

EMERGING CONTAMINANTS OCCURRENCE AND STREAMFLOW RESPONSES TO
EXTREME CLIMATE CONDITIONS IN AN AGRICULTURAL WATERSHED

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Runoff from agricultural fields is a significant non-point source of pollution to water bodies, as it transports sediments, nutrients, pesticides, and veterinary pharmaceuticals (VA). Climate change intensifies the hydrological cycle, generating more extreme hydrometeorological and climate conditions (EHCC) that lead to floods and droughts. However, there is limited information regarding those impacts on water quality in agricultural areas. The aim of this dissertation is to evaluate the occurrence of VA and streamflow response to EHCC in the Shell Creek (SC) watershed, Nebraska. Streamflow and water quality are simulated using the Soil and Water Assessment Tool (SWAT). VA are detected using Polar Organic Chemical Integrative Samplers (POCIS) and simulated using the pesticide subroutine in SWAT. Model performance is measured by the Nash-Sutcliffe Efficiency (NSE) coefficient. Streamflow response is assessed through statistical analysis of flows and loading pollutants in periods of EHCC. VA concentrations range from 0.0003 to 68 ng/L and some display significant temporal variation. The hydrologic model reproduces monthly flows with NSE of 0.40-0.92. It overestimates lower flows by 1-2 m³/s in years with very wet and dry summer. A rain gage-forced model simulates medium-flow conditions (10-90th percentiles) closer to observations, although, it overestimates lower flows ($\leq 10^{\text{th}}$) and underestimates higher flows ($\geq 90^{\text{th}}$) up to 0.1 and 1 m³/s, respectively. The water quality model adequately reproduces monthly flows, sediments, and nutrients (NSE = 0.61-0.82). However, it poorly reproduces atrazine and VA (NSE ≤ 0.01). This study demonstrates the utility of POCIS for monitoring ambient levels of pharmaceuticals, and their occurrence confirms that agricultural activities influence surface water quality. Rain gages located outside SC incorporate the spatiotemporal variation of precipitation. Their integration with radar precipitation data can support hydrologic models and bring quantitative information to watershed managers. Continuous water quality monitoring is needed for an adequate implementation of hydrological models in small agricultural watersheds.

DEDICATION

Six years ago, I began to dream of a career in science and technology. The support of my wife Melina and my daughter Antonia helped me to find the forces I needed to overcome the challenges along the way. My dream has become a reality. This achievement belongs to them too.

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Chapter 1 Introduction

Runoff from agricultural fields is a significant non-point source (NPS) of pollution to water bodies. It transports sediments, nutrients, and chemicals (e.g. pesticides) from croplands, which degrade surface water quality. Emerging contaminants such veterinary pharmaceuticals (VA) or beta agonist are found in agricultural watersheds where manure is used as soil amendment or nutrient source. VA are commonly prescribed for prevention and treatment of disease in animals. Their use has increased in recent years. Van Boeckel et al. (2015) estimated a global use of VA of 63.1 thousand tons in 2010 for livestock production, with the USA as the second largest consumer (13%). The Food and Drug Administration (2015) reports that 14,800 tons of VA were distributed in the USA in 2013, which was a 17% increase in four years.

Studies have demonstrated VA occurrence in surface waters from concentrations ranging from hundreds of ng/L to tens of $\mu\text{g/L}$ (Jaimes-Correa, Snow, and Bartelt-Hunt 2015; Bernot, Smith, and Frey 2013; Joy et al. 2013; Kurwadkar et al. 2013; Xian Zhang et al. 2012; Kim et al. 2010; Arikan, Rice, and Codling 2008; Burkholder et al. 2007; Lissemore et al. 2006; Davis et al. 2006). VA occurrence in the environment poses a risk to non-target organisms (Swanton et al. 2011) and represents a threat to public health due to the potential development of antibiotic-resistant bacteria (Truszczyński and Pejsak 2013; Hughes and Andersson 2012; Jjemba 2006). The VA occurrence in surface waters are commonly evaluated using grab sampling methods (Kurwadkar et al. 2013; Bernot, Smith, and Frey 2013; Xian Zhang et al. 2012; Arikan, Rice, and Codling 2008; Lissemore et al. 2006). However, grab samples are limited in their ability to detect low concentrations of pollutants like VA that quickly dissipate or enter the water body in discrete events. Passive samplers

such as Polar Organic Chemical Integrative Sampler (POCIS) are used less frequently (Jaimes-Correa, Snow, and Bartelt-Hunt 2015; Matthiessen et al. 2006), but POCIS is a useful tool to evaluate water-soluble compounds like VA at concentrations often below detection limits of traditional methods.

Another water quality concern from agricultural runoff is the fate of pesticides. Gilliom et al. (2006) estimated that in US agricultural areas 75% surface waters and 40% shallow groundwater in 1992-2001 contained atrazine or its metabolites. Atrazine is a synthetic herbicide to control broadleaf and grassy weeds in corn, sorghum, and sugarcane crops in the growing season. Wu et al. (2010) found atrazine as the most detected pesticide in 20 US watersheds. Official reports by USGS (2012) indicate that about 60-70 million pounds of atrazine were applied annually between 1992 and 2009 in the USA.

Atrazine application has generated a wide controversy because of human health concerns. Although evidence suggests that exposure to atrazine can induce reproductive cancers in rats and mice, it has not been determined to be its causal agent (Alavanja, Hoppin, and Kamel 2004). Moreover, atrazine has not been found to promote breast cancer (Mills and Yang 2006; Hopenhayn-Rich, Stump, and Browning 2002). On the other hand, pesticides represent a risk for aquatic organisms. Adverse effects include bioaccumulation in some invertebrates and fish, reductions in reproduction and spawning, tissue abnormalities in fish (Tillitt et al. 2010), and changes in sex of adult frogs and an excess number of females (Hayes et al. 2003). This herbicide can also inhibit photosynthesis, change community structure, and cause the mortality of aquatic flora (U.S. EPA 2006).

Extreme hydrometeorological and climatic events such as hurricanes, tornados, extreme precipitation, floods, and droughts have increased in intensity during the 20th

century, driven by climate change (Retchless et al. 2014; Alexander et al. 2006; S. J. Brown, Caesar, and Ferro 2008; Easterling, Meehl, et al. 2000). Floods and droughts represent a risk for human and agricultural infrastructure. As the climate continues to change, we anticipate more intense and frequent precipitations, and it is expected that agriculture runoff can occur at larger magnitudes and frequency. Conversely, prolonged droughts limit water supply for communities and drastically reduces agricultural yields.

Discontinuous, heterogeneous, and variability in temporally-monitored data limits diagnostic and prognostic studies of extreme climate effects on small watersheds. Multiple sources of data such as radar sensors (radar) and rain gages can complement each other to validate long-term records of precipitation and aid the analyses of extreme climate conditions, especially in rain-ungaged watersheds. While radar represents a high-resolution and high-frequency monitoring tool, rain gage integrates long-term records of climatological stations collecting punctual precipitation data. However, these sources of precipitation poorly address combined long-term and watershed-specific needs of data. Further, increasing incidence of extreme hydrometeorological and climate events and needs of analyses to manage water and agricultural resources at watershed-scale led to integrate available data and modeling resources. Thus, a representation of changes across spatiotemporal scales requires an assessment of the hydrologic responses to climate conditions at watershed scales.

Hydrological modeling of watersheds is a powerful tool that can be used for many applications, including forecasting, evaluation of management practices, assessment of future climate conditions, optimization of data collection, and representation of rainfall-runoff processes. For example, the Soil and Water Assessment Tool (SWAT) (Arnold et al. 1998) is

an open-source semi-distributed model that has been used to simulate water quantity and quality of different watersheds worldwide.

Despite the evidence that VA enter surface waters from agricultural practices and the potential human health and ecological impacts of these emerging contaminants, a few studies have evaluated not only their occurrence, but also the spatiotemporal variability in agricultural watersheds (Kurwadkar et al. 2013; Xian Zhang et al. 2012; Arikan, Rice, and Codling 2008). Furthermore, to the best of our knowledge, antibiotic occurrence at the watershed scale has not been previously simulated. A limitation on the use of numerical models for VA is the lack of monitored data.

Hence, a series of research questions were evaluated to address the lack of information and modeling on emerging contaminants. First, how does streamflow respond to extreme precipitation surplus and deficits in a highly agricultural watershed? Can the occurrence of VA be modeled using the pesticide routing of the hydrological model SWAT? To answer these questions, the aims of this dissertation are (1) Evaluate VA occurrence using POCIS in a highly agricultural watershed of Nebraska, (2) Quantify the streamflow response to extreme hydrometeorological and climatic conditions (EHCC) in an agricultural watershed using SWAT, and (3) test SWAT capability on modeling VA using its pesticide routing. This dissertation is organized as follows. Chapter 2 describes the occurrence of VA in Shell Creek, Nebraska. Chapter 3 describes the sensitivity of flow responses to EHCC using a modeling and statistical approach. Chapter 4 illustrates the water quality responses to EHCC and presents the modeling of VA using the pesticide simulation routine of SWAT. General conclusions and future directions are summarized in the final chapter.

Chapter 2 Seasonal Occurrence of Veterinary Antibiotics and a Beta Agonist in an Agricultural Watershed

This chapter is published:

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2.1 Introduction

The occurrence of veterinary pharmaceuticals in surface water is of significant concern due to their potential human health and ecological impacts. These compounds can enter surface water through illicit or accidental wastewater discharge, or in storm runoff from agricultural fields fertilized with manure from animals that were administered pharmaceuticals (Davis et al. 2006; Kim et al. 2010; Joy et al. 2013). Although there is significant evidence showing that pharmaceuticals can be transported to surface water in runoff from land-applied manure, to date a limited number of studies have evaluated the fate and persistence of veterinary pharmaceuticals in surface waters in agricultural watersheds.

Antibiotics are commonly prescribed to humans and livestock for prevention and treatment of disease. Beta-adrenergic agonists stimulate skeletal muscle growth of livestock species (Beermann 2002). Ractopamine, sold as a feed additive, is used to promote weight gain (Centner, Alvey, and Stelzleni 2014) and is administered to swine (Alder et al. 2010) and cattle (Koontz et al. 2010). The Center for Disease Control (CDC) has estimated that 50 million pounds (~2.26 million kg) of antibiotics are produced in the United States annually, with approximately 40 percent used in agriculture (Nawaz et al. 2001). Antibiotics administered to animals are excreted in manure, and up to 90% may be released unmetabolized (Jjemba 2006). Antibiotic concentrations in manure range from trace levels to hundreds of mg/kg, e.g. from 1 to 1,400 mg/kg dry weight (Joy et al. 2013; Ji et al. 2012; Zhao, Dong, and Wang 2010; Martínez-Carballo et al. 2007; Kumar et al. 2005).

The occurrence of veterinary pharmaceuticals in the environment may pose a human health risk as they may be linked to the proliferation of antibiotic resistance (Jjemba 2006; Hughes and Andersson 2012; Truszczyński and Pejsak 2013). Some are structurally similar

to pesticides (e.g. fluconazole vs. azaconazole; sulfanilamide vs. asulam) and may also impose a risk to non-target organisms (Swanton et al. 2011). For instance, lomefloxacin, sulfamethoxazole, and chlortetracycline are toxic for *Lemna gibba* at effective concentrations of 38, 37 and 114 µg/ml, respectively (Brain et al. 2004).

Potential adverse effects of veterinary pharmaceuticals on microorganisms, aquatic life, and human health have motivated the evaluation of their environmental occurrence, especially in waters receiving municipal wastewater treatment plant effluents (D A Alvarez et al. 2005; Moldovan 2006; Ying, Kookana, and Kolpin 2009; Watkinson et al. 2009). In contrast, fewer studies have analyzed the occurrence, temporal, and spatial variability of veterinary pharmaceuticals in water bodies within predominantly agricultural watersheds (Arikan, Rice, and Codling 2008; Kurwadkar et al. 2013; Xian Zhang et al. 2012). Tetracyclines, and sulfonamides and monensin have been detected in agricultural watersheds (Kurwadkar et al. 2013; Lissemore et al. 2006; Arikan, Rice, and Codling 2008; Xian Zhang et al. 2012), and evidence suggests that there are temporal trends in their concentration. Typical concentrations of veterinary pharmaceuticals measured in agricultural watersheds range from hundreds of ng/L to tens of µg/L (Lissemore et al. 2006; Kurwadkar et al. 2013).

Traditionally, grab sampling methods are used to evaluate the occurrence of pharmaceuticals in aquatic environments. The efficacy of grab samples can be limited when evaluating low concentrations of pollutants, especially pollutants that dissipate quickly or enter the water body in discrete temporal events. An alternative is to use passive samplers such as the Polar Organic Chemical Integrative Sampler (POCIS) (D A Alvarez et al. 2005). POCIS is useful for evaluation of water-soluble compounds like veterinary pharmaceuticals

where concentrations may be below detection limits in grab samples. The technique is efficient due to the ease of deployment and does not require collecting or processing multiple water samples (D A Alvarez et al. 2005). It has been used to provide TWA concentration of pharmaceuticals at locations for periods of weeks to months (David A Alvarez et al. 2004; Matthiessen et al. 2006; S. L. Bartelt-Hunt et al. 2009).

In this study, the occurrence of 12 veterinary antibiotics and a beta agonist in the Shell Creek watershed, Nebraska was evaluated. POCIS devices were deployed at eight stations simultaneously from September 2008 to October 2009. The goal was to assess the temporal variation in the occurrence of dissolved pharmaceuticals in an agricultural watershed.

