influence the surface water flow simulated by SWAT in the Zollner Creek watershed. The sensitivity analysis was conducted using the SWAT-CUP program utilizing the Sequential Uncertainty Fitting (SUFI-2) procedure. The SUFI-2 procedure is a semi-automated process in which new parameter values are selected from a defined range of possible values using a Latin hypercube sampling approach. The objective function is calculated for each parameter set comparing the model simulation results with observed data. The parameter sensitivity is determined by multiple regression of the new parameters in relation to the objective function values. A t-test is used to evaluate the relative significance of each parameter included in the analysis and provide estimates of the average change in objective function value with respect to variation of the parameters (Abbaspour et al 2004). For this study, the NSE was utilized as the objective function to evaluate the impact of parameter modification on average daily stream flow at the outlet of the Zollner Creek watershed during the 2006 to 2008 period. The parameters chosen for the sensitivity analysis (Table 3.3) included parameters that have been shown to be sensitive in hydrologic modeling in SWAT (van Griesvan et al 2005) as well as the DDRAIN, DEP_IMP, GDRAIN, and TDRAIN parameters edited to simulate the effects of tile drainage systems. The sensitivity analysis was performed on parameterization Scenario E with tile drainage modeled in 50% of the watershed area for 1000 iterations.

3.3 Results and Discussion

3.3.1 Stream Flow Results

Results of model evaluation statistics for all parameterization scenarios are shown in Table 3.4. Flow duration curves for model parameterization scenarios are presented in Figure 3.2.

The standard parameterization of the SWAT model represented by Scenario A resulted in a unsatisfactory fit of average daily stream flow compared with USGS observed flow. The Scenario A maximum average daily stream flow exceeded the maximum observed flow. In addition, simulated values exceeded observed between the 2nd and 95th percentiles of ranked average daily stream flow by as much as 480%. Average daily stream flows within the transitional flow and low flow ranges were overestimated by the model by an average of 300% while flows in the minimum flow range were overestimated by an average of 33%.

One potential cause for the overestimation of the average daily flow under parameterization Scenario A is the source of precipitation data. For parameterization Scenario A, daily precipitation measurements were obtained from a NCDC station located in Silverton, OR approximately 8km from the centroid of the Zollner Creek watershed. This weather station is located nearer to the Cascade Mountain range than the lowland Zollner Creek watershed and is located at an elevation of 124m. While the maximum elevation of areas within the Zollner Creek watershed is 149m, the elevations below 100m account for 99% of the watershed area. The proximity to the Cascade Mountains in addition to the difference in elevation could lead to orographic effects creating a difference between rainfall patterns observed at the Silverton station and those experienced in the Zollner Creek watershed. In order to account for these differences, radar based precipitation data was utilized in parameterization Scenario B to capture more localized precipitation patterns in the watershed. Comparison of the total annual precipitation from the AHPS grids within the Zollner Creek watershed and the Silverton NCDC station measurements showed differences of 287, 403, and 29 mm of precipitation in years 2006, 2007, and 2008 respectively. Statistical evaluation of SWAT simulated stream flow for Scenario B showed an improved fit of the observed flow. The inclusion of more localized precipitation data significantly improved the PBIAS. In Scenario B, the model overestimated average daily stream flow by 20% rather than 66%. Visual inspection of the simulated and observed daily hydrographs showed a more accurate estimation of peak flow events. The SWAT model still overestimated the recession flows for Scenario B, but the magnitude was less than that of Scenario A. Inspection of the flow duration curves for Scenario B show that the maximum flow estimated was similar to that observed and flows between the 15th and 88th percentiles were overestimated. Flows in the transitional and low flow ranges were overestimated by an average of 144%. Where Scenario A was able to reproduce the shape of the distribution at minimum flows, flows were underestimated by nearly 55% in this range.

The inclusion of more localized distributed precipitation inputs reduced the degree to which the SWAT model over estimates average daily stream flow, but model fit could still only be classified as satisfactory. In addition to evaluating the effects of including more precise parameterization of precipitation data, a more precise understanding of the stream morphology was also evaluated. Stream flow in the simulations described in this study was estimated in SWAT using Manning's equation for uniform flow. In this method, stream flow is calculated based on cross sectional area, hydraulic radius, slope, and the Manning's coefficient for the channel. As stated above, the cross sectional area and hydraulic radius of the channel are calculated using the bankfull channel width and depth. In the standard model parameterization, these values are determined by analyzing readily available DEM datasets. In this study, measurements of the bankfull channel width and depth were obtained as part of a survey conducted by the Marion Soil and Water Conservation district. These values were utilized to create a more precise parameterization of variables that are essential in the estimation of stream flow by the SWAT model. The inclusion of measured channel dimensions in the SWAT model parameterization did not result in a statistical improvement in model performance. While the PBIAS for this parameterization scenario was slightly improved, the 15th to 88th percentile stream flows were still overestimated by the SWAT model. The flow duration curves for both model parameterization scenarios B and C are nearly identical indicating that precise parameterization of channel dimensions does not have a significant impact on average daily stream flow estimation.

The effect of land use/land cover on stream flow estimation by the SWAT model was evaluated with model parameterization scenario D. An accurate representation of the land use/land cover present in the watershed is important to the simulation of the water balance in the system. Model parameterization Scenarios A-C utilized USDA NASS CDL data to represent the land use/land cover of the system. These datasets however are statistically designed to evaluate cropping patterns are the county scale, not at the resolution of the Zollner Creek watershed. As the CDLs were the most refined readily available land use/land cover data sets, local knowledge of the Zollner Creek watershed was necessary to refine this parameterization. Local agronomists and land owners were consulted to produce land use/land cover maps based on cropping practices in 2010 and 2011. Through consultation with these local resources, detailed knowledge of the cropping practices for 77% of the watershed area was obtained. NASS CDL data was utilized to parameterize land use/land cover for 22% of the watershed area where single crops could be identified in the delineated fields. For the remaining 1% of the watershed area where local knowledge of the land use/land cover was not available and examination of the CDLs revealed multiple identified crops, generic agricultural lands were modeled in SWAT. Based on statistical guidelines, model performance regarding stream flow was considered satisfactory. There was a slight increase in the PBIAs compared to model parameterization scenario C, however the nearly identical shape of the flow duration curves of the two model parameterization scenarios indicates that refined land use/land cover data in this case did not have a large impact on the estimated stream flow. Similar to Scenario C, the SWAT model overestimated the 15th

to 88th percentile flows and underestimated flows below the 15th percentile. The average annual evapotranspiration (ET) estimated by the model in Scenario D was 3% less than Scenario C. When compared with reference ET data, model simulated ET closely resembled annual ET for winter grains and grass seed.

Through interactions with local agronomists, land owners and local resource agents it was known that tile drainage was prevalent in the Zollner Creek watershed due to the relatively flat topography and prevalence of poorly drained soils. Fields in the watershed are subject to flooding during the winter months, particularly in the lower portion of the watershed near the confluence with the Pudding River. While the presence of tile drainage is known, the extent to which tile drains are installed and the locations are not known. In order to evaluate the impact of tile drainage on SWAT estimated daily stream flow, tile drainage simulated by random placement of tile drainage at varying percentages of the watershed area following the procedures described above. As the percentage of watershed area that was artificially drained increased from 10% to 60%, the fit of the SWAT model estimated average daily stream flow improved from satisfactory to good based on statistical guidelines for NSE and RSR. Also as the percentage of tile drainage increased, the PBIAS decreased from overestimating flow by nearly 21% on average to 20% between incorporating tile drainage in 10% to 50% of the watershed area. When tile drainage was simulated in 70% of the watershed area, the model fit of the observed data worsened due to an overestimation of all flows below the 85th percentile as well as overestimating the 98th percentile of average daily stream flows. Model parameterization scenarios E 10% through E60% also overestimated the 99th percentile of average daily stream flows during the simulation period. Model parameterization scenarios including tile drainage still over estimated flows in the high and transitional flow ranges but to a lesser degree than the previous scenarios. In model Scenario D, flows in the high range of the frequency distribution were overestimated by an average of 81%. For Scenarios including tile drainage, high flows were overestimated by an average of 79% for tile drainage simulated in 10% of the watershed area to 63% for tile drainage simulated in 60% of the watershed area. In the transitional flow range, flows were overestimated by an average of 144% in Scenario D where flows in this range were overestimated by 133% to 109% as the percentage of watershed area incorporating tile drainage was increased from 10-60%. In the low flow range of the frequency distribution, the incorporation of tile drainage overestimated these flows by an average of 118% to 97% for tile drainage incorporated in 10-60% of the watershed area. The model fit of the minimum flow range was greatly improved with the incorporation of tile drainage. In Scenarios B-D, the minimum flows were underestimated below the 85th percentile. With the incorporation of tile drainage in Scenario E, minimum flows were underestimated by 23% to 7% as the percentage of watershed area incorporating tile drainage was increased from 10-50%. For Scenario E 60%, the flows in the minimum range of the distribution were within 5% of the observed. Flows estimated by Scenario E 70% were greater than the observed for all flow ranges, particularly the low and minimum flow ranges where flows were overestimated by an average of 300% of the observed. The incorporation of tile drainage in model parameterization Scenario E improved overall model fit of the observed daily average flow data demonstrating the importance of characterizing engineered hydrologic features of the watershed. The model fit of average daily stream flow improved with increasing the percentage of watershed area incorporating tile drainage below 70% of the watershed area. Based on expert opinion, artificial drainage in fields representing 50% of the watershed area is a conservative estimate of the actual extent of tile drainage present in the watershed. SWAT model results for parameterization Scenario E support this estimate as simulations incorporating tile drainage in 40-60% of the watershed area represented the best statistical fits of the observed flow data. While transitional flows were still overestimated under these model parameterization scenarios, low and minimal flows were well characterized. Increasing the percentage of watershed area beyond this range resulted in an overestimation of the low and minimum flow portion of the cumulative flow distribution.

Model performance was evaluated by comparing the ability of the model to simulate average daily stream flows that fit both the observed hydrograph and cumulative distribution of stream flows. The simulated fit of observed data can be improved by adjusting model parameters based on refined understanding of the actual system or by identifying optimal parameter values utilizing mathematical methods. While refined understanding of the modeled system requires additional effort and resources, it also serves as a means of improving model performance based on a deeper understanding and knowledge of the system. This method was utilized in this study to evaluate the effect of localized data on model performance compared to model parameterization based solely on readily available geospatial data sets. Model performance overall was improved with the inclusion of localized precipitation data and an understanding of engineered drainage features based on local knowledge of the system. The incorporation of distributed precipitation data in the model parameterization improved model fit of peak flow events while the incorporation of tile drainage features improved the fit of recession flows following peak events and low flow conditions. The influence of measured stream channel dimensions on SWAT estimated average daily stream flow was negligible when compared to simulations where these parameters were derived from the SWAT required topographic input data sets. SWAT estimated average daily stream flow was also not greatly influenced by the inclusion of detailed local land use/land cover data compared to county level geospatial data sets.

3.3.2 Sensitivity Analysis

A sensitivity analysis of the SWAT model parameters commonly associated with variation in stream flow (van Grievsen et al 2005) as well as tile drainage parameters was conducted on SWAT model parameterization scenario E 50%. Ranks of relative parameter sensitivity are shown in Table 3.3. Of the 10 most sensitive parameters, 2 parameters are related to surface water runoff (CN2 and SURLAG) while 3 relate to drainage and baseflow conditions (ALPHA_BF, GW_DELAY, and DEP_IMP). Overestimation of peak flow events can be seen in the average daily hydrograph of the model parameterization scenario E 50% relating to an overestimation of surface runoff during these periods (Figure 3.3). The runoff estimated by the model can be adjusted by either adjusting the identified sensitive parameters, but it can also be affected by the drainage and baseflow sensitive parameters. The sensitivity of the drainage parameters is consistent with other lowland watersheds that have been modeled (Schmalz et al 2008, Schmalz et al 2010). Examination of average daily hydrograph shows that the SWAT model overestimates flows during the recession period following peak flows. Stream flows during these time periods account for the many of the flows that fall within the 15^{th} to 88^{th} percentile flows seen on the flow duration curves that are overestimated by the SWAT model. The overestimation of flow during these recession periods indicates a slow draining of the soil profile. The soil water content influences the CN2 parameter related to surface water runoff that has also been identified as sensitive. Excess soil water content can lead to increased surface water runoff which could account for over estimation of peak stream flows and overestimation of recession events. Results of the sensitivity analysis indicate that further consultation with growers to characterize tile drainage in the watershed could be beneficial in improving model performance.

3.3.3 Potential Non-point Source Pollution Areas

NPS pollution including sediment, nutrients, and pesticides transport from source areas in the terrestrial landscape to surface waters requires a transport media. In the SWAT model, water is the transport media for NPS pollution. Insight into the distribution of potential source areas of NPS pollution within a watershed can be obtained by evaluating the hydrologic contribution to surface water flow. The hydrologic contribution alone however does not indicate that a subbasin is a source for NPS pollution, only that there is a greater potential for transport. Actual NPS loading also depends on edaphic conditions, climate, topography, and chemical use practices in the subbasin in addition to an understanding of the transport potential.

The SWAT model can be used to estimate the hydrologic contribution of subbasins within a watershed to surface water flow. SWAT calculates subbasin water yield as the net hydrologic contribution to the stream reach including surface water runoff, lateral flow, and groundwater recharge on a daily time step. For this study, average annual water yield between 2010 and 2011 was evaluated at the subbasin level for SWAT model parameterization Scenarios A and E with 50% of the watershed area simulated with tile drainage to assess the influence of localized input data on the identification of potential NPS source areas. Water yields were averaged over the two year period and also normalized to subbasin area in order to identify subbasins in each simulation that contribute disproportionately to surface water flow. Subbasins that have greater hydrologic contributions per unit area represent areas with a greater potential to transport NPS pollution to surface water flow. Maps were generated to show the spatial distribution of average annual water yield per unit area over the 2010-2011 period (Figure 3.4). Cumulative average annual unit area water yield for the two simulations of the Zollner Creek watershed are similar (Figure 3.5), showing that over 50% of the unit area average annual water yield is contributed by 5% of the watershed area. The spatial distribution of the subbasins making up these contributing areas however is significantly different between the two parameterization scenarios. For model parameterization Scenario A, 3 subbasins make up the contributing area while 8 subbasins constitute the contributing area for Scenario E. This can be attributed to the difference in the level of detail incorporated into parameterization Scenario E. In order to incorporate measured channel dimensions into the model parameterization, additional subbasin outlets were added such that new stream reaches were created where average channel dimensions between measurement points varied by more than 10%. The increased number of subbasins produced during this approach allow for a finer resolution assessment of the terrestrial hydrologic contribution.

3.4 Conclusions

The SWAT model was utilized to characterize the hydrology of the Zollner Creek watershed. Model performance was evaluated by comparing SWAT simulated average daily stream flow to USGS observed stream flow at the watershed outlet. Several model parameterization scenarios were performed in order to evaluate the impact of incorporating local knowledge in the parameterization process on model performance. SWAT model results based on parameterization with readily available GIS datasets commonly utilized in SWAT applications resulted in unsatisfactory model performance based on statistical evaluation guidelines. Peak, transitional, and base flows were overestimated by the model.

The incorporation of localized distributed precipitation data resulted in an improved fit of the observed average daily stream flow data classified as satisfactory based on model evaluation guidelines. Model fit of peak flows were improved with the distributed precipitation data, however the recession to base flow conditions was still overestimated and base flows were underestimated. The inclusion of stream channel measurements and locally defined land use/land cover data did not significantly affect model performance. The incorporation of tile drainage in increasing percentages of the watershed area improved model performance to good in terms of the NSE and RSR statistics between 50-60% of the watershed area incorporating tile drainage. The incorporation of tile drainage resulted in a better fit of base flow conditions except when tile drainage was modeled in 70% of the watershed area. The improved model fit of average daily stream flow for the model parameterization scenarios modeling tile drainage in 50-60% of the watershed area were consistent with expert opinion that approximately 50% of the watershed area included tile drainage. Model performance can be improved by either improving the model input data or using mathematical methods to estimate optimal parameters. The refined parameterization of the SWAT model based on the inclusion of local knowledge in the model parameterization process resulted in an improved fit of average daily stream flow, however further improvement of model fit may require mathematical optimization.

A sensitivity analysis of the SWAT model parameterized with local knowledge of the system modeling tile drainage in 50% of the watershed area was chosen for further evaluation. A sensitivity analysis of this model parameterization indicated SWAT model simulations of the Zollner Creek watershed were sensitive to parameters relating to surface runoff, groundwater recharge, and tile drainage. These results were consistent with other SWAT simulations of lowland watersheds incorporating tile drainage features. Future research efforts should focus on local knowledge of tile drain characteristics in the Zollner Creek watershed as values for tile drainage parameters in this study were based on a simplified approach validated in watersheds in the Mid-West.

The SWAT model parameterized with local knowledge of the system modeling tile drainage in 50% of the watershed area was also used to assess areas within the watershed that demonstrated a strong hydrologic connection to surface waters in the watershed compared to SWAT model simulations based on readily available GIS datasets. Both SWAT model parameterization scenarios indicated that 5% of the watershed area contributed 50% of the hydrologic contribution; however the distributions of the subbasins within the Zollner Creek watershed that were identified were different. The incorporation of local knowledge of the system can be used to delineate subbasins within the watershed at a finer scale that can influence the identification of strongly connected terrestrial landscapes. The identification of strongly connected terrestrial environments can be used in conjunction with an understanding of the land management practices to aide in the identification of critical source areas of NPS pollution.

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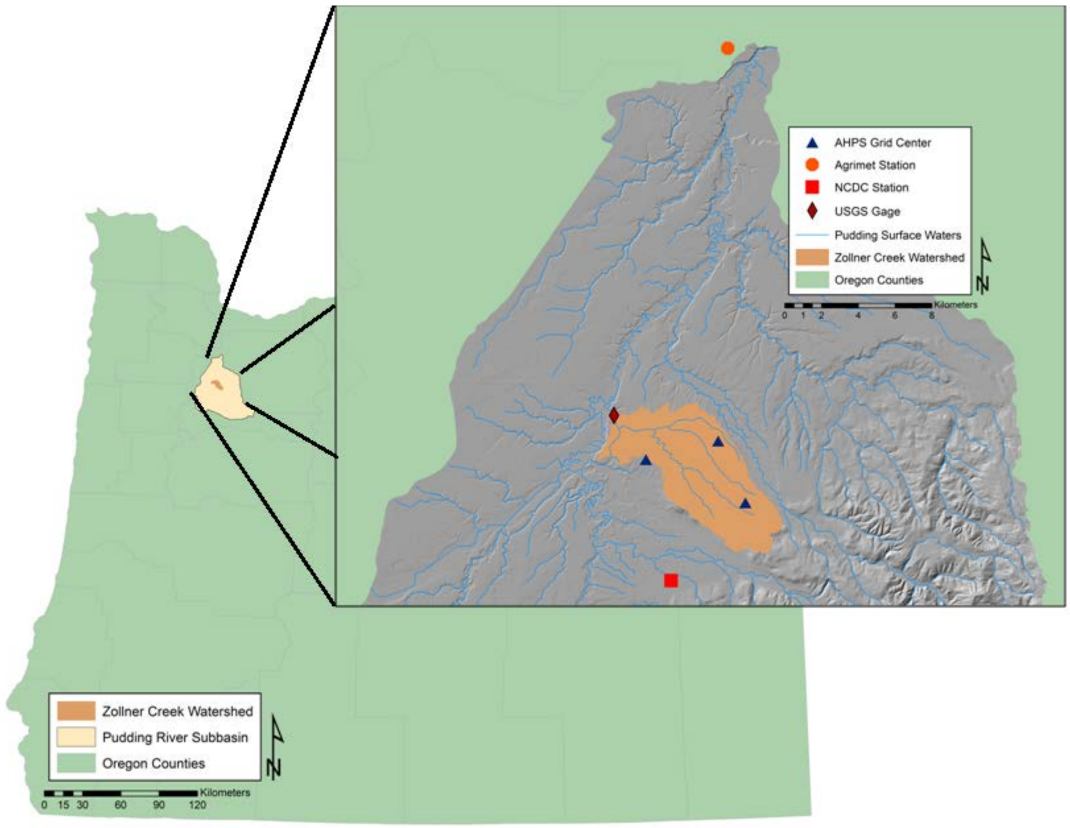


Figure 3.1. Location of the Zollner Creek watershed in relation to climate input locations.

Table 3.1. Summary of SWAT model parameterization scenarios.

Scenario	Land Use/Land Cover	Precipitation	Channel Dimensions	% Watershed Area with Tile Drainage
A	NASS CDL[a]	NCDC[b]	DEM based	-
B	NASS CDL[a]	AHPS[c]	DEM based	-
C	Local	AHPS[c]	Measured	-
D	Local	AHPS[c]	Measured	-
E	Local	AHPS[c]	Measured	10-70%

[a] National Agricultural Statistics Service Cropland Data Layer
[b] National Climatic Data Center
[c] Advanced Hydrologic Prediction Service

Table 3.2. Summary of model performance evaluation guidelines outlined in Moriasi et al 2007.

Monthly model output			Performance Rating
NSE[a]	**PBIAS[b] (%)**	**RSR[c]**	
0.75 < NSE ≤ 1.00	PBIAS < ± 10	0.00 ≤ RSR ≤ 0.50	Very Good
0.65 < NSE ≤ 0.75	±10 ≤ PBIAS < ±15	0.50 < RSR ≤ 0.60	Good
0.50 < NSE ≤ 0.65	±15 ≤ PBIAS < ±25	0.60 < RSR ≤ 0.70	Satisfactory
NSE ≤ 0.50	PBIAS ≥ ±25	RSR > 0.70	Unsatisfactory

[a] Nash-Sutcliff Modeling Efficiency Coefficient
[b] Percent Bias
[c] Root Mean Square Error-Observation Standard Deviation Ratio

Table 3.3. Parameters included in the hydrologic sensitivity analysis for parameterization Scenario E with tile drainage simulated in 50% of the watershed area. The parameters are listed in order of rank of sensitivity.