2.2 Methods

2.2.1 Study area

The Shell Creek watershed drains approximately 1,200 km² in east-central Nebraska and is located primarily in Boone, Madison, Platte and Colfax counties of Nebraska. The towns of Schuyler, Platte Center, Lindsay, and Newman Grove are located in the watershed, and the city of Columbus is directly to the south. Shell Creek has three major tributaries in the watershed: Elm Creek, Loseke Creek, and Taylor Creek (Figure 2.1).

The watershed is a heavily agricultural region with a high percentage of the land in irrigated row crops (46%). The counties comprising the watershed include approximately 1,550 farms with over 1,050,000 head of swine, cattle, and poultry (USDA-NASS 2012). Land cover types include cultivated (78.2%), herbaceous (14.6%), and forest (1.85%); while developed urban areas cover only 4.4% of the watershed (Figure 2.1b). In this region, veterinary antibiotics are commonly administered prophylactically for disease prevention as well as for disease treatment. Animals are typically raised in confined animal feeding operations (CAFO) where they are confined to production barns (swine and poultry) or feedlots (cattle). Manure from livestock facilities is typically collected and land applied to agricultural fields as a soil conditioner and fertilizer. The five towns in the watershed combined have a population of 1,675 people (U.S. Census Bureau 2010). The daily discharge at the USGS gage station (Figure 2.1a) averages 1.40 ± 5.13 m³/s in 1947-2014, and the average annual precipitation is 671 ± 159 mm/year between 1910 and 2014.

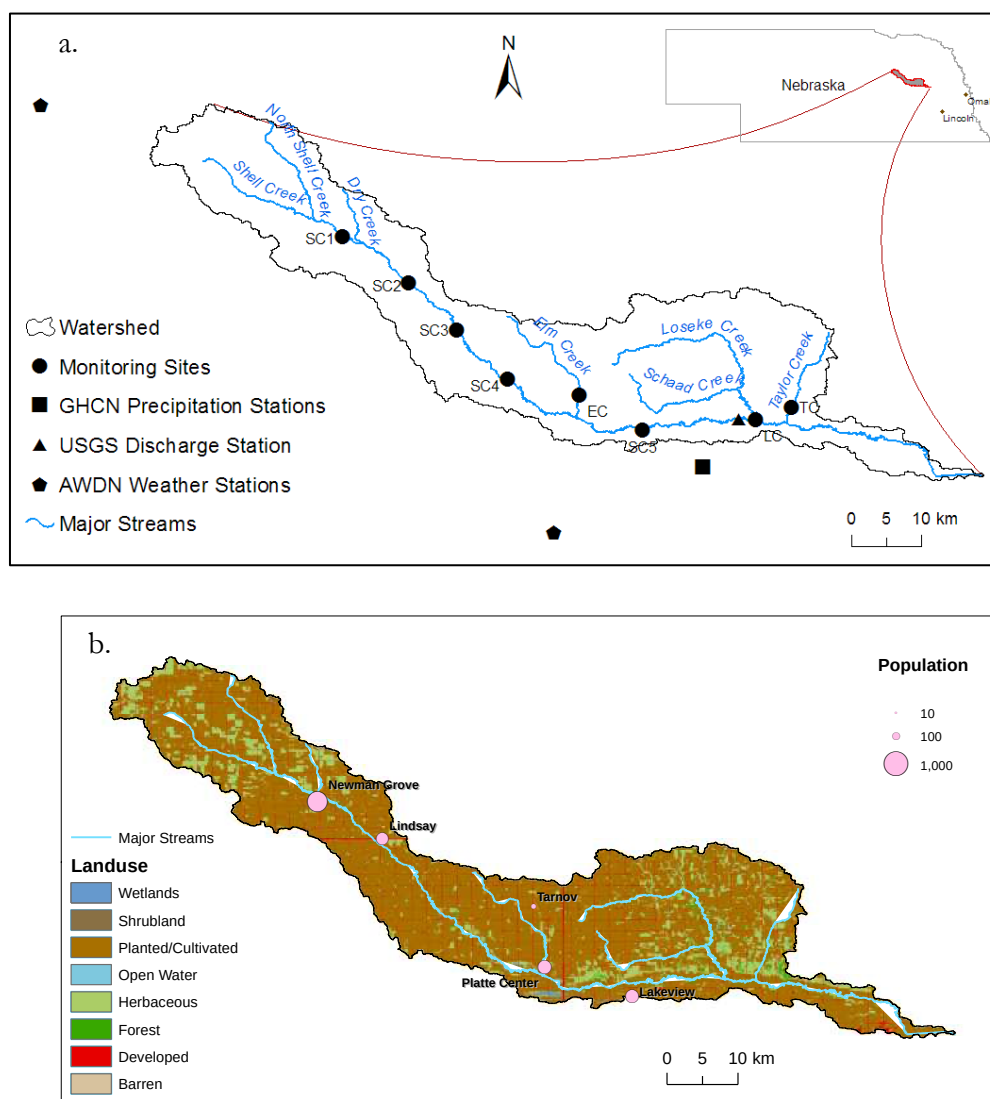


Figure 2.1 Shell Creek watershed (a) monitoring stations and (b) land use

In 2008, sampling was conducted at 7 stations within the Shell Creek watershed. Another site was included in 2009 to monitor the water quality near headwaters. Figure 2.1a shows the location of the stations. POCIS, holders, and deployment canisters were obtained from Environmental Sampling Technologies (EST Inc., St. Joseph, MO). In this study, a pharmaceutical POCIS with a surface area of 41 cm² filled with 200 mg of OasisTM HLB

sorbent (Waters Corporation, Milford, MA) were used. At each sampling station, POCIS were deployed in triplicate in a stainless steel canister and secured in place using a metal stake. POCIS were deployed in September 2008 through November 2008 and June 2009 through October 2009 at each station for exposure periods ranging from 22 to 52 days (Table 2.1). At the end of each exposure period, POCIS were retrieved, disassembled, rinsed gently with purified reagent water, and stored at -20°C until processing for analysis. Data on the mass of each compound recovered from the POCIS were converted to aqueous concentrations using the laboratory uptake rates reported in Bartelt-Hunt et al. (2011) and presented in Table 2.2.

Table 2.1 Exposure periods

Year	Month	Exposure period (days)	Collection date (mm/dd/yyyy)
2008	Sep.	22	09/26/2008
	Oct.	34	10/30/2008
	Nov.	26	11/25/2008
2009	June	26	06/18/2009
	July	32	07/20/2009
	Aug.	44	09/02/2009
	Sep.	41	10/13/2009
	Oct.	52	12/04/2009

2.2.2 Solvents and Internal Standards

Reference materials, metabolites, and standards were obtained from Sigma-Aldrich (St. Louis, MO). Phenyl-¹³C₈-sulfamethazine, used as a labeled internal standard, was purchased from Cambridge Isotopes (Andover, MA). Roxithromycin (Sigma-Aldrich, St. Louis, MO) was used as an internal standard for macrolide group antibiotics and lincomycin.

Solvents used in sample preparation were high purity grade (OPTIMA, Fisher Scientific, Waltham, MA).

2.2.3 POCIS Extraction Methodology

Handling and elution of POCIS followed procedures described previously (David A Alvarez et al. 2004; Jones-Lepp et al. 2004). After disassembly, the sorbent contents of each POCIS were transferred using approximately 20 mL of high-purity methanol directly into silane-treated vials. Vials containing the methanol and sorbent were held at -20°C until they could be processed for analysis.

Target compounds were eluted from the sorbent by loading the slurry and passing an additional 50 mL of high-purity methanol through silane-treated glass gravity flow chromatography columns into 120 mL evaporation tubes (RapidVAP, Labconco, Kansas City, MO). Approximately 1 ng phenyl-¹³C₈-sulfamethazine, doxycycline, and roxithromycin internal standards were added to the elute and used for quantification. Extracts were evaporated under nitrogen to approximately 1 mL and quantitatively transferred to autosampler vials for analysis by liquid chromatography tandem mass spectrometry (LC/MS/MS). Standards and spiking solutions were prepared from stock solutions (5 µg/µL) in methanol. Calibration solutions (2, 5, 12.5, 25, and 50 pg/µL) were prepared in 50:50 methanol and water. All standards and extracts were stored in amber vials at -20°C.

2.2.4 Liquid Chromatography-Tandem Mass Spectrometry

POCIS extracts were analyzed for thirteen veterinary pharmaceuticals, as listed in Table 2.2. These pharmaceuticals were selected for analysis as they are commonly used in animal production. Standards and extracts were analyzed on a Quattro Micro triple quadrupole with a Waters 2695 high-pressure liquid chromatography (HPLC) and

autosampler. Electrospray ionization in positive ion mode was used for detection of target compounds by multiple reaction monitoring (MRM) with argon collision gas. A Thermo (Bellefonte, PA) Betabasic-18 column (250x2.1 mm, 5 μ m, 50°C) was used for separation at a flow rate of 0.2 ml/min with a gradient of methanol with 0.1% formic acid in water. Mass spectrometer operational parameters were optimized by infusing each compound separately. The source conditions were: capillary 2.5 kV, extractor 2 V, RF lens 0.8 V, source temp 90°C, desolvation temp 400°C, cone gas flow at 30 L/hr, and desolvation gas flow at 700 L/hr. Compound retention times, ionization modes and MRM transitions are listed in Table 2.2.

A five-point internal standard calibration curve was used for quantification of each analyte. Phenyl-¹³C₈-sulfamethazine was used for sulfa antibiotics, and roxythromycin was used as the internal standard for all other target compounds. Based on the variability of the lowest standard (2 pg/ μ L), the estimated detection limits for most compounds are less than 1 pg/ μ L, corresponding to 1 ng recovered from the POCIS. Recovery of target compounds was checked by analysis of fortified blanks spiked with known amounts of each compound and ranged between 62.2% and 153% (Table 2.2). Two laboratory reagent blanks were processed with the POCIS samples, with all compounds below instrument detection limits. Additional information on the analytical methods and determination of uptake rates is included in Bartelt-Hunt et al. (2011) and Bartelt-Hunt et al. (2011).

2.2.5 Statistical analysis

Initially, a one-way ANOVA to assess differences for mean concentrations of veterinary pharmaceuticals was performed. Secondly, for each antibiotic, one-way ANOVAs were used to determine significant differences ($p < 0.01$) within stations (e.g. SC1, SC2),

years (2008 and 2009) or months (June-November). The ANOVA tests the null hypothesis that all samples in a group have the same mean. If the p -value tends to zero, the null hypothesis can be neglected and suggests that at least one sample mean is significantly different. When such difference exists in mean concentrations of samples within a group, the Tukey's multiple comparison tests were applied to evaluate which samples are significantly different at the 95% confidence interval ($p < 0.05$).

Table 2.2 Uptake rates, LC/MS/MS analytical parameters, and method detection limits for the veterinary pharmaceuticals evaluated

Compound	Use	CAS No. †	Molecular Weight	Rs‡ (L/d)	Retention time (min)	Precursor ion (m/z)	Product ion (m/z)	MDL (ng/g)	Reporting limits (ng/g)	Recovery (%)
Veterinary and Human Antibiotics										
Erythromycin	Macrolide antibiotic	114-07-8	733.93	0.253	10.6	733.9	575.9	0.023	0.02	86.8
Lincomycin	Macrolide antibiotic	154-21-2	406.54	0.233	7.2	407	359	0.011	0.02	111.9
Monensin	Ionophore antibiotic	17090-79-8	670.88	0.205	13.2	688.1	635.2	0.001	0.02	62.2
Sulfachloropyridazine	Sulfonamide antibiotic	23282-55-5	306.7	0.177	7.7	285	156	0.015	0.02	153.3
Sulfamethazine	Sulfonamide antibiotic	57-68-1	278.33	0.243	7.5	279.1	156	0.008	0.02	105.7
Sulfadimethoxine	Sulfonamide antibiotic	122-11-2	310.33	0.291	8	311.1	156	0.002	0.02	124.0
Sulfamethazole	Sulfonamide antibiotic	144-82-1	270.34	0.066	7.7	271.1	156	0.012	0.02	108.2
Sulfamethoxazole	Sulfonamide antibiotic	723-46-6	253.28	0.118	7.7	254.1	156	0.014	0.02	102.9
Sulfamerazine	Sulfonamide antibiotic	127-79-7	264.31	0.191	7.4	265.1	156	0.014	0.02	100.5
Sulfathiazole	Sulfonamide antibiotic	72-14-0	255.32	0.187	7.3	256.1	156	0.014	0.02	125.5
Tylosin	Macrolide antibiotic	1401-69-0	916.1	1.33	9.7	915.9	771.9	0.002	0.02	64.4
Tiamulin	Antimicrobial	55297-96-6	609.82	0.314	10.6	493.9	191.9	0.018	0.02	83.1
Growth Promotants										
Ractopamine	beta-agonist	97825-25-7	301.38	0.302	7.3	302.2	164.2	0.007	0.02	134.4

†CAS: Chemical Abstracts Service Registry Numbers. ‡Rs: Turbulent sampling rates at 22°C. Sources: ^{33,35}

2.3 Results and discussion

2.3.1 Occurrence of veterinary pharmaceuticals

The TWA concentrations (ng/L) of thirteen veterinary pharmaceuticals were determined at each of eight sampling stations in Shell Creek between September 2008 and October 2009 (Table 2.3 and Table 2.4). Twelve pharmaceuticals were detected in at least one sampling event with concentrations ranging from 0.0003 ng/L to 68 ng/L as shown in Figure 2.2, where the split box shows the 25th, 50th, and 75th percentiles, and whiskers indicate the 5th and 95th percentiles. Erythromycin was only found at station SC5 in July 2009 with an estimated concentration of 0.024 ng/L, and sulfathiazole, at station LC in October 2009, at a concentration of 0.75 ng/L. One compound, sulfamerazine, was detected at concentrations below the detection limit in POCIS extracts (0.02 ng/g) at all sampling locations.

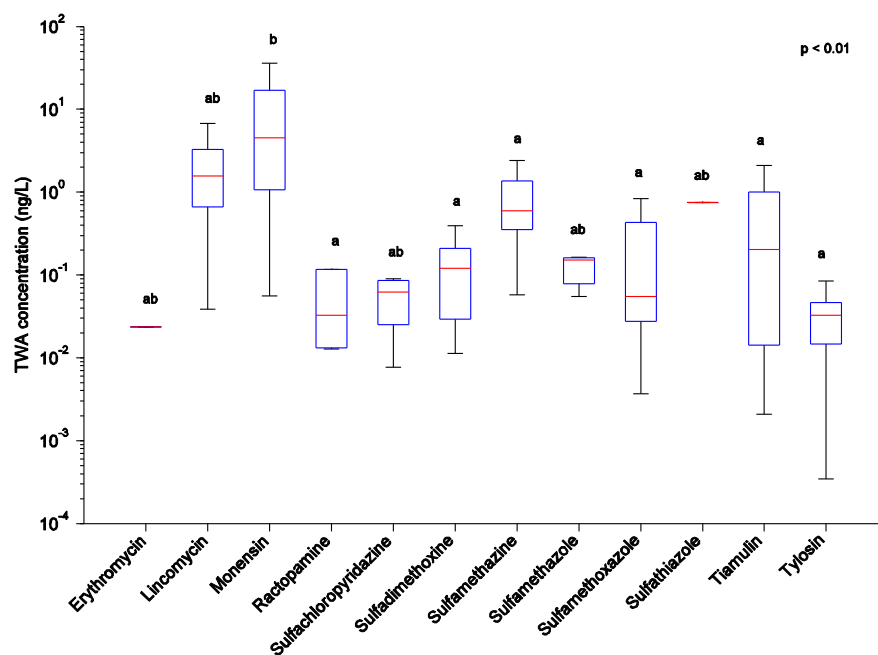


Figure 2.2 Distribution of pharmaceutical concentrations in Shell Creek, 2008-2009

The compounds detected at the highest TWA concentrations in Shell Creek were lincomycin (68 ng/L) and monensin (49 ng/L). Tiamulin, sulfadimethoxine, and sulfamethazine had maximum concentrations of 2.6, 3.9, and 13 ng/L, respectively. Dissolved concentrations of the beta agonist, ractopamine, three sulfonamide group antibiotics sulfachloropyridazine, sulfamethazole, sulfamethoxazole, and the macrolide tylosin were estimated at average concentrations less than 1 ng/L.

ANOVA reveals significant differences in mean concentrations of veterinary pharmaceuticals ($p < 0.01$). Results from Tukey's multiple comparison test are represented by letters. Antibiotics with similar letters (e.g. 'a' and 'ab') had no significant differences in mean concentrations ($p > 0.05$) while different letters (e.g. 'a' and 'b') had significant differences ($p < 0.05$).

2.3.2 Detection frequencies

Lincomycin (85.5%), monensin (94.5%), tiamulin (89.1%), and sulfamethazine (94.5%) exhibited detection frequencies consistent with a study in the Grand River, Canada. It reported frequencies of lincomycin, monensin, and sulfamethazine of 91.2%, 75.2%, and 32.8%, respectively (Lissemore et al. 2006). The high detection frequencies of sulfonamides and lincosamides ($> 40\%$) confirmed that agricultural runoff from soils receiving animal manure influences the surface water quality of Shell Creek.

Table 2.3 Concentration of pharmaceuticals in Shell Creek in 2008

station	month	Lincomycin		Monensin		Sulfamethazine		Tiamulin		Tylosin	
		mean	SD [¶]	mean	SD	mean	SD	Mean	SD	mean	SD
SC2	Sep.	0.088	0.086	0.53	0.90	0.47	0.30	0.0027	0.0016	0.022	0.0097
	Oct.	0.77	0.30	11	2.6	1.4	0.99	0.0088	0.0035	0.039	0.0052
	Nov.	0.74	0.081	--	--	0.58	0.055	0.0025	0.0010	0.014	0.0032
SC3	Sep.	--	--	0.32	0.54	0.45	0.21	0.0091	0.0094	0.020	0.011
	Oct.	1.6	0.54	27	12	0.94	0.14	0.028	0.0082	0.043	0.024
	Nov.	0.66	0.19	1.5	1.3	1.4	0.69	0.0055	0.0065	0.020	0.0035
SC4 [†]	Sep.	2.1	0.95	18	5.6	0.60	0.13	0.061	0.054	0.038	0.0093
	Oct.	1.8	0.48	35	14	0.70	0.16	0.040	0.012	0.053	0.018
	Nov.	16	16	7.1	3.1	1.0	0.41	0.14	0.12	0.035	0.011
SC5	Sep.	1.8	0.23	5.1	5.1	0.45	0.020	0.0021	0.0014	0.024	0.0046
	Oct.	0.49	0.38	3.6	5.2	0.32	0.14	0.0079	0.0060	0.044	0.032
EC [‡]	Sep.	4.6	0.42	--	--	1.3	0.53	0.0026	0.0010	0.033	0.011
	Oct.	0.85	0.21	2.9	3.0	0.22	0.062	0.014	0.0096	0.081	0.050
	Nov.	0.95	0.21	0.056	0.089	0.26	0.15	0.0057	0.0046	0.079	0.0083
LC	Sep.	2.9	2.7	23	15	1.2	0.51	--	--	0.060	0.012
	Oct.	3.4	0.45	32	2.6	1.6	0.11	0.027	0.0062	0.066	0.0041
	Nov.	6.3	1.6	16	7.6	1.7	0.39	0.014	0.0022	0.063	0.010
TC	Sep.	2.8	1.2	--	--	0.44	0.033	--	--	0.011	0.0029
	Oct.	0.93	0.56	3.9	2.1	0.38	0.091	0.0066	0.0043	0.012	0.0038
	Nov.	0.78	0.28	0.54	0.92	0.39	0.075	0.0041	0.0053	0.015	0.0024

[¶]Concentration units in ng/L; SD: standard deviation of three replicates for each measurement event. -- Below detection limit in POCIS extracts. [†] Ractopamine had **0.013**(0.019) and **0.12**(0.10) ng/L in October and November 2008, respectively, at station SC4. [‡]Sulfadimethoxine had **4.0**(3.2) and **0.21**(0.37) ng/L in September and October 2008, respectively, at station EC. Station SC1 was not monitored this year.

Table 2.4 Concentration of pharmaceuticals in Shell Creek in 2009

station	Month	Lincomycin		Monensin		Sulfadimethoxine		Sulfamethazine		Sulfamethoxazole		Tiamulin		Tylosin	
		mean	SD†	mean	SD	mean	SD	mean	SD	Mean	SD	mean	SD	mean	SD
SC1	June	--	--	0.26	0.25	--	--	0.23	0.11	0.030	0.037	2.1	1.4	--	--
	July	1.6	1.5	0.17	0.17	--	--	0.12	0.17	--	--	1.3	1.2	--	--
	Aug.	--	--	0.25	0.23	--	--	0.082	0.12	--	--	0.55	0.84	--	--
	Sep.	--	--	1.3	0.61	0.10	0.034	0.48	0.14	--	--	0.036	0.058	--	--
	Oct.	0.039	0.063	0.15	0.17	--	--	0.071	0.079	--	--	0.99	1.6	--	--
SC2	June	--	--	6.3	0.41	--	--	0.70	0.11	0.83	0.057	2.0	0.71	--	--
	July	0.68	0.66	0.84	0.47	--	--	0.39	0.16	0.027	0.035	2.1	1.9	--	--
	Aug.	0.42	0.25	7.3	1.5	--	--	1.3	0.41	0.026	0.036	--	--	--	--
	Sep.	0.53	0.29	3.1	1.3	0.11	0.082	0.48	0.16	0.63	0.15	0.39	0.68	--	--
	Oct.	--	--	4.0	1.1	--	--	--	--	--	--	0.22	0.23	--	--
SC3	June	6.8	7.1	12	3.9	0.078	0.11	0.31	0.22	0.082	0.072	--	--	0.0075	0.012
	July	0.077	0.13	0.52	0.14	0.19	0.24	0.20	0.28	0.046	0.069	1.6	0.94	--	--
	Aug.	2.2	1.1	49	6.5	0.32	0.29	3.4	1.2	--	--	1.6	0.58	0.085	0.026
	Sep.	0.41	0.18	2.8	1.8	0.15	0.23	0.50	0.28	0.53	0.23	1.0	0.75	--	--
	Oct.	1.0	0.89	16	6.2	--	--	13	0.72	0.0037	0.0007	0.028	0.045	0.0086	0.011
SC4	June	0.34	0.49	28	5.5	0.026	0.020	1.2	0.27	--	--	0.057	0.094	--	--
	July	--	--	0.82	0.17	0.16	0.072	0.34	0.084	--	--	0.49	0.10	--	--
	Aug.	1.8	0.88	25	6.3	0.029	0.025	3.1	0.22	--	--	1.1	0.52	0.037	0.012
	Sep.	2.7	1.3	2.0	0.50	--	--	0.31	0.093	0.11	0.11	0.20	0.078	--	--

	Oct.	0.99	0.47	9.9	7.3	--	--	5.3	1.1	--	--	0.16	0.13	--	--
SC5 †	June	15	8.1	44	24	0.15	0.069	1.2	0.29	--	--	2.6	1.2	0.023	0.039
	July	--	--	0.56	0.46	--	--	0.18	0.15	--	--	2.1	0.45	--	--
	Aug.	3.0	0.80	19	12	0.065	0.11	1.9	0.53	--	--	0.82	1.4	0.0007	0.0005
	Sep.	3.6	1.6	5.0	1.4	0.027	0.025	0.53	0.15	0.055	0.048	0.89	0.81	--	--
	Oct.	0.83	0.74	2.7	0.94	--	--	3.0	0.56	--	--	0.036	0.060	--	--
EC **	June	68	27	1.8	1.4	0.016	0.023	0.36	0.62	--	--	0.95	1.4	0.016	0.021
	July	5.9	3.1	0.44	0.42	0.11	0.18	0.057	0.094	--	--	1.2	0.26	--	--
	Aug.	2.9	2.2	1.9	0.45	0.39	0.094	1.0	0.25	--	--	2.6	0.15	--	--
	Sep.	0.32	0.40	3.6	1.7	0.011	0.016	--	--	--	--	0.53	0.32	--	--
	Oct.	0.088	0.11	6.1	2.5	0.75	0.061	--	--	--	--	--	--	0.038	0.0069
LC ‡*§	June	25	8.9	19	12	--	--	2.4	1.4	--	--	--	--	--	--
	July	0.42	0.15	6.2	1.0	0.025	0.038	0.67	0.13	--	--	0.76	0.83	--	--
	Aug.	1.6	0.70	18	3.7	0.21	0.27	2.2	1.1	--	--	0.97	1.0	0.0003	0.0001
	Sep.	4.0	3.0	36	23	--	--	1.3	0.31	--	--	0.65	0.62	--	--
	Oct.	8.5	3.1	8.1	2.8	0.13	0.079	2.9	0.27	--	--	0.026	0.032	--	--

¶ Concentration units in ng/L; SD: standard deviation of three replicates for each measurement event. -- Below detection limit in POCIS extracts. † Erythromycin had **0.024**(0.036) ng/L on July 2009 at station SC5. ‡ Sulfathiazole had **0.75**(0.68) ng/L on October 2009 at station LC. * Ractopamine was found in four months with a maximum of **0.54**(0.38) ng/L on June 2009 at station LC. ** Sulfachloropyridazine was found in four months with a maximum of **0.090**(0.15) ng/L on August 2009 at station EC. § Sulfamethazole was found in three months with a maximum of **0.16**(0.27) ng/L on August 2009 at station LC.

2.3.3 Comparison with other Agricultural watersheds

Although various studies investigating antimicrobial occurrence in agricultural watersheds have considered different compounds and commonly utilized grab sampling methods, some comparisons can be made (Table 2.5). The peak concentration of lincomycin detected in Shell Creek (68 ng/L) is similar to found in Sugar Creek, Indiana (45 ng/L) (Bernot, Smith, and Frey 2013). However, it is lower than in the Grand River, Canada (355 ng/L) (Lissemore et al. 2006). Monensin concentrations in Shell Creek (49 ng/L) are considerably lower than maximum values reported in the Grand River, Canada (1,172 ng/L) (Lissemore et al. 2006), and Bosque River, Texas (3,410 ng/L) (Kurwadkar et al. 2013). Song et al. (Song et al. 2010) also detected monensin concentrations varying from 75 to 189 ng/L in surface waters surrounding animal feeding operations such as swine, cattle, dairy, and poultry.

The highest concentration of sulfamethazine in Shell Creek is comparable to measurements in Maryland and Indiana, but lower than in Canada and China (Table 2.5). The maximum concentration of sulfadimethoxine in Shell Creek is similar to those values in Maryland and China, but smaller than that in Canada. Concentrations of erythromycin, sulfachloropyridazine, and sulfamethoxazole in Shell Creek were lower than the concentrations reported for other agricultural watersheds. Temporal and spatial differences in usage, persistence through treatment and handling, and proximity to sources very likely determine maximum concentrations of individual pharmaceutical residues in each watershed.