Parameter	Description (units)	Parameter Range	Rank
CH_K2	Channel effective hydraulic conductivity (mm/hr)	0-150	1
ALPHA_BF	Baseflow alpha factor (days)	0-1	2
CN2	Initial SCS CN II value	±25% of value	3
CH_N2	Channel Manning's n value	0-1	4
EPCO	Plant uptake compensation factor	0-1	5
SURLAG	Surface runoff lag coefficient	0-10	6
GW_DELAY	Groundwater delay (days)	±10 to value	7
SMFMX	Melt factor for snow on June 21 (mm H_20/°C day)	0-10	8
DEP_IMP	Depth to impervious layer in soil profile (mm)	±25% of value	9
SMTMP	Snow melt base temperature (°C)	±25% of value	10
TIMP	Snow pack temperature lag factor	0-1	11
SLSUBBSN	Average slope length (m)	±25% of value	12
SOL_AWC	Available soil water capacity (mm H_20/mm soil)	±25% of value	13
REVAPMN	Threshold depth of water in shallow aquifer required for revap to occur (mm H_20)	±100 to value	14
GDRAIN	Drain lag time (hrs)	±25% of value	15
BIOMIX	Biolocial mixing effciency	0-1	16
CANMX	Maximum canopy storage (mmH_2O)	0-1	17
GWQMN	Threshold depth of water in shallow aquifer for return flow to occur (mm H_2O)	±1000 to value	18
TDRAIN	Time to drain soil to field capacity (hrs)	±25% of value	19
SOL_ALB	Moist soil albedo	±25% of value	20
SFTMP	Snow fall temperature (°C)	0-5	21
GW_REVAP	Groundwater revap coefficient	±0.036 to value	22
ESCO	Soil evaporation compensation factor	0-1	23
DDRAIN	Depth of subsurface drain (mm)	±25% of value	24
SMFMN	Melt factor for snow on December 21 (mm H_20/°C day)	0-10	25
TLAPS	Temperature lapse rate (°C/km)	0-50	26
SOL_Z	Soil depth (mm)	±25% of value	27
SOL_K	Soil effective hydraulic conductivity (mm/hr)	±25% of value	28
BLAI	Maximum potential leaf area index	0-1	29

Table 3.4. Results of statistical evaluation of SWAT model performance compared to USGS observed flow measured at station ID: 14201300. Statistics are based on comparison of average daily stream flow estimated by the SWAT model and measured values.

Scenario	% Watershed Area with Tile Drainage	NSE	PBIAS	RSR
A	-	0.22	-66.04	0.78
B	-	0.54	-19.97	0.46
C	-	0.54	-19.39	0.46
D	-	0.54	-21.17	0.46
E	10	0.57	-20.96	0.43
	20	0.59	-20.91	0.41
	30	0.61	-20.91	0.39
	40	0.63	-20.70	0.37
	50	0.65	-20.39	0.35
	60	0.66	-20.54	0.34
	70	0.58	-20.38	0.42

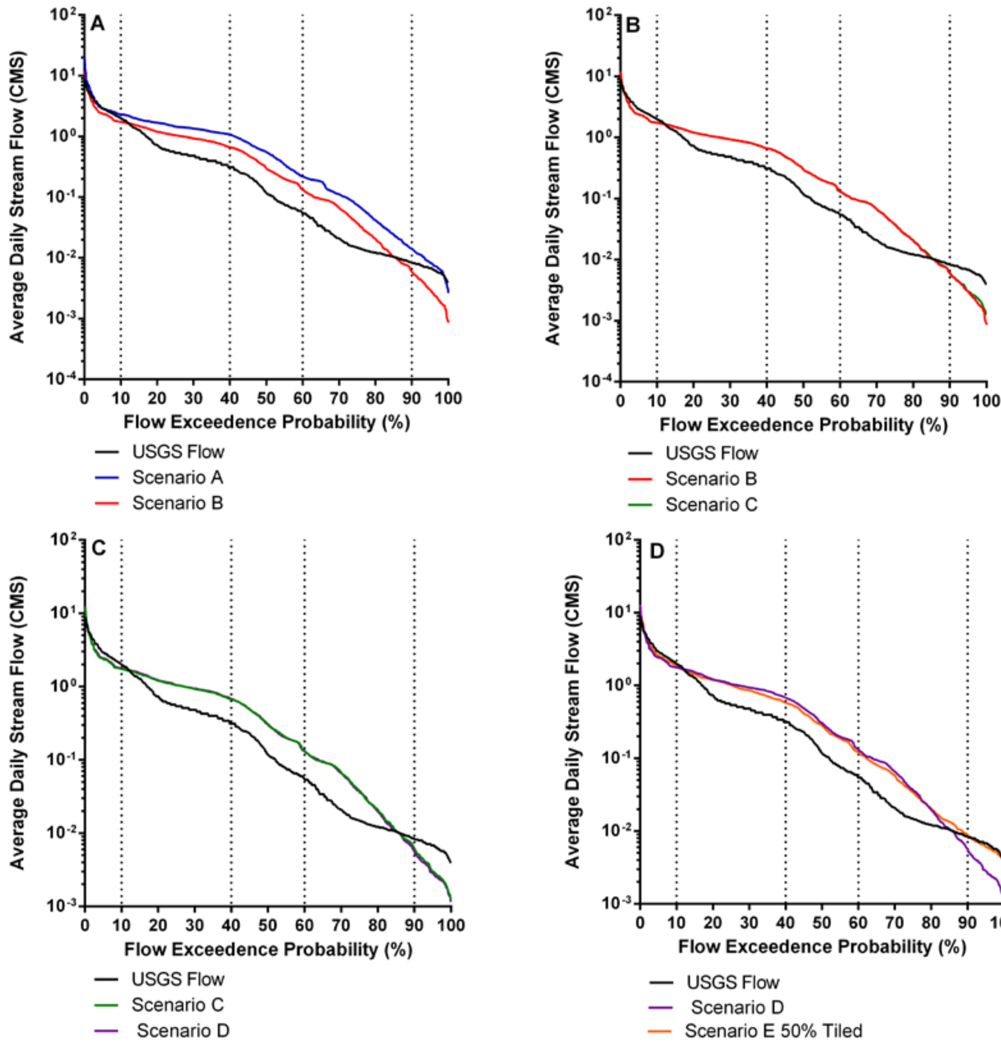


Figure 3.2. Comparison of cummulative distribution of SWAT parameterization scenario estimations and USGS observed (Station ID: 14201300) average daily stream flow. SWAT parameterization scenarios (summarized in Table 3.1) are presented as follows: A) Scenarios A and B, a comparison of precipitation inputs, B) Scenarios B and C, a comparison of channel dimension inputs, C) Scenarios C and D, a comparison of land use/land cover inputs, D) Scenarios D and E 50%, a comparison of tile drainage. Flows can be categorized according to ranges in the exceedance probability where 0-10% are peak flows, 10-40% are high flows, 40-60% are transitional flows, 60-90% are low flows, and >90% are minimum/baseflows.

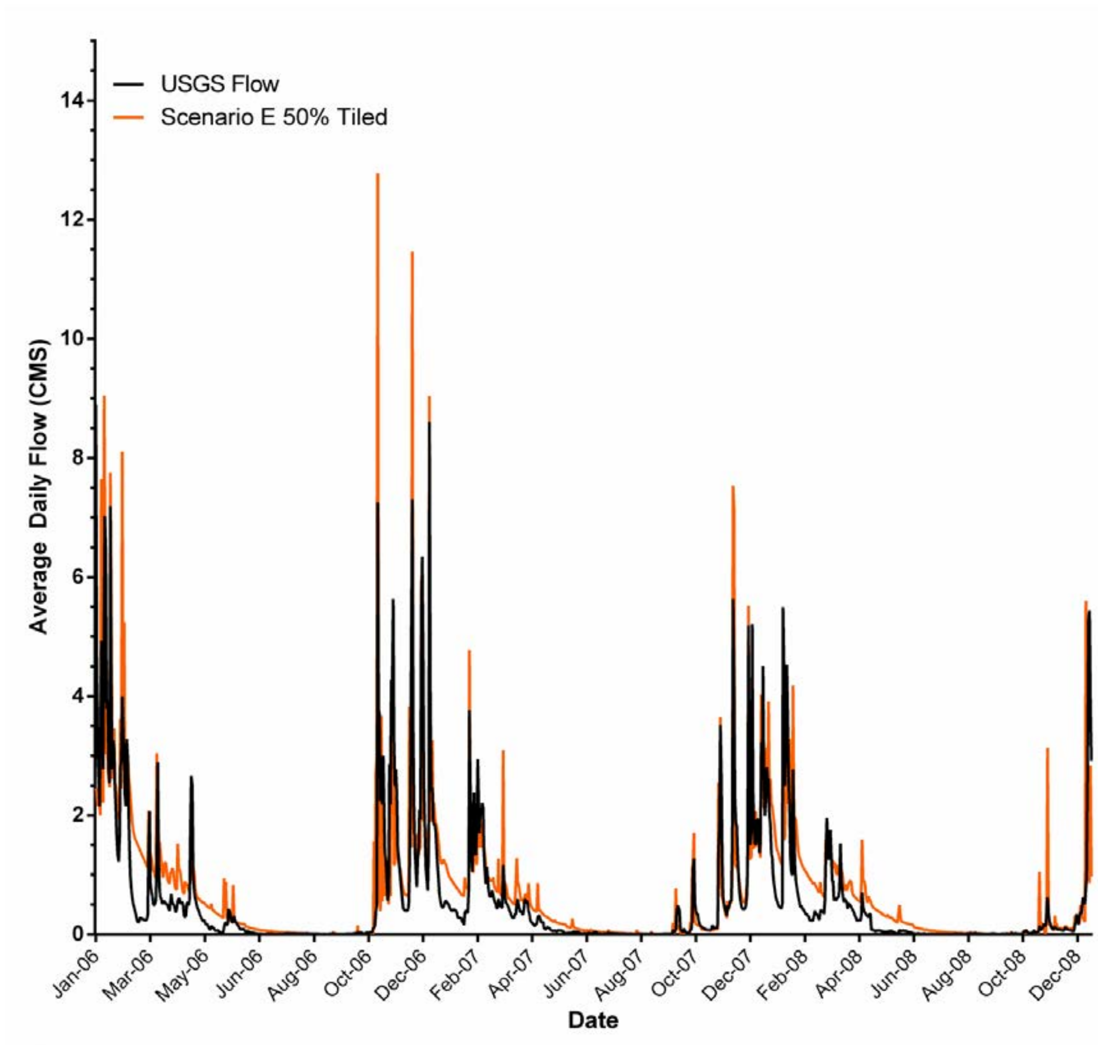
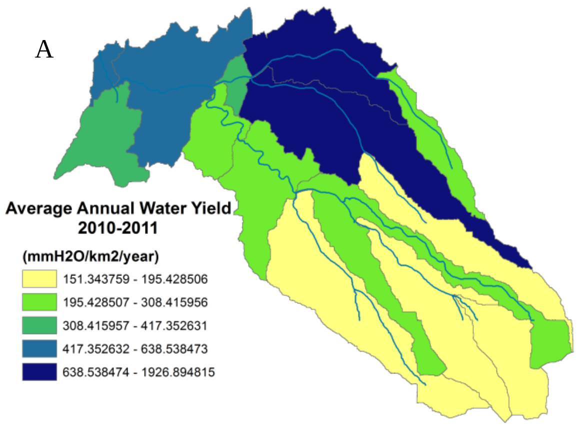


Figure 3.3. SWAT parameterization Scenario E 50% estimated and observed average daily hydrograph at outlet of the Zollner Creek watershed between 2006 and 2008.