Table 2.5 Concentrations of pharmaceuticals in surface waters of agricultural watersheds

Watershed	Location	Area (km ²)	Streamflow (m ³ /s)	Erythromycin		Lincomycin		Monensin		Sulfachloropyridazine		Sulfadimethoxine		Sulfamerazine		Sulfamethazine		Sulfamethoxazole		Sulfathiazole		Tylosin		Reference
				Max. [¶]	Mean [¶]	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	
Grand River	Canada	Na	1.21-13.51	51	5.6	355	12	1,172	44	7	3.6	56	0.66	nd	nd	408	3.2	9	2.8	-	-	tr	tr	(Lissemore et al. 2006)
Jiulongjiang River	China	14,000	na	-	-	-	-	-	-	-	-	1.90	0.89	nd	nd	775.50	170.9	58.30	15.98	-	-	-	-	(Xian Zhang et al. 2012)
Sugar Creek	IN, USA	246	0.046-7.6	-	-	45	5.5	-	-	-	-	bl	bl	bl	bl	60	6 [§]	30	3.9	bl	bl	-	-	(Bernot, Smith, and Frey 2013)
Choptank River	MD, USA	Na	na	-	-	-	-	-	-	5	5	9	2	694	350	6	6	7	3	4	4	-	-	(Arikan, Rice, and Codling 2008)
Shell Creek	NE, USA	1,200	0.33-26.9	0.024	0.024	68	4.5	49	10.2	0.090	0.055	4.0	0.33	bl	bl	13	1.3	0.83	0.22	0.75	0.75	0.085	0.034	This study

[¶] Concentration units in ng/L. - not analyzed. na = not available. nd = not detected. bl = below detection limit. [§] mean. tr = trace

Land uses in Shell Creek are comparable to those reported for other agricultural watersheds where pharmaceutical occurrence in surface water has been assessed. The Shell Creek watershed is characterized by cattle and swine feeding operations, and ~19% of the area is utilized for grazing (Van Liew, Feng, and Pathak 2012). Similarly, the Sugar Creek watershed, Indiana has ~50 animal agricultural sites, and 18 swine and cattle CAFOs (Bernot, Smith, and Frey 2013). The Grand River, Canada receives inputs from livestock operations for cattle, swine, and poultry (Lissemore et al. 2006). Also, the Bosque River watershed, Texas, has 11.7–31.3% of the area used for manure application, and 26.9–45%, for pasture (Kurwadkar et al. 2013). The Choptank River watershed, Maryland, has 62% agricultural land like corn and soybean fields, and it is characterized by poultry houses (Arikan, Rice, and Codling 2008). As all of these watersheds are predominantly agricultural, the occurrence of veterinary pharmaceuticals in the surface waters within these watersheds can be attributed to the land application of manure and other livestock production activities. As observed in Table 2.5, the estimated concentrations are higher in the larger watersheds, which may be due to their larger contributing land area or amounts of livestock waste applied. However, factors contributing to the occurrence of veterinary pharmaceuticals in surface waters in agricultural watersheds have not been elucidated. While land use is one important aspect, parameters such as soil type, slope, and seasonality strongly influence the occurrence of veterinary pharmaceuticals in runoff and surface water.

2.3.4 Spatial and temporal variations

The results from ANOVA analysis indicate there is a significant difference ($p < 0.01$) in mean concentrations of veterinary pharmaceuticals in Shell Creek. Tukey's multiple comparison test is illustrated in Figure 2.2. It reveals that average concentration of monensin (10 ng/L) is significantly ($p < 0.05$) higher compared to ractopamine, sulfadimethoxine,

sulfamethazine, sulfamethoxazole, tiamulin, and tylosin (0.034–1.3 ng/L). Nevertheless, there is no significant difference ($p > 0.05$) between concentrations of erythromycin, lincomycin, sulfachloropyridazine, sulfamethazole, and sulfathiazole (0.024–4.5 ng/L) and any other pharmaceutical.

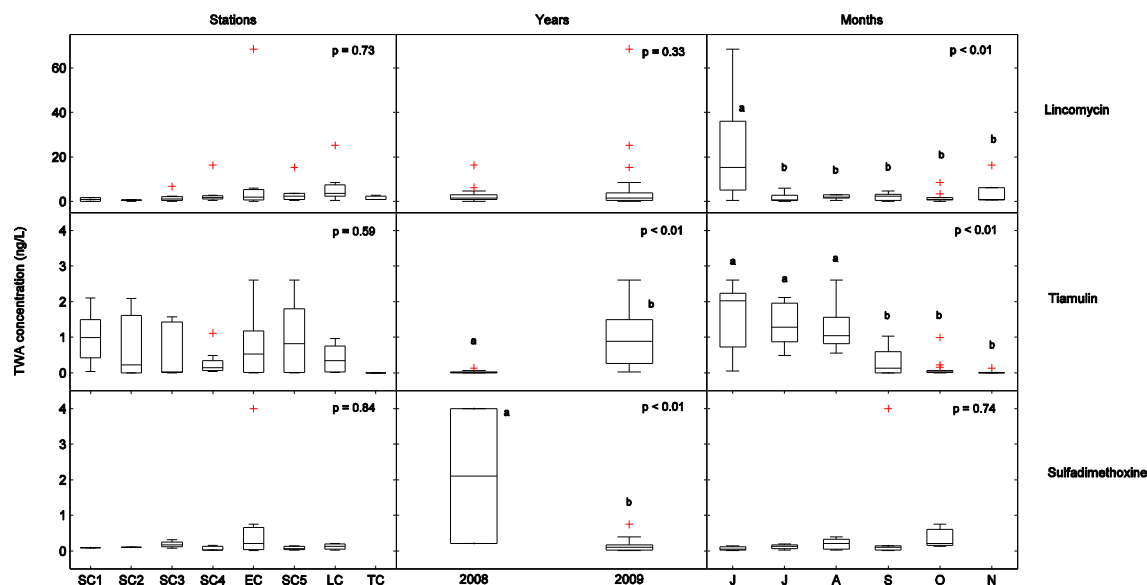


Figure 2.3 Comparison of lincomycin, tiamulin, and sulfadimethoxine concentrations within stations, years, and months in Shell Creek. The split box shows the 25th, 50th, and 75th, whereas whiskers show the 5th and 95th percentiles. ANOVA p -values are shown for each group (stations, years, and months). Significant differences using Tukey's multiple comparison test ($p < 0.05$) are illustrated by different letters.

The veterinary pharmaceuticals detected in Shell Creek do not display a significant ($p > 0.01$) spatial variation. Only lincomycin, tiamulin and sulfadimethoxine show any significant ($p < 0.01$) temporal variation as illustrated in Figure 2.3. Tiamulin and sulfadimethoxine exhibit significant differences ($p < 0.01$) between 2008 and 2009 years. While mean concentration of tiamulin was significantly ($p < 0.05$) higher in 2009 (0.97 ng/L) compared with 2008 (2.1 ng/L), sulfadimethoxine was significantly ($p < 0.05$) lower in 2009

(0.15 ng/L) relative to the previous year (2.1 ng/L). Tiamulin and lincomycin have significant differences ($p < 0.01$) in monthly mean concentrations. Tiamulin is significantly ($p < 0.05$) higher in summer months (1.3–1.5 ng/L) when compared with fall months (0.028–0.32 ng/L). Lincomycin is significantly ($p < 0.05$) higher in June (23 ng/L) than other months (1.6–4.3 ng/L).

Temporal variation of monensin and lincomycin among monitoring stations in Shell Creek are illustrated in Figure 2.5. The maximum concentration of monensin (49 ng/L) occurred on August 2009 at station SC3 while the highest concentration of lincomycin was found during June 2009 at station EC (68 ng/L) (Figure 2.5). Pulses of these antibiotic concentrations could increase driven by rainfall-runoff events in October 2008 and June 2009 (Figure 2.4). Lissemore et al. (2006) observed similar pulses of antibiotic concentrations in the Grand River, Canada, with fluctuations of monensin in July and August, and lincomycin in July and October. Bernot et al. (2013) also detected peaks of lincomycin in July.

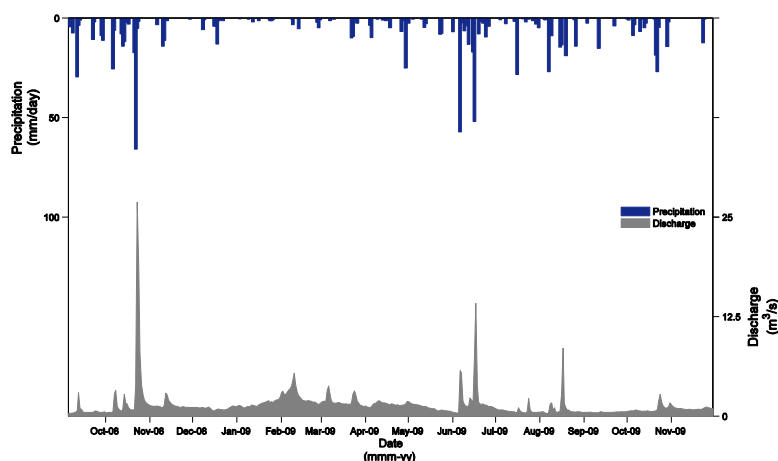


Figure 2.4 Discharge and precipitation in Shell Creek over the study period . Sources: Discharge data from the U.S. Geological Survey (USGS) for the stream site USGS 06795500 at Shell Creek near Columbus, NE. Precipitation data from the Global Historical Climatology Network (GHCN) for the station USC00251825, named COLUMBUS 3 NE.

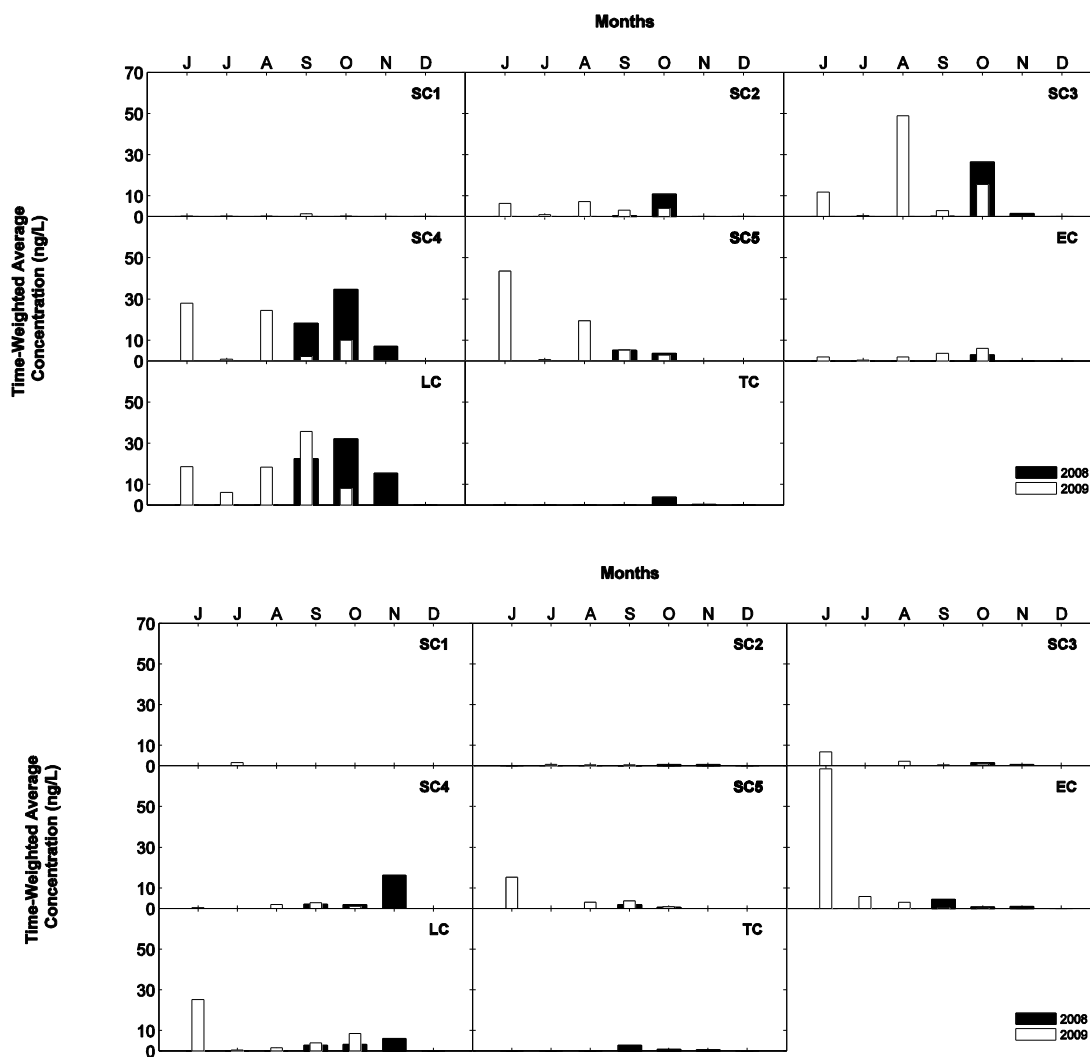


Figure 2.5 Temporal variation of (a) monensin and (b) lincomycin in monitoring stations

2.4 Conclusions

The seasonal occurrence of veterinary pharmaceuticals in the Shell Creek watershed was evident. The study demonstrates the utility of passive samplers like POCIS for the evaluation of low concentration of veterinary pharmaceuticals in surface waters. The high frequencies (40–94.5%) of veterinary pharmaceuticals detected (lincomycin, monensin, tiamulin, sulfadimethoxine, and sulfamethazine) confirms that Shell Creek is heavily influenced by agricultural activities such as land application of manure and livestock production. We identified pulses of monensin and lincomycin concentrations occurring in summer months, corresponding to seasonal rainfall and surface runoff events. Lincomycin, tiamulin, and sulfadimethoxine show a significant temporal difference ($p < 0.01$) in years and months. Results are consistent with other studies that have demonstrated a summer pulse of veterinary pharmaceutical concentrations in agricultural watersheds.