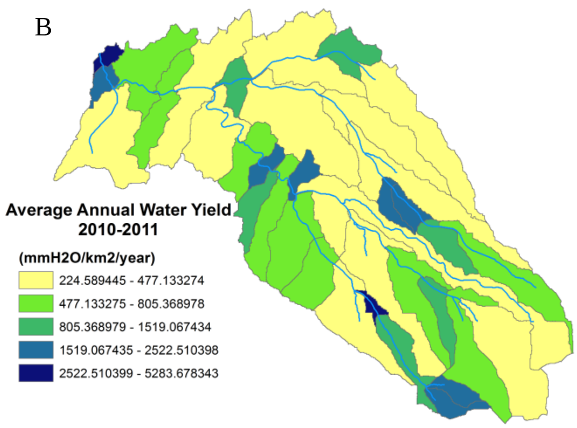


Figure 3.4. Zollner Creek average annual water yield (mm H_2O/km^2/year) 2010-2011 simulated by SWAT for model parameterization scenarios A (Fig 3.4A) and E with 50% of the watershed area simulated with tile drainage (Fig 3.4B).

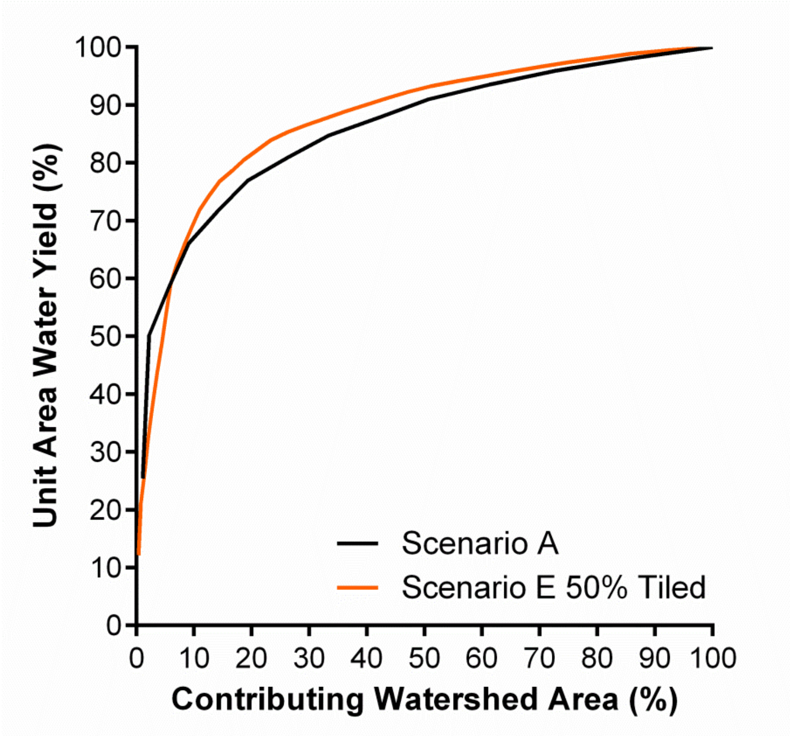


Figure 3.5. Cumulative average annual water yield per unit area for the 2010-2011 period by the percent contributing watershed area for SWAT model simulations of the Zollner Creek watershed under parameterization Scenarios A and E with 50% of the watershed area tiled.

Chapter 4 - Modeling Pesticide Surface Water Loading and Continuous Exposure in the Zollner Creek Watershed – Pacific Salmonid Critical Habitat

4.1 Introduction

Surface water monitoring has demonstrated the widespread occurrence of pesticides in the western United States (Gilliom et al 2006, Carpenter et al 2008, Lisker et al 2011, Tuttle 2014). Portions of the surface waters included in these surface water monitoring studies include critical habitat defined for 26 evolutionarily significant units (ESUs) listed as threatened or endangered under the Endangered Species Act (Good et al 2005). Concern regarding the potential impact of water quality degradation due to pesticide contamination on Pacific salmonid critical habitat has led to ESA mandated consultations between the US Environmental Protection Agency (EPA) and the NOAA National Marine Fisheries Service (NFMS). The result of these consultations has been a series of Biological Opinions (BOs) which represent comprehensive assessment of risks to ESA listed Pacific salmonids that may result from exposure to products containing 37 pesticide active ingredients registered for use within the geographic range of the ESUs (NMFS 2008, 2009, 2010, 2011, 2012a, 2012b). Characterizing risk to individuals

NFMS assessments are focused on assessing the potential of registered pesticide products to jeopardize the continued existence of the listed Pacific salmonid ESUs or adversely modify or destroy critical habitat (National Research Council 2013) and require assessment of impacts on individuals within the ESU to extrapolate population level impacts (Hanson et al 2012). Characterizing risk to individuals within ESUs requires an understanding spatial and temporal co-occurrence of listed Pacific salmonids and pesticides in surface waters (Macneale et al 2010). Due to the spatial and temporal variability of salmonid distribution within freshwater environments, characterizing co-occurrence with pesticides in surface waters is challenging (Teply et al 2011). In addition to the spatial and temporal variability of salmonid presence, pesticide concentrations in surface waters can be highly variable and have been shown to fluctuate on monthly, daily, and even hourly scales (Leu et al 2004, Gilliom et al 2006, Johnson et al 2011). Pesticide transport to surface waters is a complex process that is influenced by application timing, amount, placement, and formulation; physiochemical properties of the pesticide; soil properties and conditions; landscape topography; climate; and land management practices (Wauchope 1978, Grover 1988, Cheng 1989). Due to the complexity of evaluating pesticide exposure at the ESU scale, exposure patterns were assumed to be uniform throughout ESU geographic boundaries (Poletika et al 2011, Teply et al 2011). Under this assumption, pesticide exposure was estimated based on monitoring data collected within the geographic boundaries of listed Pacific salmonids (Gilliom et al 2006, Lisker et al 2011, Tuttle 2014) as well as field scale pesticide fate models (National Research Council 2013). Based on the variability of pesticide occurrence related to the variables described above, pesticide exposure is unlikely to be uniform over the geographic extent of list Pacific salmonid ESUs. Evaluation of trends in pesticide concentrations at 15 National Water Quality Assessment (NAWQA) demonstrated the variable nature of pesticide use (Johnson et al 2005).

Additionally, pesticide concentrations have been shown fluctuate at the daily and hourly time steps often in response to runoff events, often at levels that exceed toxicologically relevant concentrations (Holvoet et al 2007a, Liess et al 1999, Leu et al 2004). Grab sampling monitoring programs designed to characterize long term trends in pesticide concentrations typically collect samples at regular intervals and fail to capture these episodic events which can lead to inaccurate characterization of exposure (Holvoet et al 2007b, Stehle et al 2012). Continuous sampling systems can be utilized characterize these episodic fluctuations in pesticide surface water concentrations (Holvoet et al 2007a, Leu at al 2004, Liess et al 1999), however these sampling strategies still present logistical difficulties (Holvoet et al 2007a, Shaw et al 2008). Passive sampling devices (PSDs) provide several advantages including the ability to capture episodic fluctuations in contaminant concentrations over the period of deployment and provide time-weighted average (TWA) contaminant concentrations (Namiesk et al 2005, Vrana et al 2005). Additonally, PSDs sequester the freely dissolved or bioavailable fraction of contaminants in aquatic systems similar to passive biological uptake (Huckins et al 2006, Allan et al 2012).

While there are many benefits the use of PSDs, the TWA concentration normalizes the episodic fluctuations in contaminant concentration over the deployment period. This can be a disadvantage in the case of pesticides where the peak concentrations that may represent toxicological concern can be normalized with lower concentrations over a deployment period and underestimate acute exposure. When characterizing risk associated with pesticide exposure, short term pulses of pesticides have been shown to affect aquatic community structure (Schulz 2004, Liess et al 2005, Colville et al 2008). Diversity in natural prey abundance and diversity has been shown to impact salmonid population growth (Macneale et al 2014). As such, it is important to characterize the acute exposure patterns in listed Pacific salmonid habitats.

The use of water quality models in conjunction with sampling can provide a means of characterizing water quality conditions (Holvoet et al 2007b, Gavaert et al 2009). Ecohydrological models such as the Soil and Water Assessment Tool (SWAT) provide a tool to simulate the processes that influence pesticide fate. SWAT is a physically-based, process model developed to simulate the impact of land management practices on hydrology and water quality at the watershed scale (Arnold et al 1998). SWAT has been widely utilized to assess hydrologic and non-point source (NPS) pollution primarily related to erosion and nutrients and to a lesser degree pesticides (Gassman et al 2007, Gassman et al 2014). Fohrer et al (2014) provide a summary of applications of the SWAT model to simulate pesticides. SWAT has been applied diverse watersheds internationally and shown the ability to simulate pesticide fate.

The goal of this study was to demonstrate the utility of coupling passive sampling techniques and watershed scale ecohydrological modeling in evaluating the relationship between pesticide surface water concentrations and assessing exposure of juvenile salmonids to pesticides. SWAT was used to simulate the fate of chlorpyrifos and trifluralin, the two current use pesticides identified most frequently in PSD monitoring, in the Zollner Creek watershed. The ability of the SWAT model to estimate temporal trends in pesticide concentrations was evaluated by comparing model estimated TWA concentrations with PSD observations. SWAT model estimations of pesticide fate were also used to estimate acute pesticide exposure patterns from PSD TWA concentrations based on land management practices, landscape characteristics, climate, soil conditions, and hydrology in the Zollner Creek watershed during PSD sampling between June 2010 and September 2011.

4.2 Methods and Materials

4.2.1 Study Site

The Zollner Creek watershed a 3885 ha watershed located within the Molalla-Pudding subbasin (HUC8:1709009) in Marion County, OR. The Zollner Creek watershed is predominately situated on the Willamette Valley floor, one of the most agriculturally diverse regions in the world. Land use within the Zollner Creek watershed is primarily agricultural, with a range of field, vegetable, fruit, and orchard crops accounting for more than 90% of the watershed area. The Zollner Creek watershed can be characterized as a relatively flat lowland catchment with elevations ranging from 35 to 193 m asl with a median elevation of 67 m als. Additionally, more than 50% of the watershed area having a slope less than 2%. Soils in the watershed are predominately characterized as poorly drained hydrologic group C and D soils with silt loam and silt clay loam textures. Weather in the Willamette Valley is characterized by cool, wet winters followed by warm, dry summers (Ulrich & Wentz 1999). The Zollner Creek watershed receives on average 966 mm of rainfall annually, with the majority of rainfall occurs between October and April.

4.2.2 SWAT Model Description

SWAT is a watershed scale ecohydrologic model developed by the USDA Agricultural Research Service that simulates the impacts of land management on water, sediment and chemical yields in large, variable basins. SWAT uses physical characteristics of the landscape including land use/land cover, soil types and topography along with weather data and physical chemical properties of compounds to perform mathematical simulations of the processes that dictate routing of water, chemicals and sediment (Arnold et al 1998, Neitsch et al. 2005). SWAT is a physically based model that operates on a daily time step capable of performing continuous simulation of weather, hydrology, soil conditions, plant growth, nutrient cycling and transport, pesticide fate, bacteria transport, and land management practices over long periods (Gassman et al 2007).

SWAT simulates watershed scale processes by first dividing the watershed into subbasins based on watershed topography. Each subbasin is further divided into hydrologic response units (HRUs) that consist of unique combinations of land use/land cover, soils, and slope. The HRUs are operational units of the model where daily simulations terrestrial processes are performed (Neitsch et al 2005). The driving force of SWAT simulations is the terrestrial water balance characterizes soil water content as a function of precipitation, surface runoff, evapotranspiration, percolation, and groundwater return flow (Arnold et al 1998, Neitsch et al 2005). For simulations in this study, surface water runoff was estimated using the Curve Number method (USDA 1972) and evapotranspiration was estimated using the Penman-Monteith method (Monteith 1965). Crop growth and development in the SWAT model are based on the Erosion Impact Calculator (EPIC) model (Williams 1990). Pesticide terrestrial fate processes in SWAT are based on the Groundwater Loading Effects on Agricultural Management Systems (GLEAMS) model (Leonard et al 1987) and include foliar wash-off and degradation, volatilization, surface and subsurface soil-water partitioning, infiltration, surface water runoff, lateral flow, and degradation. Pesticides can be transported from HRUs in both the dissolved and particulate bound phases. Currently, SWAT is not capable of simulating pesticide drift resulting from application (Holvoet et al 2008, Gevaert et al 2010) or distinguishing pesticide transport via tile drainage from overall lateral flow (Fohrer et al 2014).

Water and contaminants generated in the HRUs are added to stream reach in the associated subbasin. Hydrologic routing in this study was simulated using the variable-storage rate method (Williams 1969). Pesticide fate in the stream including degradation, partitioning, volatilization, settling of particulate bound residues, and resuspension and burial of sediment bound residues are simulated following a model described by Chapra (1997).

4.2.3 Model Parameterization

For this study, ArcSWAT version 2009.93.7b was used to simulate hydrology and pesticide fate in the Zollner Creek watershed. ArcSWAT is an ArcGIS interface for the SWAT model that has been developed to derive SWAT input variables from readily available GIS data sources (Olivera et al 2006). SWAT model parameterization to simulate the hydrology of the Zollner Creek is described in Chapter 3. The model parameterization scenario that produced the best fit of the observed daily hydrograph and was representative of tile drainage in the watershed based on expert opinion was Scenario E with tile drainage simulated in 50% of the watershed area. Briefly, topography of the watershed was characterized using a 10m resolution digital elevation model (DEM); county level soils data was extracted from the SSURGO data set for Marion County, OR; precipitation was characterized using Advanced Hydrologic Prediction Service (AHPS) gridded daily precipitation data; daily minimum and maximum temperature data were obtained from the National Climatic Data Center (NCDC) for a station located in Silverton, OR (COOPID: 357823) located approximately 8 km outside of the watershed boundary; and daily values of wind speed, solar irradiation, and relative humidity were simulated based on historical data for an AgriMet weather station located in Aurora, OR approximately 24 km outside of the watershed boundary.

Land use/land cover data for simulations in this study was based on analysis of cropping practices in the watershed in 2010 and 2011. Land use/land cover GIS datasets were produced by delineating individual field boundaries from FSA National Agriculture Imagery Program (NAIP) aerial imagery of the watershed during the 2009 and 2011 growing seasons. Field shapes displayed a high degree of fidelity between the 2009 and 2011 aerial images. Land use/land cover in the delineated fields was determined through a series of consultations with local growers from the Zollner Creek watershed and agronomists that advised growers within the Zollner Creek watershed, windshield surveys of the watershed, and evaluation of USDA National Agricultural Statistics Service (NASS) Oregon Cropland Data Layers (CDLs) for the 2010 and 2011 growing seasons. Land use/land cover for 70% of the watershed area was defined through consultations with growers and agronomists along with windshield surveys, 22% of the watershed area was defined by identifying the crop type identified in the field through the NASS CDLs, and 8% of the watershed area was defined as generic agricultural land use due to the inability to define the land use/land cover through the previously described methods. A total of 52 land uses were identified in the watershed with approximately 23% of the watershed area represented by grass seed/sod grass, 17% representing 15 different vegetable crops, 12% representing fruit crops, and 11% wheat.

In addition to assistance defining land use/land cover in the watershed, consultations with growers and agronomists provided insight into crop management timelines for the crops identified in the watershed (Dennis Roth, personal communication). Pesticide use practices for chlorpyrifos and trifluralin simulated in the SWAT model were based on agronomist recommended programs in conjunction with limited grower records. Chlorpyrifos applications were recommended for 6 crops identified in the Zollner Creek watershed representing nearly 10% of the watershed area. Pre-plant incorporated applications of chlorypyrifos were recommended for 5 of the crops, while later season applications were recommended for 2 of the crops. Pre-plant incorporated trifluralin applications were recommended for 3 crops representing nearly 3.5% of the watershed area.

4.2.4 SWAT Pesticide Fate Analysis

Results of SWAT simulations of chlorpyrifos and triflualin fate in the Zollner Creek watershed were compared to results of continuous pesticide surface water monitoring utilizing low-density polyethylene passive sampling devices (PSDs) collected near the watershed outlet described in Chapter 2. Briefly, PSDs were deployed in Zollner Creek for approximately 3 week periods from June of 2010 to September of 2011. Chlorpyrifos was detected in 100% of the PSD samples with TWA concentrations ranging from 0.69-12.5 ng/L. Trifluralin was also detected in 100% of the PSD samples with TWA concentrations ranging from 0.21-15.4 ng/L. These pesticides were chosen for model analysis as high frequencies of detection provide continuous estimates of the freely dissolved concentrations over the entire sampling period which is desirable for comparison to model estimates.

The SWAT model simulates the mass of pesticides in both the dissolved and bound phases entering and exiting surface water on a daily time step. In order to compare SWAT model estimates to PSD monitoring results, the simulated dissolved mass of the pesticides exiting the stream reach on a daily time step was used to estimate average daily concentration. The dissolved fraction was chosen as the PSDs sample the freely dissolved fraction of pesticides in the water column while the pesticide mass exiting the reach was chosen as the PSDs were located at the point defined as the watershed outlet. Daily pesticide concentrations were calculated in ng/L by dividing the mass of dissolved pesticide by the daily volume of water in the stream reach which was obtained by converting the average daily flow reported in m^3/s to liters as follows:

$$Conc\ \left(\frac{ng}{L}\right) = \frac{SOLPST\_OUT(mg) * 1x10^6 (\frac{ng}{mg})}{FLOWOUT\left(\frac{m^3}{s}\right) * \frac{1000L}{1m^3} * \frac{86400s}{1day}}$$

where SOLPST_OUT is the dissolved mass of pesticide exiting the stream reach and FLOWOUT is the average daily flow out of the stream reach. These daily concentrations were used to calculate the TWA concentrations of pesticides over the same sampling periods as the PSDs were deployed in the watershed. SWAT model performance was evaluated through visual evaluation of the data as well as the Nash-Suttcliff Modeling Efficiency Coefficient (NSE) (Nash & Suttcliff 1970), and the coefficient of determination as described in Krause et al 2005.

4.3 Results and Discussion

4.3.1 SWAT Pesticide Modeling

We evaluated the utility of SWAT to characterize the relationship between land management practices and pesticide surface water loading in the Zollner Creek watershed by comparing simulated chlorpyrifos and trifluralin TWA concentrations to measured values described in Chapter 2. For both chlorpyrifos and trifluralin, visual assessment shows that simulated TWA concentrations generally follow the pattern of measured values, particularly during periods with peak concentrations (Figure 4.1). The maximum simulated chlorpyrifos TWA concentration occurs during the same sampling interval as the maximum measured value. In general, over the period of continuous monitoring fluctuations in simulated and measured chlorpyrifos TWA concentrations show a similar pattern. The maximum simulated trifluralin TWA concentration also occurs during the same sampling interval as the maximum measured value. However, over the period of continuous monitoring fluctuation in trifluralin measured TWA concentrations is not a pronounced as the simulated values. These observations are generally consistent with other applications of SWAT for evaluating the fate of these pesticides at the watershed scale (Neitsch et al 2002, Parker et al 2007, Boithias et al 2011, Lou et al 2008, Luo et al 2009, Zhang et al 2008, Ficklin et al 2013).

Similar patterns of simulated and measured TWA concentrations indicate reasonable model performance in simulating pesticide use patterns, as well as processes responsible for transport from application sites to Zollner Creek.

For both pesticides the simulated TWA concentrations consistently underestimate measured values; statistics are shown in Table 4.1. The mean of simulated chlorpyrifos TWA concentrations underestimates the mean of measured values by a factor of 10, and the chlorpyrifos maximum simulated TWA concentration underestimates the maximum measured value by a factor of fewer than 4. For trifluralin the mean and maximum of simulated TWA concentrations are 2 orders of magnitude below measured values. Figure 4.2 shows a positive relationship, r^2 of 0.34 and 0.50, respectively, for chlorpyrifos and trifluralin simulated TWA concentrations regressed with measured values. However, for both chlorpyrifos and trifluralin, if slope deviation from unity is considered and the r^2 values are appropriately weighted (Table 4.2), the transformed r^2 values are reduced (Krause et al 2005).

The media for mass transport of pesticides in the SWAT model is water (Nietsch et al 2005). As such, accurate characterization of hydrology is necessary to simulate pesticide fate (Holvoet et al 2005). The parameterization of the SWAT model utilized to simulate chlorpyrifos and trifluralin fate is described in detail in Chapter 3 as model parameterization Scenario E with 50% of the watershed area simulated with tile drainage. Model performance in terms of hydrology was considered satisfactory based in part on NSE = 0.65. Using the NSE to evaluate SWAT performance in simulating pesticide fate, values for chlorpyrifos and trifluralin were -1.4 and -0.56 respectively. Due to the satisfactory fit of the hydrology that transports pesticides and similar patterns of pesticide TWA concentration between the model and observed data, the most likely source of bias is insufficient knowledge of pesticide use practices. As the NSE is a function the sum of the squared differences between the simulated and measured values divided by the sum of the squared difference between the measured value and its mean, a large difference between simulated and measured values will likely result in a low (unsatisfactory) NSE. As simulated TWA concentrations consistently underestimate measured values, the NSE for both chlorpyrifos and trifluralin is a negative value indicating unsatisfactory model performance.