Chapter 3 Streamflow response to extreme wet and dry conditions in a rain-ungaged and agriculturally driven watershed

This chapter is in preparation to submit:

Jaimes-Correa, J. C., Bartelt-Hunt, S. L., & Munoz-Arriola, F. (2017). Streamflow response to extreme wet and dry conditions in a rain-ungaged and agriculturally driven watershed (in preparation). *Journal of Hydrology*.

3.1 Introduction

The occurrence of extreme hydrometeorological and climate events is increasing as a consequence of climate change (Alexander et al. 2006; Easterling, Meehl, et al. 2000; Retchless et al. 2014). Annual precipitation totals have increased at 37% of monitoring stations worldwide in the last century (Alexander et al. 2006) and extreme events in the United States have led to a 10% increase in annual precipitation (Karl and Knight 1998). Projections also suggest an increase in runoff of 10-40% at high latitudes and reduction in runoff of 10-30% at mid-latitudes in western North America by 2050 (Milly, Dunne, and Vecchia 2005). At the watershed scale, tracking the impact of extreme climatic conditions rely on data and models that can capture the changes in the hydrological processes as well as the influence of human activities. The goal of this work is to identify the sensitivity of flow generation to high-order changes in hydrometeorology and climate, represented by intraseasonal and interannual changes in extreme wet and dry conditions.

Understanding the cause-effects between climate change and watershed responses is complex (Van Liew, Feng, and Pathak 2012) due to nonlinear relationships of hydro-meteorological processes and water quantity/quality effects in addition to the lag effects in watershed response. Physical properties of a watershed such as land use, soil type, and topography affect flow generation. Two similar-size agricultural watersheds located 80 km apart in northeastern Nebraska responded differently to wet conditions. Logan Creek (1,990 km²) received 15% less annual precipitation in 1980-2000, but it generated streamflow 50% greater than Shell Creek (1,214 km²) (Van Liew, Feng, and Pathak 2012). Thus, watershed responses are site-specific, and responses vary according to variations in climate. However, it is unclear if such changes in a particular watershed are magnified by very wet and dry conditions and how these changes can be characterized.

Within watersheds, different techniques have been implemented to measure precipitation, from traditional rain gages to field sensors (Next-Generation Radar - NEXRAD) to remote sensing (Global Precipitation Mission –GPM, Tropical Rainfall Measurement Mission -TRMM). Advantages and disadvantages exist for rain gage and radar techniques. Rain gage data accurately estimate precipitation at a single point, although, their locations can be coarse in space and discontinuous in time. The deployment can be constrained by equipment maintenance, cost, and accessibility in remote areas. Nevertheless, rain gage is still the most affordable and accessible source of precipitation data from the field- to watershed-scale, which is critical for farmers and local water managers.

Radar had a finer spatial distribution of precipitation and shorter sampling frequency of interval record. It was developed to address operational needs in precipitation estimates (e.g. Zhang and Srinivasan (2010)), weather and flood forecasting. Radar indirectly estimates precipitation (P) from radar reflectivity (Z) through Z-P relationships, and bias in measures are commonly corrected with rain gage estimates (e.g. Beeson et al. (2011), Zhang and Srinivasan (2010)). Constraints with radar data include a limited historical records and data processing. Raw data requires the development of automatic techniques for extraction, formatting, transformation, and processing of large amounts of information (e.g. Zhang and Srinivasan (2010), Kalin and Hantush (2006), Xie et al. (2005)).

A few studies have evaluated the simulated flow responses to extreme climate conditions with the use of point and distributed precipitation measurements. Moon et al. (2004) found that radar precipitation produced better-simulated flows than rain gage as judged by Nash-Sutcliffe efficiency (NSE) coefficient (Nash and Sutcliffe 1970) of 0.55 and 0.39, respectively for the 10% of daily highest flows. The probability of exceedance of monthly flows matched observations with the use of radar, although, it underestimates the

greatest flows (Tobin and Bennett 2009). Use of radar and rain gage precipitation data can lead to different flow responses within a watershed. Price et al. (2014) reported that radar forcings accurately reproduce high-flow conditions, although, it underestimated medium and low flows while rain gage underestimates all three flow regimes.

Temporal variation in the occurrence of wet and dry periods can also influence simulated flow responses. Tobin and Bennett (2009) reported greater NSE in wet periods (0.47 to 0.82) than dry ones (-2.24 to 0.47) for the Middle Nueces Basin using rain gage, radar, and TRMM forcings, but there was no difference in another studied watershed. It suggests that occurrence of extreme climate conditions influence flow responses in a manner that is site specific. Gali et al. (2012) found that a model performance improved from NSE of 0.35 to 0.61 after removing the five largest flows.

The analysis of flow responses to extreme climate conditions is relevant for urban planning and agricultural management. Reliable and continuous long-term records to support these studies are needed (Easterling, Evans, et al. 2000; Huntington 2006). In the USA, a monitoring weather network with more than 8,000 stations provides precipitation records since the late 1800s. However, lack of high-quality hydrometeorological data still exists. Only 10.2% of 5,948 precipitation stations from 3 international daily datasets, including the Global Historical Climatology Network, had at least 80% records over the past century (Alexander et al. 2006). An integrative and complementary monitoring data set is required to fill those gaps.

Watershed hydrologic models are one potential solution to the previously described data limitations to evaluate impacts of extreme climate conditions on water resources. The models rely on high-quality input data and forcings for accurate flow predictions. Both rain

gage and radar products have been successfully used for hydrologic modeling of watersheds (e.g. Zhang et al. (2012), Beeson et al. (2011), Golden et al. (2010)).

To better understand the influence of extreme hydrometeorological and climate conditions on streamflow responses, first, rain gage data were validated using radar estimates. Later, long-term simulations performed and watershed responses assessed through statistical analysis in extreme climate and streamflow conditions. The first objective of this chapter is to evaluate the streamflow generation in a rain-ungaged watershed using rain gage-based forcings located outside the study area. The simulated flows using radar forcings and rain gage data from neighboring watersheds were compared. Another objective is to evaluate the model sensitivity to high- and low-flow conditions in the last century by simulating flows in a long-term period using rain gage forcings.

3.2 Methods

3.2.1 Study area

The Shell Creek watershed is a heavily agricultural and rain-ungaged watershed located in east-central Nebraska. It drains 1,233 km² on a mostly flat topography (Figure 3.1a). Streamflows are monitored at the USGS stream gage station No. 06795500 near the watershed outlet. The daily mean streamflow in 1947-2014 was 1.40 ± 5.13 m³/s. Corn (49%) and soybean (27%) dominates land use, whereas urban areas cover only 4.4% (b). The five greatest state towns have 1,675 inhabitants (U.S. Census Bureau 2010). The soil is characterized by sandy clay loam and prone to low infiltration rates and high runoff (Soil Survey Staff. Natural Resources Conservation Service. United States Department of Agriculture 2016).

Corn is the primary USA feed grain with 95% of total feed grain production and use (USDA-Economic Research Service 2017). It is also used as energy ingredient in livestock feed and ethanol production. The country is the largest corn producer and exports 10-20% worldwide. Corn production is concentrated in the corn-belt region that comprises Illinois, Iowa, Indiana, eastern portions of South Dakota and Nebraska, western Kentucky, and Ohio, and the northern Missouri. Advances in technology and production practices (e.g. fertilizer, pesticides, irrigation, crop rotation) have led to corn yield increase between 1926 and 2016 from 25 to 175 bushels per harvested acre while planted area, remained constant (~80 million acres). Location and land use characteristics of the Shell Creek watershed represent a typical agricultural area in the USA corn-belt. This study becomes relevant for watershed managers to assess water availability under extreme climate conditions in the region.

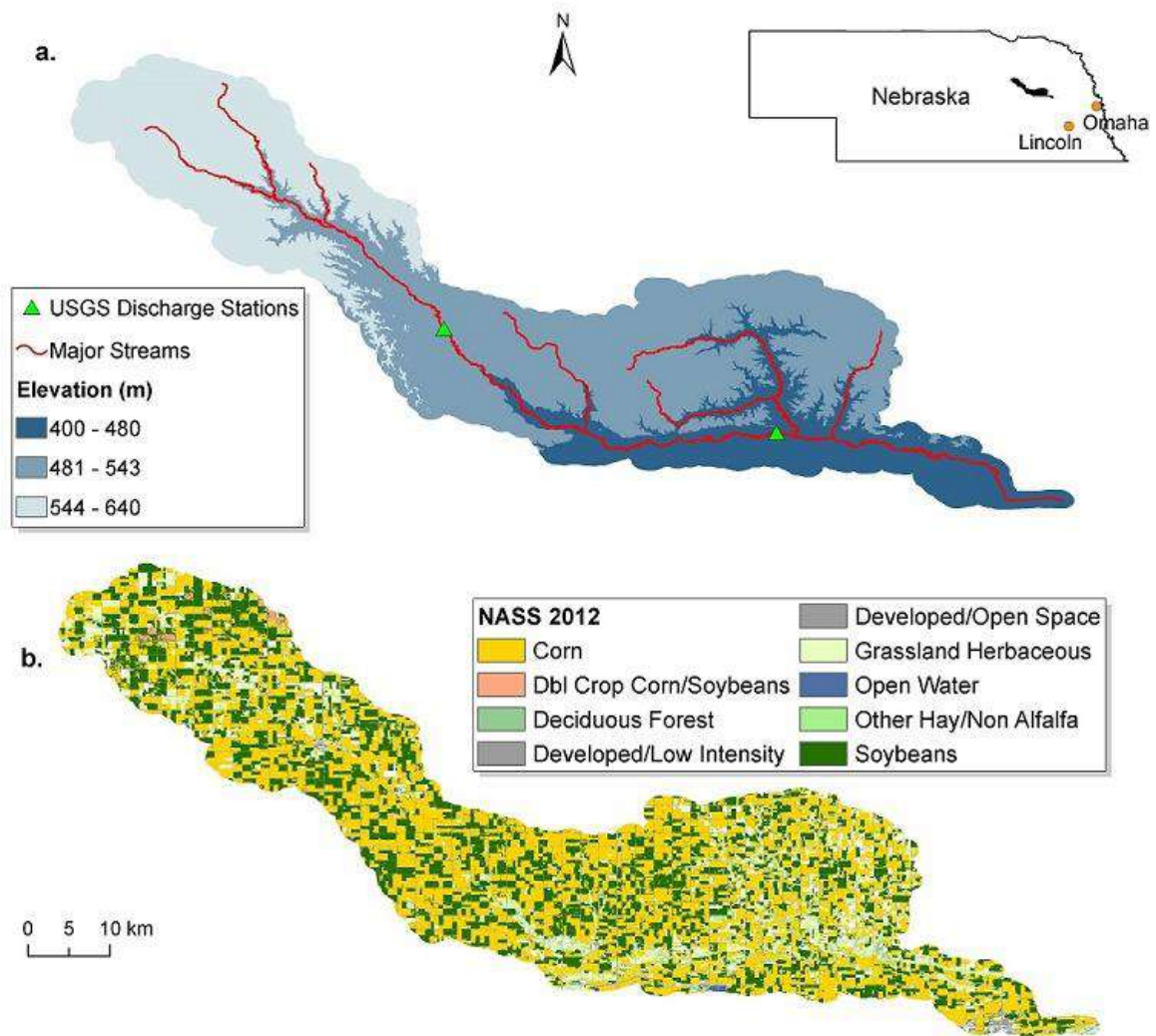


Figure 3.1 Shell Creek (a) streamflow network and (b) spatial distribution of landuses.
Source: (a) The National Elevation Dataset (D. B. Gesch 2007; D. Gesch et al. 2002); (b) USDA-NASS (2012)

3.2.2 Precipitation data

We used two available public datasets to study the spatiotemporal characteristics of precipitation in the Shell Creek watershed: rain gages and radar.

3.2.2.1 Rain gages

Rain gages around the Shell Creek watershed were identified. Ten stations belong from the National Oceanic and Atmospheric Administration (NOAA)'s National Climatic Data Center (NCDC) in the Global Historical Climatology Network (GHCN)-Daily database (Menne et al. 2012). Additionally, two stations, to the High Plains Regional Climate Center (HPRCC)'s Automated Weather Data Network (AWDN). The stations with longer records in 1910-2014 and more than 90% of daily observations were kept, otherwise, disregard. After screening, eight stations were finally selected.

Rain gage precipitation follows a seasonal variation (Figure 3.2) with wet summers and dry winters. Summer (June-August) receives an average precipitation of 3 ± 8.9 mm/day. Autumn (September-November) and winter (January-March) have precipitations of 1.5 ± 5.5 and 0.6 ± 2.5 mm/day, respectively. In spring, precipitation averages 2.2 ± 6.3 mm/day, when melting snowfall contributes to the flow generation and deep aquifer recharge, relevant for crop irrigation.