Except for studies conducted under controlled conditions or studies conducted in California where pesticide use reporting is required, one of the greatest uncertainties in pesticide fate modeling is application amount, timing, and frequency. In this study, chlorpyrifos and trifluralin applications were based on agronomist recommended crop management programs (Dennis Roth, personal communication). Based on these recommendations we assumed that between June 2010 and October 2011 chlorpyrifos was applied to 6 crops and trifluralin applied to 3. These recommendations are deemed approximate to actual pesticide use practices, and because during this period there were 144 chlorpyrifos and 137 trifluralin labeled uses in Oregon, including labeled uses for many of the crops found in the Zollner Creek watershed, we assume that pesticide applications are underrepresented and therefore a likely source of bias in model simulations that consistently underestimate measured TWA concentrations in Zollner Creek.

When pesticide application records are available there is greater opportunity for improved simulation. For example, in studies conducted in California (Lou et al 2008, Luo et al 2009, Zhang et al 2008, Ficklin et al 2013) SWAT simulated chlorpyrifos concentrations were on same order of magnitude as measured values. In another SWAT simulation, Boithias et al 2011 parameterized trifluralin applications based on actual application records submitted over a 3 year period. In the Sugar River Basin studies (Neitsch et al 2002, Parker et al 2007) trifluralin use (pre-plant only) on corn and soybeans was estimated by NASS records of progression – percentage of acres treated by date – a detailed surrogate for application records. In this case SWAT simulations were also aided by the narrow application window and lack of diversity in cropping practices.

In addition to consideration of application temporal attributes, spatial analysis suggests that hydrologic connectivity may also influence pesticide stream loading. Figure 3.4 shows average annual unit area water yield for Zollner Creek watershed subbasins. Eight of 36 subbasins show strong hydrologic connection to Zollner Creek, contributing 50% of the hydrologic yield to surface waters in the Zollner Creek watershed. Overlaying pesticide use locations (crops with use recommendations) with these subbasins results in 16% of chlorpyrifos simulated applications occurring in 6 of these subbasins in 2010 and 11% in 5 in 2011, while 16% of trifluralin simulated applications were made in 2 these subbasins in 2010 and 15% in 3 in 2011. This analysis suggests that consideration of both temporal and spatial attributes of pesticide applications relative to hydrologic connectivity may improve model fit of measured pesticide surface water concentrations.

4.3.2 Deconvolution of PSD Time-weighted Average Concentrations

For sampling periods during which the maximum TWA concentrations of chlorpyrifos and trifluralin were detected, SWAT estimations of the daily fluctuation in pesticide concentration were utilized to differentiate potential patterns at time steps less than the period of deployment which produced the integrated average concentrations reported. Fluctuations within the approximately 21 day TWA concentrations were evaluated at 1, 2 and 4 day exposure periods commonly associated with acute toxicity testing. SWAT estimates of 1, 2, and 4 day TWA pesticide concentrations were used to determine the proportion to which the exposure period concentrations contributed to the simulated 21 day TWA concentration. Proportions derived from the SWAT simulation were then applied to PSD TWA concentration to estimate the potential fluctuation in pesticide concentration over the PSD deployment period.

The maximum chlorpyrifos TWA concentration of 12.5 ng/L occurred between October and November of 2010. SWAT estimated chlorpyrifos concentrations during this time period exceeded 75th percentile of concentrations simulated during all of 2010 and included the maximum estimated daily chlorpyrifos concentration. Estimates of daily, 2 day, and 4 day average chlorpyrifos concentrations derived from measured TWA concentrations based on daily SWAT estimates are shown in Figure 4.3 in relation to precipitation and average daily stream flow during the PSD deployment period. Estimated concentrations remained below the measured TWA concentration prior to the first run-off event. Following this first run-off event, chlorpyrifos estimates rose above the TWA concentration until concentration estimates fall below the TWA again when flows begin to recede in early November. Estimated daily concentrations that exceeded 12.5 ng/L represented 36% of the concentrations estimated from the PSD TWA concentration based on SWAT modeled variation in concentration. The maximum daily, 2 day, and 4 day average chlorpyrifos concentrations estimated from monitoring data based on SWAT simulations were 24.0, 20.3, and 17.7 ng/L, respectively. When compared with chlorpyrifos acute aquatic life benchmarks (Table 2.5) and NMFS salmonid levels of concern (Table 4.2), all concentration estimates are below the lowest measures of acute toxicity by a factor of 1.7.

The maximum trifluralin TWA concentration of 15.4 ng/L was detected in the Zollner Creek watershed in June of 2010. Estimates of daily, 2 day, and 4 day average trifluralin concentrations derived from measured TWA concentrations based on daily SWAT estimates are shown in Figure 4.4 in relation to precipitation and average daily stream flow during the PSD deployment period. This sampling period was characterized by precipitation events in the early part of June that mobilized the soil applied herbicide. Estimates of the daily, 2 day, and 4 day concentrations derived based on SWAT simulation data were below the TWA concentration of 15.4 ng/L during high flows resulting from runoff events. As the flows receded following these events, the estimated concentrations of trifluralin increased due to decreased dilution capacity of the stream reach. Following runoff events at the beginning of the sampling period, flows continually receded for the remainder of the deployment period. Estimated concentrations of trifluralin following the runoff events followed bell shaped curves observed for the dissipation of concentrations following discrete input events (Hartley and Graham-Bryce 1980). The maximum daily, 2 day, and 4 day average concentrations for trifluralin derived from the measured TWA concentration based on SWAT simulations were 35.6 ng/L, 35.1 ng/L, and 30.4 ng/L respectively. Comparison of the estimated peak concentrations with trifluralin acute aquatic life benchmarks (Table 2.5) and NMFS levels of concern for fish, aquatic macroinvertebrates, and primary producers (Table 4.3), all estimated concentrations are below the lowest measures of acute toxicity by a factor of 84.

The 4 day (96hr) maximum concentrations estimated based on the results of SWAT simulations for both chlorpyrifos and trifluralin were lower than those estimated based on a proportional analysis of PSD data (Chapter 2.4). Proportional analysis of the maximum TWA concentrations of chlorpyrifos and trifluralin was used to calculate a compressed TWA concentration assuming that the entirety of the mass of pesticides sequestered by the PSDs occurred with one 96 period. Applying these assumptions to the maximum chlorpyrifos and trifluralin PSD concentrations in the Zollner Creek watershed results in chlorpyrifos and trifluralin concentrations of 65.6 ng/L and 80.8 ng/L respectively. Maximum 96 hour concentrations for chlorpyrifos and trifluralin based on SWAT simulations however were 17.7 ng/L and 30.3 ng/L respectively. The maximum 96 hour concentrations based on the SWAT simulations represent a more realistic assessment of the potential acute exposures to the pesticides modeled. The SWAT simulations estimated fluctuations in pesticide concentration representative of the pesticide use practices as well as the climatic, edaphic, and hydrologic conditions that influence pesticide fate. Coupling passive sampling data with ecohydrological models can provide a means of estimating the variation in pesticide concentrations that contribute to the TWA concentrations measured based on simulations of the relationship between pesticide use practices and surface water loading.

4.4 Conclusions

One of the areas of uncertainty in the exposure assessment identified in the NMFS BOs was a limited understanding of the relationship between pesticide use practices and pesticide surface water monitoring data (NFMS 2008, 2012). The goal of this study was to utilize the ecohydrological model SWAT coupled with PSD pesticide surface water monitoring to evaluate the influence pesticide use practices on temporal trends in surface water concentrations and evaluate potential acute exposure patterns. The SWAT model was able to simulate the temporal trends in chlorpyrifos and trifluralin TWA concentrations observed in PSD monitoring between June 2010 and September 2011. The similarity in the temporal patterns of chlorpyrifos and trifluralin concentrations indicate that pesticide use practices and pesticide fate were reasonably represented by the SWAT model. However, simulated TWA concentrations consistently underestimated measured values. Our analysis suggests that the likely source of bias is underrepresented pesticide use practices. Pesticide applications were simulated based crop management plans developed in conjunction with growers and agronomists in the Zollner Creek watershed. These plans contain recommendations and therefore do not represent actual pesticide use practices. A more refined understanding of pesticide use practices within the Zollner Creek watershed is likely to greatly improve simulation of pesticide surface water loading and pesticide surface water concentrations.

PSDs represent a useful tool in assessing pesticide surface water concentrations. Monitoring programs to characterize pesticide surface water concentrations traditionally rely on grab samples collected at regular intervals that may miss peaks in pesticide concentration due to episodic events. PSDs offer the advantage of being able to capture these episodic events and provide TWA concentrations. The TWA concentrations however can be viewed as a disadvantage with respect to ecological risk assessment as these peak concentrations that have been shown in many cases to approach and exceed levels of toxicological concern are normalized into a single concentration. Coupling PSD monitoring results with an ecohydrological model such as SWAT can be used to deconvolute the TWA concentrations and provide an estimate of the fluctuations in pesticide concentration that contributed to the average concentration over the deployment period. As SWAT was able to represent the temporal trends in chlorpyrifos and trifluralin concentration, daily simulated concentrations were utilized to estimate the proportion of the TWA concentrations that were contributed on daily, 2 day, and 4 day basis throughout the deployment period of the PSDs representing the maximum pesticide levels detected. Using the SWAT model simulations to represent the daily variability in pesticide concentrations allows for the estimation of acute exposure patterns based on complex processes of pesticide surface water loading. While there is still uncertainty in the representation of actual pesticide use practices, the coupling of PSD monitoring data with the SWAT model can be a beneficial tool in assessing the relationship between land management practices and the potential exposure of juvenile salmonids to pesticides.