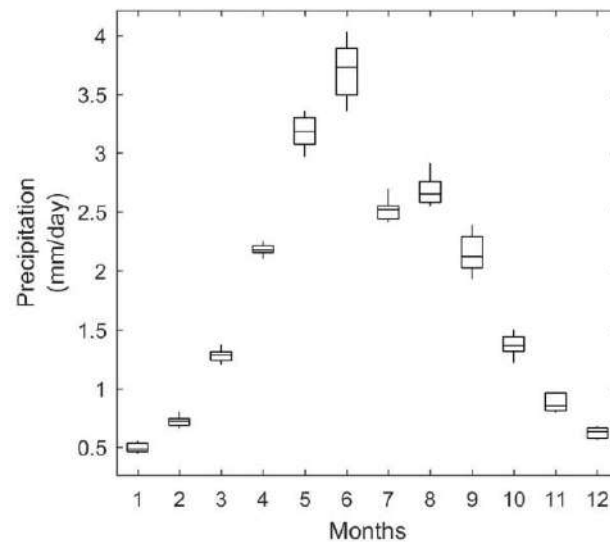


Figure 3.2 Distribution of monthly precipitation from rain gage data, 1910-2014

3.2.2.2 Radar

The NCEP Stage IV is a nationwide mosaic of multi-sensor (radar and gages) precipitation analyses (MPEs), produced by the 12 River Forecast Centers (RFC). It offers real-time, hourly/6-hourly precipitation analyses since 2002 at grid centroids of 4 km resolution (Lin and Mitchell 2005). Daily values are summed up from the 6-hourly analysis and data might have manual quality control.

Figure 3.3 shows the spatial distribution of radar precipitation between 2002 and 2013 in Shell Creek. Precipitation is homogeneous across the watershed. It averages 3 mm/day in summer and less than 1.2 mm/day in winter. These results are in agreement with rain gage estimates, indicating that radar data were corrected to produce similar precipitation. It also suggests that rain gages can represent temporal variation and spatial distribution of precipitation in Shell Creek. Despite radar accuracy and spatial resolution, the simpler access and longer records of rain gage make it more attractive for local water users such as farmers or ranchers, and policy makers.

Variation of monthly precipitation in agricultural watersheds, dry winters and wet summers where crop yield might rely on deep-aquifer or rain-fed irrigation, highlights the importance to study streamflow responses to climate intensifications. This water resources availability would represent key information for water resources infrastructure design and planning. The aim of this study is to evaluate the streamflow sensitivity, through a hydrologic model approach, to extreme hydrometeorological conditions.

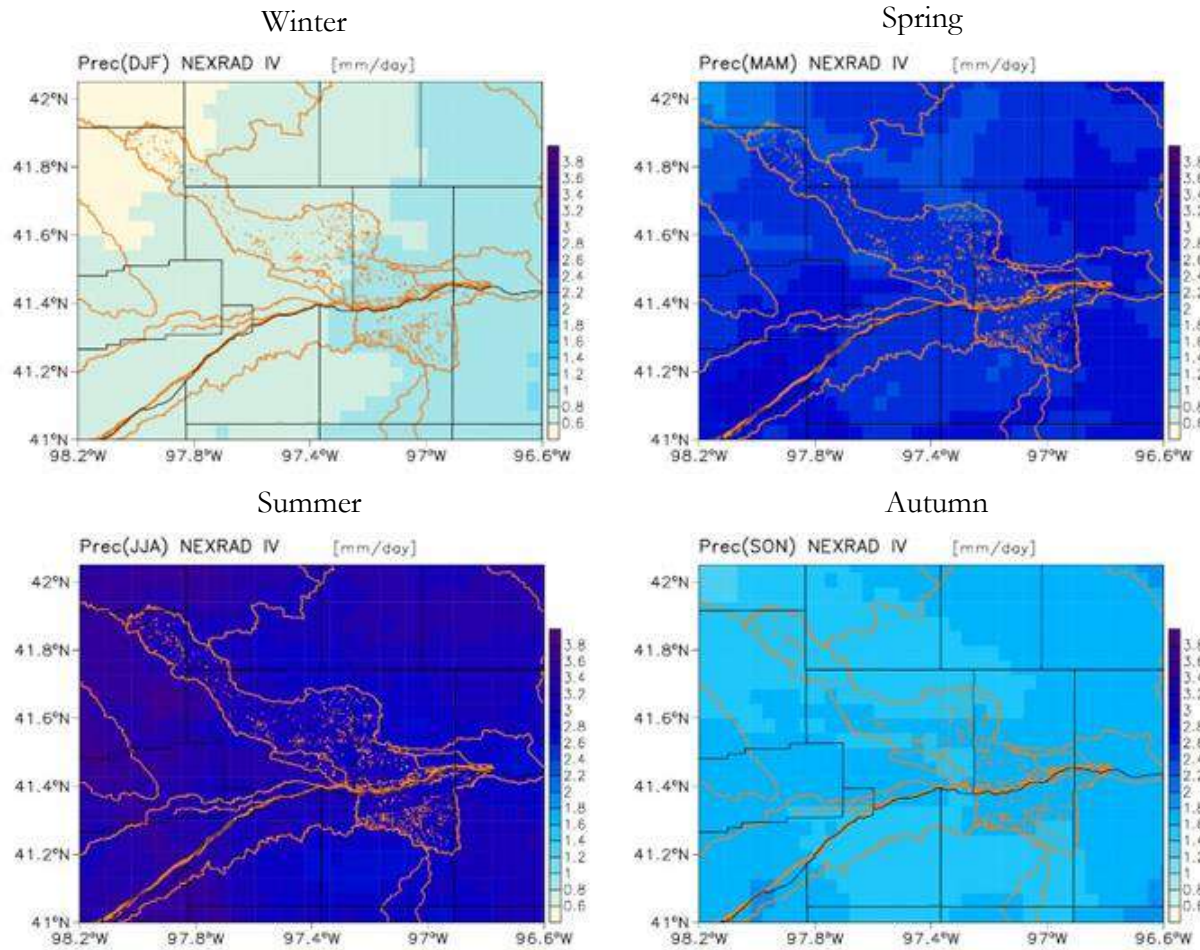


Figure 3.3 Seasonal mean precipitation across Shell Creek. Spatial distribution at the grid level for seasonal mean precipitation in SC watershed using NEXRAD data (4 km x 4 km resolution). Trends show rainy and dry seasons in summer and winter, respectively. Precipitation data 2002-2013, NCEP (Lin and Mitchell 2005).

3.2.3 The hydrologic model

A hydrologic modeling for the Shell Creek watershed was built in the Soil and Water Assessment Tool (SWAT) (Arnold et al. 2012; Neitsch et al. 2011; Arnold et al. 1998).

SWAT is a semi-distributed, physically-based software program that simulates hydrologic processes (e.g. infiltration, overland flow, evapotranspiration, shallow, and ground water), crop growth, fate and transport of nutrients and chemicals in soils and surface waters. The watershed is discretized in Hydrological Response Unit (HRU) defined by soil physical properties, land use, management practices, and topography. After a precipitation event, HRUs generate the same amount of runoff volume per unit area and routing it to the subbasin streams.

SWAT can compute the surface runoff volume using the Green and Ampt infiltration method, although, it requires sub-daily precipitation data to calculate infiltration based on the wetting front matric potential and effective hydraulic conductivity (Neitsch et al. 2011). The precipitation estimates that forced the SC model were records at daily time steps. Thus, the Soil Conservation Service (SCS) curve number method (USDA-NRCS 2004) was selected for estimation of surface runoff. It is an empirical model commonly used in the USA since the 1950s. Additionally, the channel routing and evapotranspiration were estimated using the Muskingum (Williams 1969) method, and the Penman-Monteith approach (Monteith 1965).

In the Equation 3-1, Q_{surf} is the accumulated runoff (mm), R_{day} is the daily rainfall depth, I_a is the initial abstraction including surface storage, interception, and infiltration before runoff, and S is the retention parameter (Equation 3-2). The S parameter depends on soils, land use, management, and slope and soil water content.

$$Q_{\text{surf}} = \frac{(R_{\text{day}} - I_a)^2}{(R_{\text{day}} - I_a + S)}$$

Equation 3-1 SCS curve number equation. Units in mm.

$$S = 25.4 \left(\frac{1000}{\text{CN}} - 10 \right)$$

Equation 3-2 Retention parameter. Where CN is curve number for the day.

3.2.3.1 Input data

To build the Shell Creek model in SWAT, spatial data such as soil types, land use, and topography were input. Soil types were obtained from the digital US General Soil Map so named STATSGO2 database that is pre-installed in ArcSWAT. Land use at a spatial resolution of 30 m cell size raster came from the USDA-NASS (2012). The National Elevation Dataset (NED) (D. B. Gesch 2007; D. Gesch et al. 2002), courtesy of the USGS at 1 arc-second (~30 m), the National Hydrography Dataset (NHD) (U.S. Geological Survey 2014), and the Watershed Boundary Dataset (WBD) (United States Department of Agriculture-Natural Resources Conservation Service (USDA-NRCS), United States Geological Survey (USGS), and Environmental Protection Agency (EPA) 2014) were downloaded from *The National Map* (Dollison 2010). The NHD and WBD were used for the stream network delineation.

Climatologic data was also input to the model. Meteorological records, since 1988, including relative humidity, solar radiation, air temperatures, and wind speed and were obtained from two stations that belonged to the HPRCC's AWDN. The weather generator incorporated in SWAT, which preserves the normal monthly averages of climate data,

produced any missing meteorological data. SWAT assigns the weather station closer to the mass centroid of each subbasin for the water balance calculations.

The spatial data were preprocessed using ArcSWAT, the ArcGIS-ArcView extension and graphical user interface for the SWAT2012, Revision 637. The ArcSWAT run in the ArcGIS version 10.2.2. The threshold for flow accumulation was set to 2,230.9 ha that equals 30,000 upslope grid cells. A total of 54 sub-basins were delineated with an area mean of 22.3 km² (Figure 3.4).

The model was forced independently with rain gage and radar precipitation estimates. Six (6) rain gages and 40 grid centroids (treated as “virtual rain gages” in SWAT) forced the SC model, independently. Comparison between simulated streamflows using either forcing tested these as forcings for the hydrologic modeling of Shell Creek.

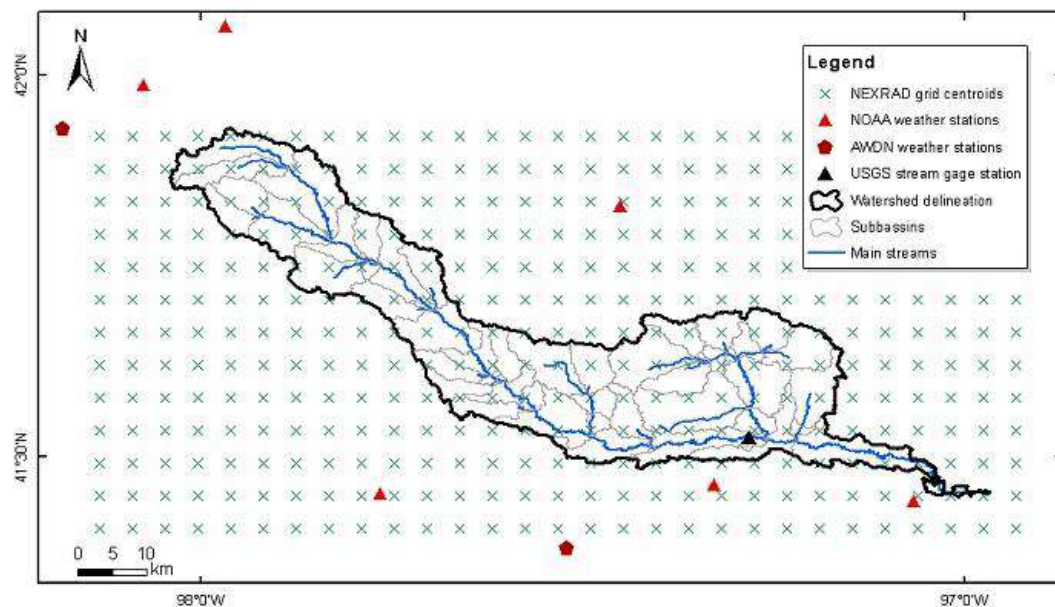


Figure 3.4 Rain gage stations and radar grid centroids used as forcings of the Shell Creek model in SWAT

3.2.3.2 Model performance

The NSE assessed the model performance. It compares observed and simulated monthly flows (Equation 3-3). NSE can range from $-\infty$ to 1. A better model performed when it tends to or equals 1. When NSE is below 0 indicates that the model performance decreases. In addition, the percent bias, PBIAS (Equation 3-4), and the ratio of the root-mean-squared error and the standard deviation, RSR (Equation 3-5) were calculated. A negative/positive PBIAS (%) evidences an over-/under- estimation of flows by the model. Regardless the PBIAS sign, it would quantify the bias magnitude. RSR can become any positive number from zero. Lower RSR values indicate a better model fit. In equations 1-3, for a simulation i , time steps t varies from 1 to n ; O and S represent the observed and simulated flows, respectively; and $\bar{O}$ is the O average. In the Equation 3-5, $RMSE$ indicates the root mean square error, and σ_o , the standard deviation of observed flows.

$$NSE_i = 1 - \left[\frac{\sum_{t=1}^n (O_t - S_t)^2}{\sum_{t=1}^n (O_t - \bar{O})^2} \right]$$

Equation 3-3 Nash-Sutcliffe efficiency (NSE) coefficient

$$PBIAS_i = \frac{\sum_{t=1}^n (O_t - S_t) * 100}{\sum_{t=1}^n O_t}$$

Equation 3-4 Percent bias

$$RSR_i = \frac{RMSE}{\sigma_o} = \frac{\sqrt{\sum_{t=1}^n (O_t - S_t)^2}}{\sqrt{\sum_{t=1}^n (O_t - \bar{O})^2}}$$

Equation 3-5 Ratio of the root-mean-squared error and the standard deviation

3.2.3.3 Calibration and validation

Due to radar data are available from 2002 to 2013 at the time of this study, the 12 years-long records were split as follows. Seven years for calibration (2002-08) and five for validation (2009-13). The hydrologic models were also calibrated through the Sequential Uncertainty Fitting ver. 2 (SUFI-2) procedure. First, an LHS generated a set of 400 parameters-value combinations within the initial ranges of the most sensitive parameters (Table 3.1). Processes involved are ground water (gw), routing (rte), sub-surface (sub), management (mgt), basin (bsn), and soil (sol).

After simulations run, SUFI-2 procedure narrows the range limits, which reduces the uncertainty associated with the value of parameters. Since the new ranges might fall beyond the initial values, these were visually checked and manually adjusted when needed. The objective function was the NSE, which identified the best simulation. Second, these “best” ranges were set for another iteration. Again, 400 parameters-value combinations were generated, and simulations run. Here, if the NSE improved at least 5%, iterations would continue passing the “best” ranges to a next iteration. Otherwise, iterations should stop and the ranges kept for the validation without any further change. In the validation, another precipitation time-frame was input. A set of 400 parameters-value combinations within the

“best” ranges from the last iteration of calibration step, was generated and simulations run.

NSE calculation tested the model performance.

Table 3.1 Parameters evaluated in sensitivity analysis

Parameter	File Ext.*	Definition
ALPHA_BF	gw	Baseflow alpha factor (days)
CH_COV2	rte	Channel cover factor
CH_K1	sub	Effective hydraulic conductivity in tributary channel alluvium
CH_K2	rte	Effective hydraulic conductivity in main channel alluvium
CH_N1	sub	Manning's "n" value for the tributary channels
CH_N2	rte	Manning's "n" value for the main channel
CH_S1	sub	Average slope of tributary channels
CH_S2	rte	Average slope of main channel
CN2	mgt	SCS runoff curve number factor
EPCO	bsn	Plant uptake compensation factor
ESCO	hru	Soil evaporation compensation factor
FFCB	bsn	Initial soil water storage expressed as a fraction of field capacity water content
GWQMN	gw	Threshold depth of water in the shallow aquifer required for return flow to occur (mm)
GW_DELAY	gw	Groundwater delay (days)
GW_REVAP	gw	Groundwater "revap" coefficient
HRU_SLP	hru	Average slope steepness
OV_N	hru	Manning's "n" value for overland flow
RCHRG_DP	gw	Deep aquifer percolation fraction
REVAPMN	gw	Threshold depth of water in the shallow aquifer for "revap" to occur (mm)
SFTMP	bsn	Snowfall temperature
SLSUBBSN	hru	Average slope length
SMFMN	bsn	Minimum melt rate for snow during the year (occurs on winter solstice)
SMFMX	bsn	Maximum melt rate for snow during year (occurs on summer solstice)
SMTMP	bsn	Snow melt base temperature
SNO50COV	bsn	Snow water equivalent that corresponds to 50% snow cover
SNOCOVMX	bsn	Minimum snow water content that corresponds to 100% snow cover
SOL_AWC	sol	Available water capacity of the soil layer
SOL_K	sol	Saturated hydraulic conductivity
SPCON	bsn	Linear parameter for calculating the maximum amount of sediment that can be re-entrained during channel sediment routing
SURLAG	bsn	Surface runoff lag time
TIMP	bsn	Snow pack temperature lag factor

3.2.4 Streamflow responses

3.2.4.1 Point and spatial precipitation

A hydrologic model of Shell Creek was built in SWAT using the meteorological and spatial data (topography, soil types, and land use/cover). The watershed configuration had 54 sub-basins. Then, a copy of the model set-up was made, and two identical models were forced with rain gages and radar data. Since radar captures the spatial distribution of precipitation, it validates rain gage estimates to incorporate such spatial variation into the model. Conversely, since rain gage accurately measures precipitation at ground sites, it validates radar records to reproduce the temporal variation.

A sensitivity analysis was performed to compare the physics of model effects on flow generation regarding rain gage and radar forcings. We used the SUFI-2 algorithm in the SWAT-CUP software, version 5.1.6 (Abbaspour, Vejdani, et al. 2007). A conceptual model of SWAT consistent of 31 parameters associated to flow generation (e.g. groundwater, flow routing, sub-surface, crop management and soil processes) were analyzed. A Latin Hypercube Sampling (LHS) generated a set of 150 parameters value combination within initial ranges (Table 3.4). Then, the models run for a year-long simulation.

In the global sensitivity analysis, the *t-test* estimates the sensitivity of each parameter and the *p-value* indicates their significance (Abbaspour, Vejdani, et al. 2007). The most sensitive parameters have larger *t-test* absolute values. We assumed that the sensitivity was significant when the *p-value* was ≤ 0.1 . Additionally, SUFI-2 considers most sources of uncertainty (driving variables, conceptual model, parameters, and measured data), which can be measured by two factors. Firstly, the *P-factor* quantifies the degree (in percentage) of the uncertainty of measured data within the 95% prediction uncertainty (95PPU). Secondly, the *d-factor* measures the strength of simulations using the mean thickness (from 0 to infinity) of

the 95PPU band divided by the standard deviation of the observed data. If *P-factor* and *d-factor* are closer to 1 and zero, respectively, the simulations are closer to the observations.

3.2.4.2 *Extreme hydrometeorological and climate conditions*

The Shell Creek flows have complete records since 1950, suitable to validate long-term simulations. After rain gage had been validated for the hydrologic modeling of the watershed, the model was forced for a long-term simulation (1950-2010). Similar than the validation step, “best” calibrated ranges were kept, and the set of 400 parameters value combination reused. Then, the simulation run and model performance evaluated.

First, a statistical approach is used to analyze the flow conditions of Shell Creek watershed. A gamma distribution was fitted and the probability density function estimated to observed and simulated flows. Using the inverse gamma cumulative distribution function in MATLAB, the flow percentiles were calculated. Flow conditions were identified as follows. High flows were assumed to be equal or greater than the 90th percentile flow, medium flow ranged between the 20th and 80th, and low-flows were lower than the 10th.

Second, the 3-month Standard Precipitation Index (SPI) identified years with extreme hydrometeorological and climate conditions in Shell Creek (Figure 3.5). For instance, very wet/dry summer and winter.

Rain gage data were used since they offer time frame records longer than radar. Larger absolute SPI value indicates an extreme condition. Here, a very wet condition is defined when SPI is between 1.25 and 2, and a very dry condition when SPI becomes negative, from -2 to -1.25. In Shell Creek, wet summers tend towards wetter condition, while dry summers seemed to drier conditions (Figure 3.5). However, a linear regression fit for the SPI evidence no significant trend in summer ($r^2=0.01$, $p=0.27$) or winter ($r^2<0.01$, $p=0.35$). Wet summer has a larger average precipitation of 2.16 mm/day in comparison with dry

summer of 1.36 mm/day (Table 3.2). Additionally, exceedance probability of monthly averages and maximum annual streamflow was estimated.

Table 3.2 Statistics of rain gage precipitation in extreme climate conditions

Years	Mean (mm/day)	Standard deviation (mm/day)
Historical	1.82	6.47
Wet summer ⁺	2.16	7.30
Dry summer ⁺	1.36	5.18

⁺ Very wet summer has SPI > 1, and very dry, SPI < -1.

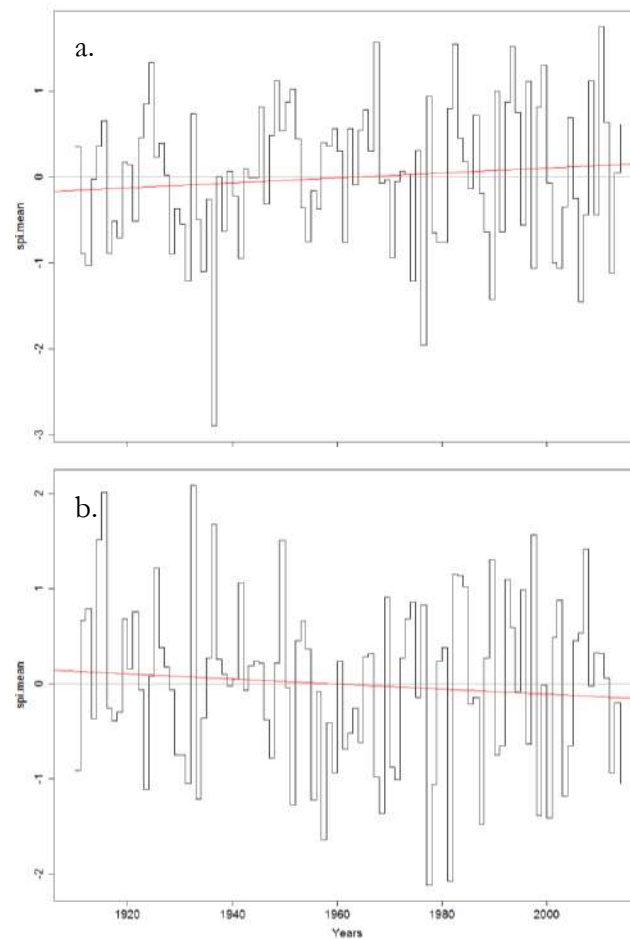


Figure 3.5 Shell Creek mean 3-month SPI in (a) summer and (b) winter, 1910-2014. Source of precipitation data: NOAA (Menne et al. 2012)

3.3 Results

3.3.1 Sensitivity of streamflow to forcings

Figure 3.6 presents the global sensitivity analysis of parameters associated to flow generation when radar and rain gage were used as model forcing data. Results show similarities in the sensitive parameters for both forcings. The most sensitive parameter was the runoff curve number (CN2) as indicated by lower P-values (< 0.10) and longer absolute t-Stats values. The initial soil water storage expressed as a fraction of field capacity water content (FFCB) was another sensitive parameter followed by the effective hydraulic conductivity in the main channel alluvium (CH_K2) and the average slope of tributary channels (CH_S1). The model that used radar precipitation was also sensitive to the soil evaporation compensation factor (ESCO), which reflects the water evaporated from bare soils and croplands.

Figure 3.7 displays the areal distribution of annual mean evapotranspiration (ET) before calibration of the Shell Creek model. The uncalibrated model using rain gage forcing displayed a more different ET estimates across sub-basins. Also, ET seemed greater than the radar-forced model.

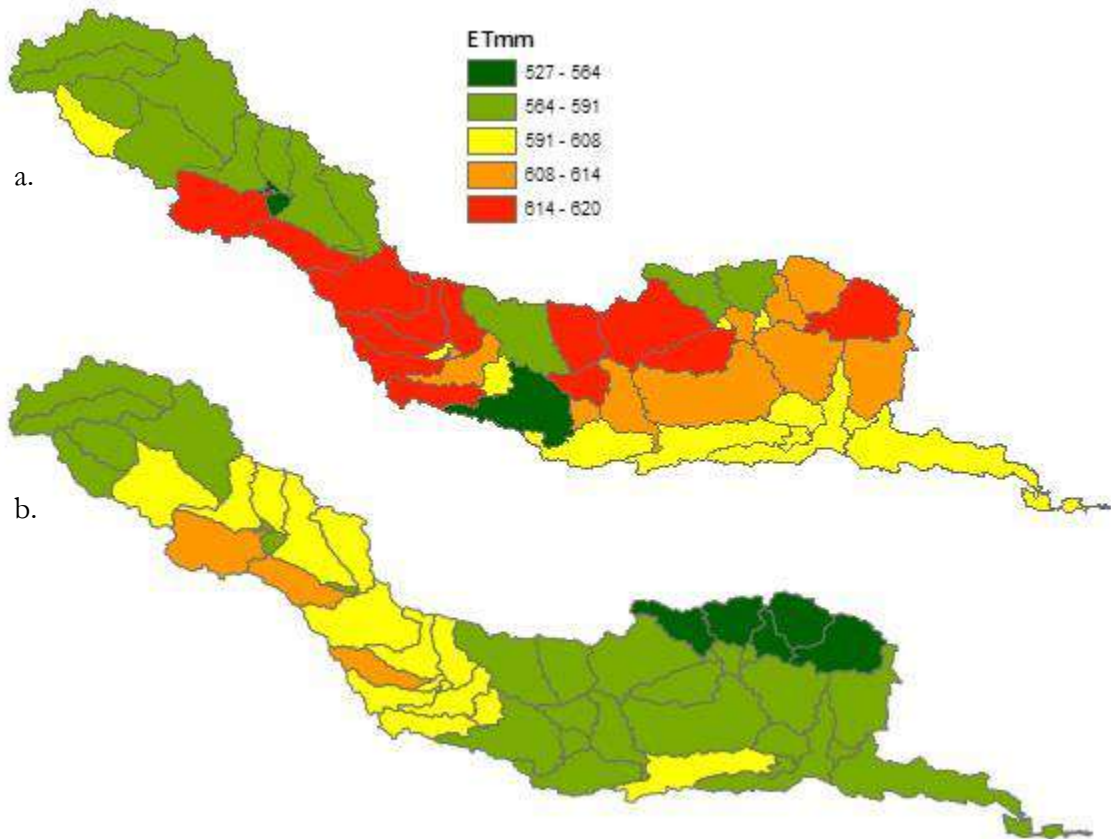


Figure 3.7 Annual mean actual evapotranspiration of the uncalibrated model using (a) rain gage and (b) radar forcings. Units are in mm.

The Shell Creek model using rain gage and radar forcings was successfully calibrated and validated, as judged by the statistics shown in Table 3.3 and Figure 3.8. Table 3.4 shows the parameters “best” range and fitted values. The models performed well with very similar NSE (0.58-0.60, 0.92-0.92) between calibration and validation periods (Table 3.3). However, when evaluating the performance in the entire time-frame (2002-13), radar displayed slightly greater NSE (0.75), lower RSR (0.50) and smaller PBIAS (3%) than rain gage (0.71, 0.54, and -12.1%, respectively).