4.5 Acknowledgements

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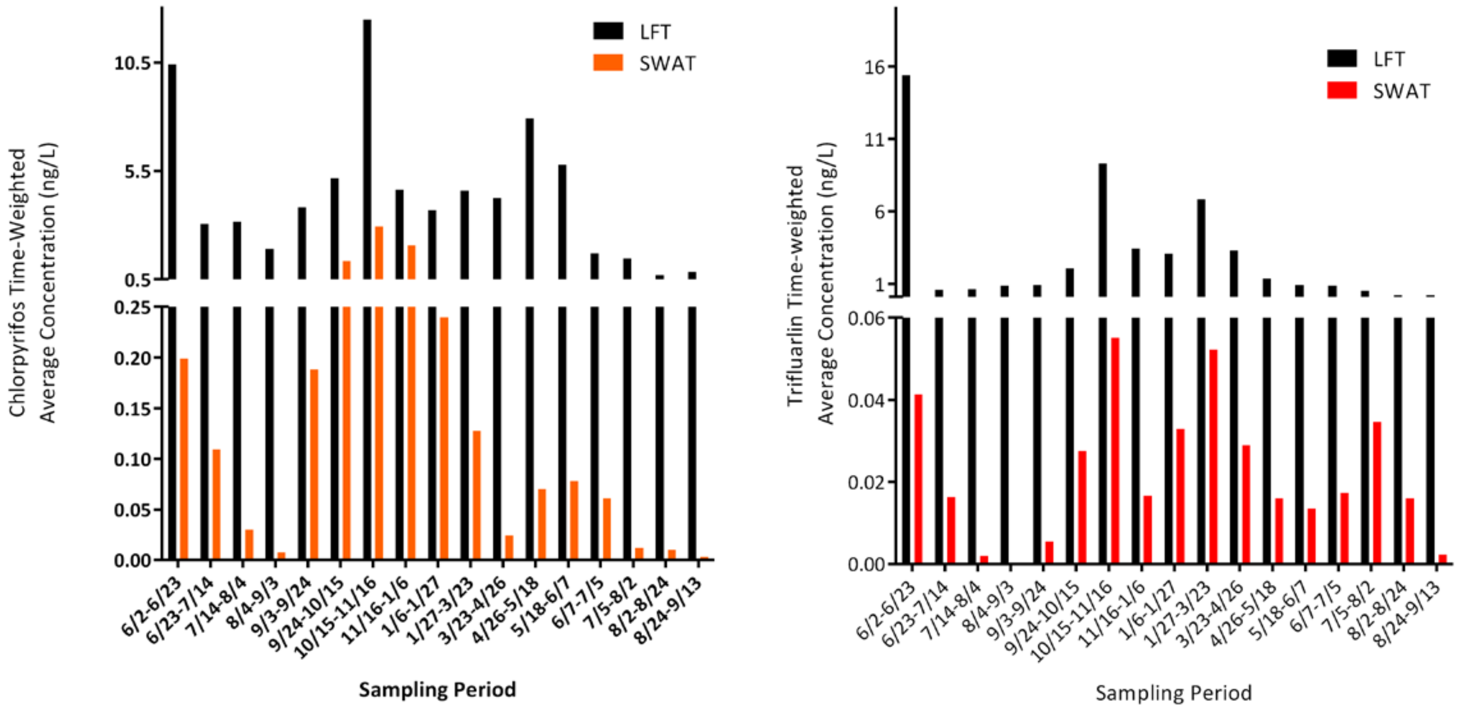

Figure 4.1. Time-weighted average concentrations of chlorpyrifos and trifluralin simulated by SWAT compared to PSD measurements in the Zollner Creek watershed.

Table 4.1. Descriptive statistics of chlorpyrifos and trifluralin TWA concentrations measured by PSDs and simulated by the SWAT model for the Zollner Creek watershed and results of statistical evaluation of SWAT model performance.

		Min	Mean	Max	NSE	r^2	a	b	wr^2
Chlorpyrifos	PSD	0.695	4.44	12.5	-1.4	0.33	-0.23	0.15	0.05
	SWAT	0.003	0.442	2.93					
Trifluralin	PSD	0.206	2.98	15.4	-0.56	0.50	0.014	0.003	0.002
	SWAT	0.0002	0.022	0.055					

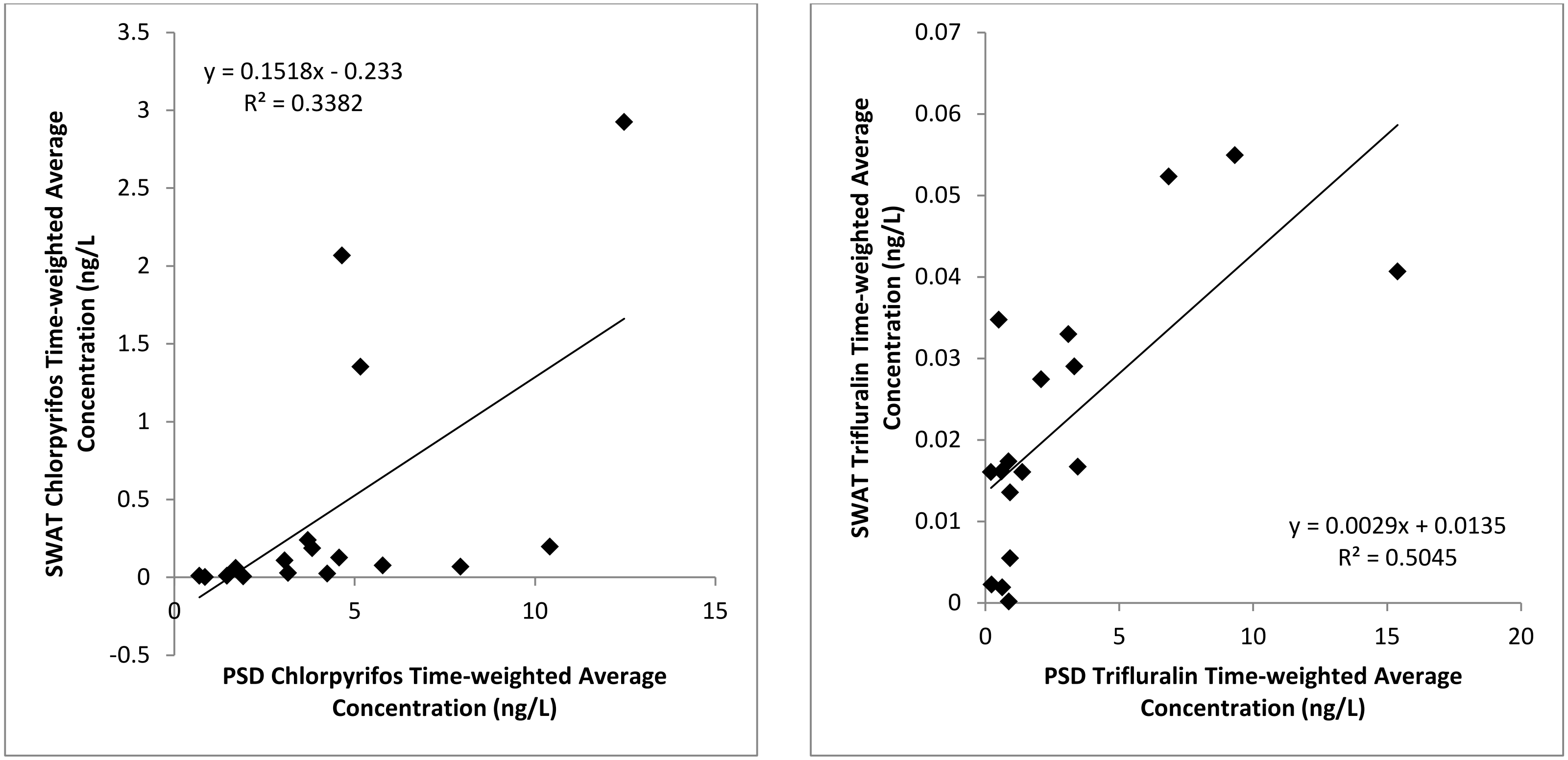

Figure 4.2. SWAT estimated TWA concentrations of chlorpyrifos and trifluralin compared to PSD measured TWA concentrations.

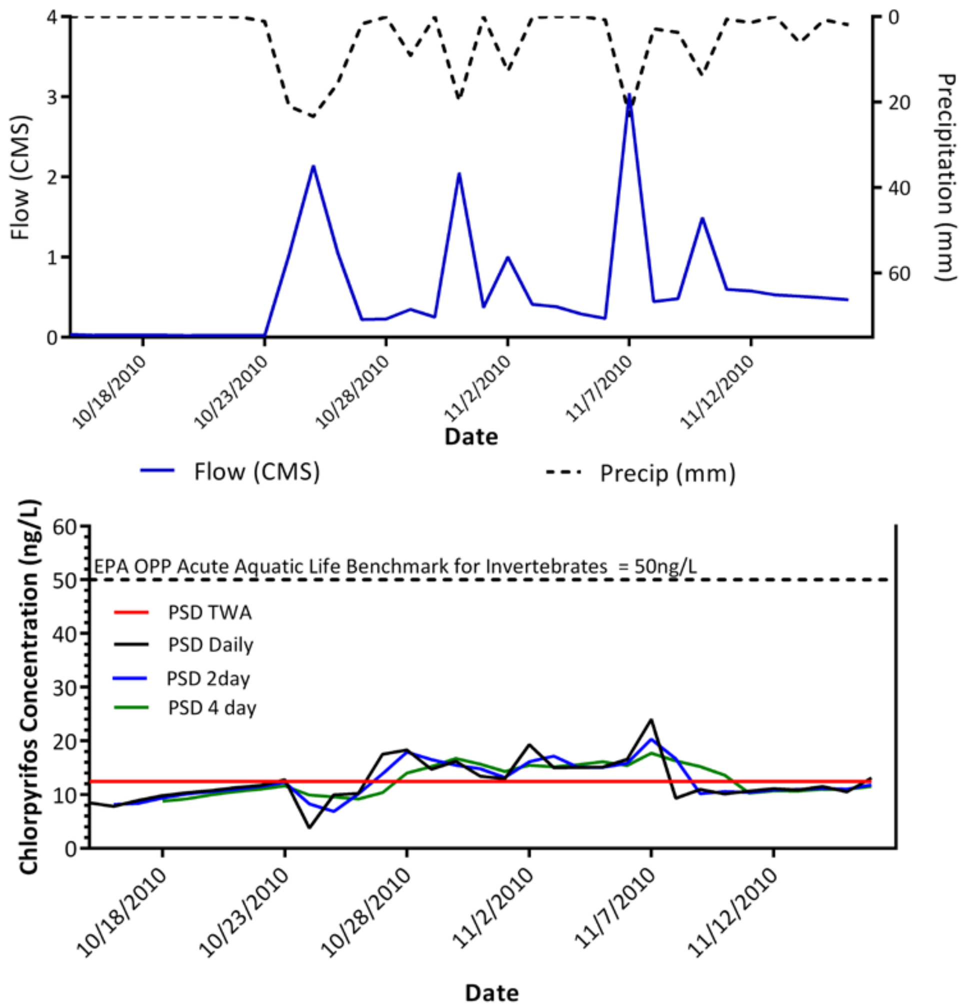

Figure 4.3. Daily precipitation and flow during chlorpyrifos maximum TWA deployment period. Potential 1, 2, and 4 day chlorpyrifos concentrations contributing to PSD TWA concentration.

Table 4.2. Daily, 2 day, and 4 day average peak concentrations of chlorpyrifos derived from maximum PSD TWA concentrations based on SWAT model simulations compared with acute toxicological endpoints evaluated in NMFS Biologcal Opinion (NMFS 2008) reported as ng/L.

		Concentration Range of Observed Effect (ng/L)			
	Estimated Maximum Concentration (ng/L)	Fish Survival (LC50)	Swimming Behavior	Olfactory-Mediated Behaviors	Prey Survival (LC50)
Daily	24	800-22000000	300-400	625-2500	40-600
2 Day	20.3				
4 Day	17.7				

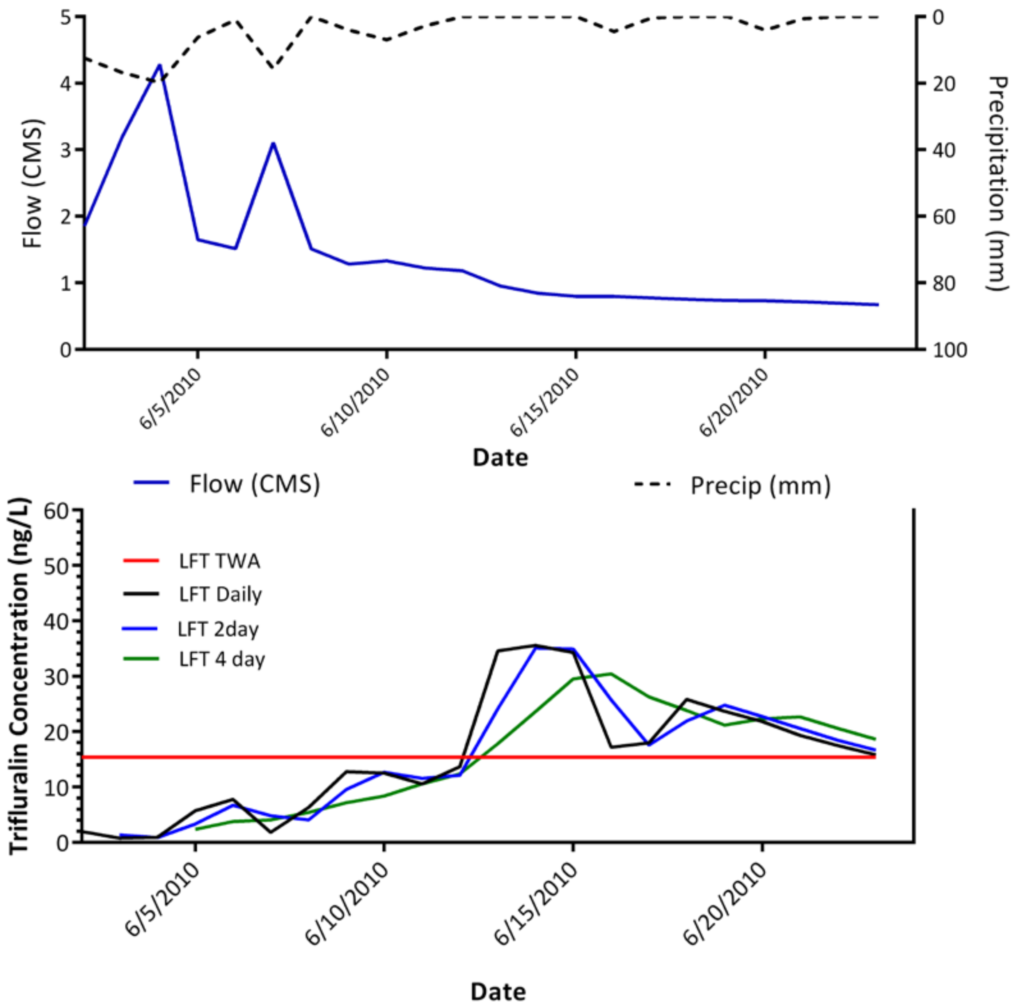

Figure 4.4. Daily precipitation and flow during trifluralin maximum TWA deployment period. Potential daily, 2 day, and 4 day trifluralin concentrations contributing to PSD TWA concentration.

Table 4.3. Daily, 2 day, and 4 day average peak concentrations of trifluralin derived from maximum PSD TWA concentrations based on SWAT model simulations compared with acute toxicological endpoints evaluated in NMFS Biological Opinion (NMFS 2012) reported as ng/L.

		Concentration Range of Observed Effect (ng/L)					
	Estimated Maximum Concentration (ng/L)	Fish Survival (LC50)	Vertebral Deformities (NOAEC, 16-96hr Exposure)	Swimming Behavior	Olfactory-Mediated Behaviors	Prey Survival (EC50)	Aquatic Plant (EC50)
Daily	35.6	13000-660000	3000-23000	-	-	251000	22000-81000
2 Day	35.1						
4 Day	30.4						

Chapter 5 – Conclusions

Pesticide exposure in surface waters can be assessed using two methods, through monitoring or modeling. Monitoring data has the advantage of providing actual measures of concentrations to which organisms may be exposed. However, due to the variability in pesticide concentrations in surface waters as a function of site specific conditions, the number of samples that is required to characterize the full range of exposure concentrations is virtually impossible to collect using sampling techniques commonly employed in pesticide surface water monitoring. Modeling on the other hand is used to estimate expected environmental concentrations based on mathematical descriptions of the processes that influence pesticide fate. This can be advantageous as it can provide estimates of exposure concentrations over a wide range of scenarios that can be tailored to represent expected environmental conditions. Models, no matter how well parameterized, are estimations of exposure rather than actual measures. A third option is to utilize both monitoring and modeling methods to inform each other and provide a better understanding of potential exposure patterns. The goal of this dissertation was to demonstrate the use of passive sampling techniques and watershed scale ecohydrological modeling to provide a systems based approach to reducing uncertainty in pesticide exposure to juvenile salmonids in sensitive habitats. The use of continuous monitoring in conjunction with a model that is able to characterize the complex environmental processes that result in off-target pesticide leverage the benefits of both tools in assessing exposure.

Characterizing exposure of juvenile salmonids in freshwater environments as a result of co-occurrence with pesticides presents a challenge given the spatial and temporal variability of both salmonid and pesticides. The use of passive sampling techniques demonstrated in Chapter 2 allows for continuous monitoring or pesticide concentration in critical habitats defined for ESA listed Pacific salmonids. Continuous monitoring reduces the temporal uncertainty in characterizing exposure as it provides a measure of exposure at any time period when juvenile salmonids might be present. Additionally, passive sample devices can be used to characterize exposure of juvenile salmonids in off-channel and shallow water habitats. The longer deployment periods allow for the PSDs to sequester and concentrate trace contaminants such as pesticides in freshwater habitats that are not routinely sampled. Given the concern regarding pesticide exposure in off-channel habitats, PSD monitoring showed that under current use practices in the Pudding River subbasin time-weighted average concentrations of 8 current use pesticides did not exceed any levels of concern in relation to chronic exposure of either juvenile salmonids themselves or components of their critical habitat. Realizing that PSD monitoring results in time-weighted average concentrations and that pesticide concentrations in surface waters can fluctuate on a scale of hours to months, additional characterization of the system is necessary to estimate the potential for acute exposures within the deployment period of the PSD to occur.

The SWAT model was used to evaluate pesticide use practices in the Zollner Creek watershed in relation to the PSD monitoring results. Zollner Creek was chosen for this evaluation due to the higher frequency of detections and often higher levels of detections of pesticides in the monitoring study. Zollner Creek represents a watershed that is potentially sensitive to pesticide surface water loading due to the high percentage of agricultural lands and low flow conditions compared to other watersheds sampled.

As pesticide fate in the SWAT model is driven by hydrology, it was important to parameterize the model such that it could reasonably simulate hydrologic conditions in the watershed. Model simulations based solely on readily available GIS data sets that are commonly used to parameterize SWAT model applications resulted in an unacceptable fit of observed stream flow in the watershed. Refinements in model parameterization were focused on incorporating more local knowledge of the watershed rather than mathematical optimization of input variables. Model simulations were most improved when utilizing spatially distributed precipitation data rather than data from a single gage station outside of the watershed. The change in precipitation inputs improved model estimations of peak flows and reduced the overestimation of recession flows following peak events. While the inclusion of stream channel measurements and refined land use/land cover data did not have a significant impact on stream flow, they did provide important knowledge of the system that was used to evaluate hydrologic contributions as well as pesticide fate. The incorporation of artificial drainage in watershed simulations also improved model performance providing a better fit of baseflow conditions. With a more accurate characterization of precipitation and representation of tile drainage in the system, the SWAT model was able to provide a good fit of average daily stream flow which indicates an accurate characterization of hydrology.

The SWAT model was able to simulate the patterns of pesticide concentration observed in the PSD monitoring for chlorpyrifos and trifluralin. Knowing that pesticide transport to surface waters is driven by hydrology in the SWAT model and based on the fit of the hydrologic data, the ability of the model to recreate the patterns of pesticide concentration indicate that pesticide fate processes were well characterized. While the patterns of pesticide concentrations estimated by the model were similar to the observations, the magnitude of the concentrations was not. The inability of the model to accurately simulate the magnitude of chlorpyrifos and trifluralin time-weighted average concentrations is most likely due to limitations and uncertainty in the pesticide used data used to parameterize the model. Pesticide applications in the model were parameterized based on recommended practices and not actual use records. With a better understanding of the actual pesticide used practices within the watershed, model performance would be expected to improve due to the ability of the model to simulate pesticide fate.

A demonstration of leveraging modeling with monitoring was also presented. The similarity between patterns of chlorpyrifos and trifluralin time-weighted average concentrations estimated by the model and observed with PSDs, particularly for peaks in concentration, suggest that model simulation of pesticide fate processes are well characterized by that model. As such, the daily fluctuations in pesticide concentration simulated by the model can be used to estimate the fluctuations in pesticide concentration sampled by the PSDs that were integrated into the time-weighted average concentration measured. The model in this case provides the systems level understanding of the site specific variables that influence pesticide fate and the PSDs provide the real world measures of the result of these processes. Combining the data can be used to extract acute exposure patterns from the time-weighted average and provide a means to estimate the peak concentrations to which juvenile salmonids or components of their critical habitat may be exposed.

Demonstration of the combination of modeling and continuous monitoring in the Zollner Creek watershed helps to verify the ability of the SWAT model to simulate pesticide fate at the watershed scale. However, several issues still need to be addressed. First, SWAT model performance was evaluated only in relation to two pesticides that fall within the sampling capabilities to the PSDs utilized in the study. In addition to these pesticides, there are many more that are recommended for use in the Zollner Creek watershed that are not sequestered by the LFT PSDs. Further characterization of the temporal trends in the concentrations of these pesticides might be evaluated utilized PSDs constructed of different polymers such as silicone and used to verify SWAT model performance. Second, the ability to characterize exposure to a limited range of pesticides does not fully address the issue of exposure to mixtures of pesticides. With a model verified for a wider range of pesticides and adequate records of pesticide use practices, the model could be used to assess exposure patterns to mixtures of pesticides applied in the watershed. Finally, pesticide exposures evaluated in this study are characteristic of practices in the Pudding River subbasin. This subbasin of the Willamette River only represents a small portion of the critical habitat defined for the Upper Willamette River Chinook and Steelhead ESUs. Geospatial analysis can be utilized to identify additional watersheds within the geographic boundaries of the Upper Willamette River ESUs that demonstrate similar characteristics to the Zollner Creek watershed. The modeling could be used in these similar watersheds to assess potential exposure patterns in other portions of the critical habitat defined for ESA listed Pacific salmonids.

The focus of this work was to demonstrate the utility of employing passive sampling techniques and watershed scale to develop an understanding of the complex relationship between land management practices and aquatic pesticide exposure. Uncertainty will always be an issue in pesticide exposure characterization due to the dynamic nature of pesticide transport. The coupling of monitoring and modeling methods to develop a systems level understanding of the complex processes associated with pesticide transport however can provide a means of reducing that uncertainty in order to more accurately characterize exposure and assess risk.

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