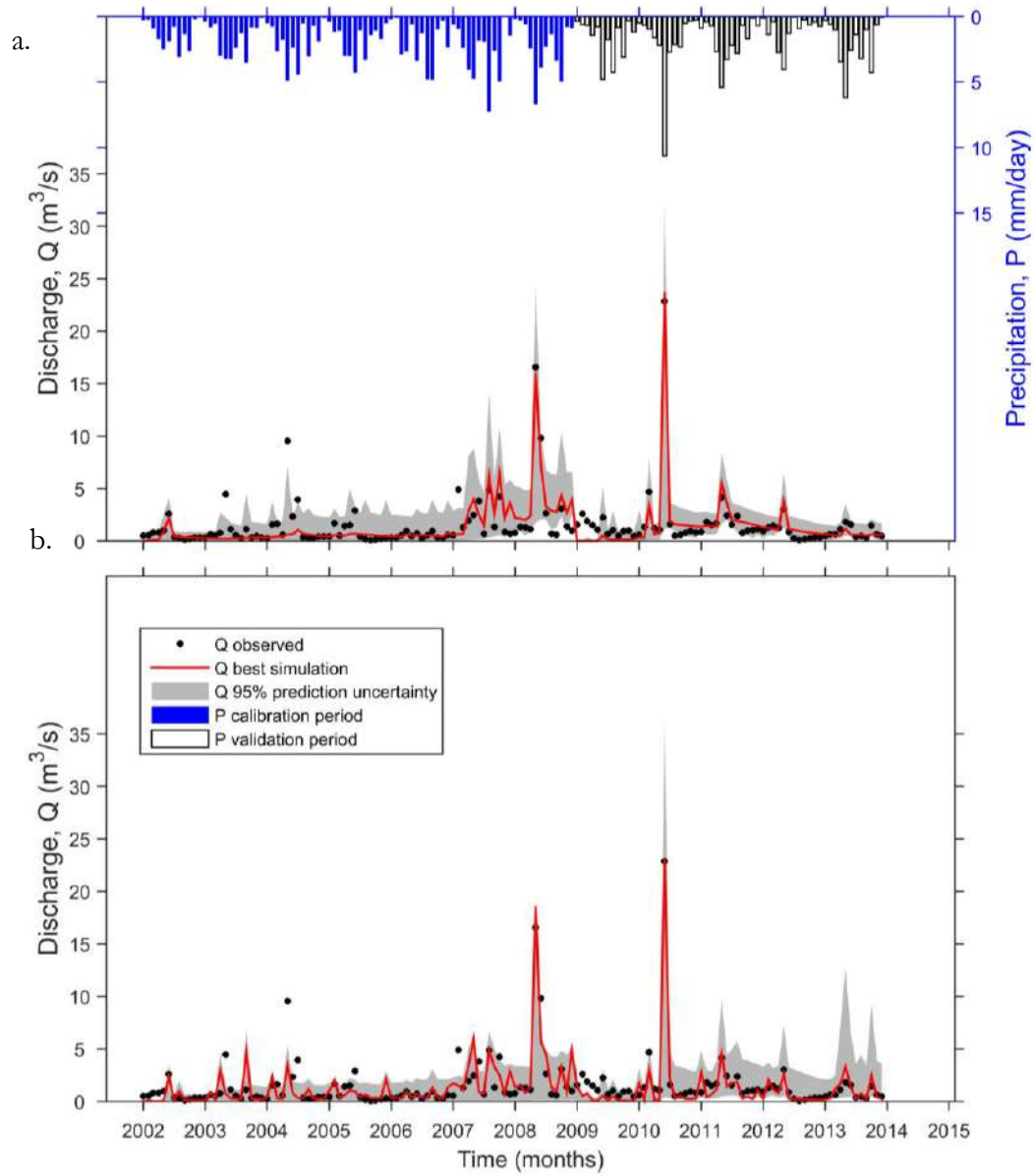


Figure 3.8 Calibrated and validated Shell Creek model using (a) rain gage and (b) radar forcings. Rain gage- and radar-forced models display NSE of 0.71 and 0.75, respectively in the period 2002-13

Table 3.3 Performance of calibrated and validated models using rain gage and radar forcings

Statistics	Rain gage			Radar		
	Calibration	Validation	2002-13	Calibration	Validation	2002-13
NSE	0.58	0.92	0.71	0.60	0.92	0.75
RSR	0.65	0.28	0.54	0.63	0.28	0.50
PBIAS (%)	8.31	6.09	-12.1	5.54	20.7	3.0

Table 3.4 Parameters fitted values of Shell Creek model using rain gage and radar forcings

Parameter	Description	Initial range	Method ⁺	“Best” range		Fitted value	
				Rain gage	Radar	Rain gage	Radar
CH_K2	Hydraulic conductivity in main channel alluvium	0.1 to 150	v	0.1 to 87.15	0.1 to 78.13	27.27	6.24
CH_S1	Average slope of tributaries	-0.005 to 0.01	r	0.002 to 0.01	0.005 to 0.01	0.0092	0.0072
CN2	Curve Number	-0.2 to 0.2	r	-0.136 to 0.087	-0.057 to 0.2	-0.024	0.086
ESCO	Soil evaporation compensation factor	0.001 to 1	v	NA	0.37 to 1	NA	0.75
FFCB	Initial soil water storage	0 to 1	v	0.49 to 1	0.23 to 0.74	0.98	0.49

⁺ Indicates that original value was either multiplied (r) or replaced (v) by another value within the initial range. NA: Not applicable since sensitive analysis of the parameter had a P-Value > 0.10.

3.3.2 Extreme flow regimes

The model was forced to a long-term (1910-2010) simulation using rain gage forcings. Figure 3.9 shows the observed, simulated flows and the prediction uncertainty band after a 1000-runs iteration. Again, the model displayed good performance for monthly streamflows as judged by NSE and RSR of 0.58 and 0.65, respectively. A PBIAS of -6.25% indicates that the model overestimates observed flows.

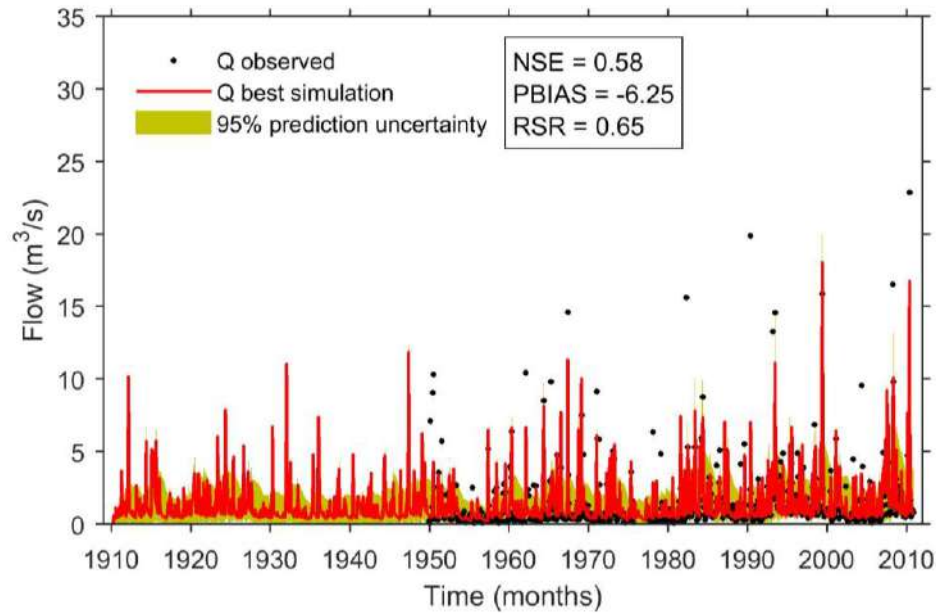


Figure 3.9 Long-term simulated streamflows in Shell Creek using rain gage forcings. A 1,000-runs simulation of monthly flows (Q) with rain gage precipitation forcings. Precipitation data source: NOAA's NCDC in GHCN (Menne et al. 2012); climatological data from SWAT weather generator (1950-1987), and HPRCC's AWDN (1988-2010). Observed flows (1950-2010) at gage station No. 06795500 (U.S. Geological Survey 2012); no streamflow records between 1/10/1975 and 9/30/1977.

A gamma distribution was fit to monthly streamflows with a shape and scale values of 0.93 and 1.51, respectively. Figure 3.10 shows a comparison of simulated and observed high-, medium- and low-flows. The rain gage-forced model can reproduce medium-flows closer to observations. However, the model overestimates low-flows while underestimates high-flow. Simulated flows differed less than $0.1 \text{ m}^3/\text{s}$ from observations. The model predicts low-flows at the 5th and 10th percentile with an uncertainty larger than any other percentile, as judged by the distance between the first and third quantile of the distribution. Moreover, medium-flows within the 50th and 80th percentiles were better reproduced as best simulation matches observed flows. The model underestimated high-flows (90th-99th percentiles), more evident at the 99th percentile by one (1) m^3/s .

Figure 3.11a presents the exceedance probability of average monthly flows.

Comparison of simulated and observed curves indicates that the rain gage-forced model reproduced flows that have probabilities to be exceeded between 0.1 and 1. However, the model underestimated the largest observed flows ($> 5 \text{ m}^3/\text{s}$), which probabilities to be exceeded are lower (< 0.1).

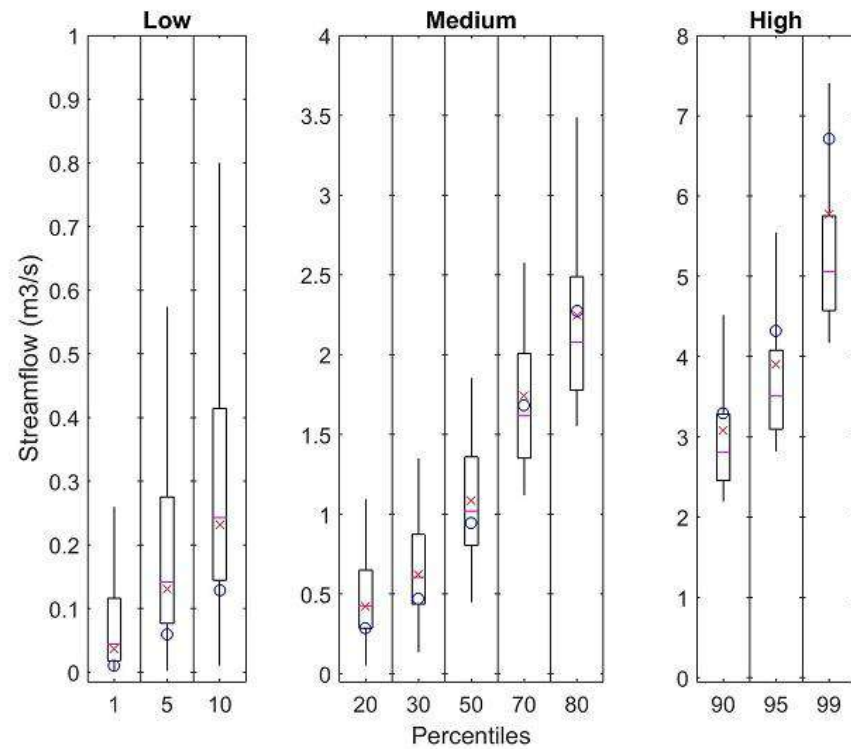


Figure 3.10 Low, medium, and high simulated streamflows using rain gage forcings, 1950-2010. Boxes represent lower (25th), medium (50th), and upper (75th) quartiles while whiskers represent 5th and 95th interquartile. Best simulated (x) and observed (o) flows.

3.3.3 Effects of wet and dry climate conditions on streamflow generation

The model performance under extreme climate conditions was evaluated as follows.

Shell Creek is an agricultural watershed with a crop season that onsets in the spring and

summer that depends on aquifer recharge and rainfed irrigation. Also, the highest precipitations occur in summer. Then, the analysis of flow responses was focused on that season. Previously, the 3-month SPI was measured for June-August from the gage precipitation data. Years with very wet and dry hydrometeorological and climate conditions were identified. SPI above 1 indicated a wet summer condition while below -1 was considered dry summer.

Table 3.5 presents the model performance of simulated flows in years with different climate conditions during the summer. Results indicate that streamflows are better reproduced in years with wet summers (NSE=0.48) in comparison with dry summers (NSE=0.23). The model captures the very wet hydrometeorological and climate conditions as measured in the simulated flows. However, the model poorly reproduces streamflows in dry conditions.

Table 3.5 Model performance in different climate conditions of summer

Years	NSE	RSR	RMSE	PBIAS	R2
Historical (1950-2010)	0.58	0.65	1.47	-6.25	0.59
Wet ⁺	0.48	0.72	2.26	-6.6	0.71
Dry ⁺	0.23	0.88	0.67	7.37	0.53
Normal [§]	0.23	0.88	1.35	9.67	0.47
Normal and dry	0.24	0.87	1.3	9.52	0.47
Normal and wet	0.36	0.8	1.52	5.8	0.58

⁺ Selection of years based on 3-month SPI estimates. Very wet summer has SPI > 1 while very dry, SPI < -1. [§] Normal years did not account for any year with very wet/dry summer.

Figure 3.11b compares exceedance probability of simulated and observed maximum annual flows, in years with wet and dry summers. The model reproduces accurately lower

flows ($< 5 \text{ m}^3/\text{s}$), which might be exceeded more frequently. The greater flows ($5\text{-}20 \text{ m}^3/\text{s}$) that have lower exceedance probabilities (< 0.3) were underestimated by the model.

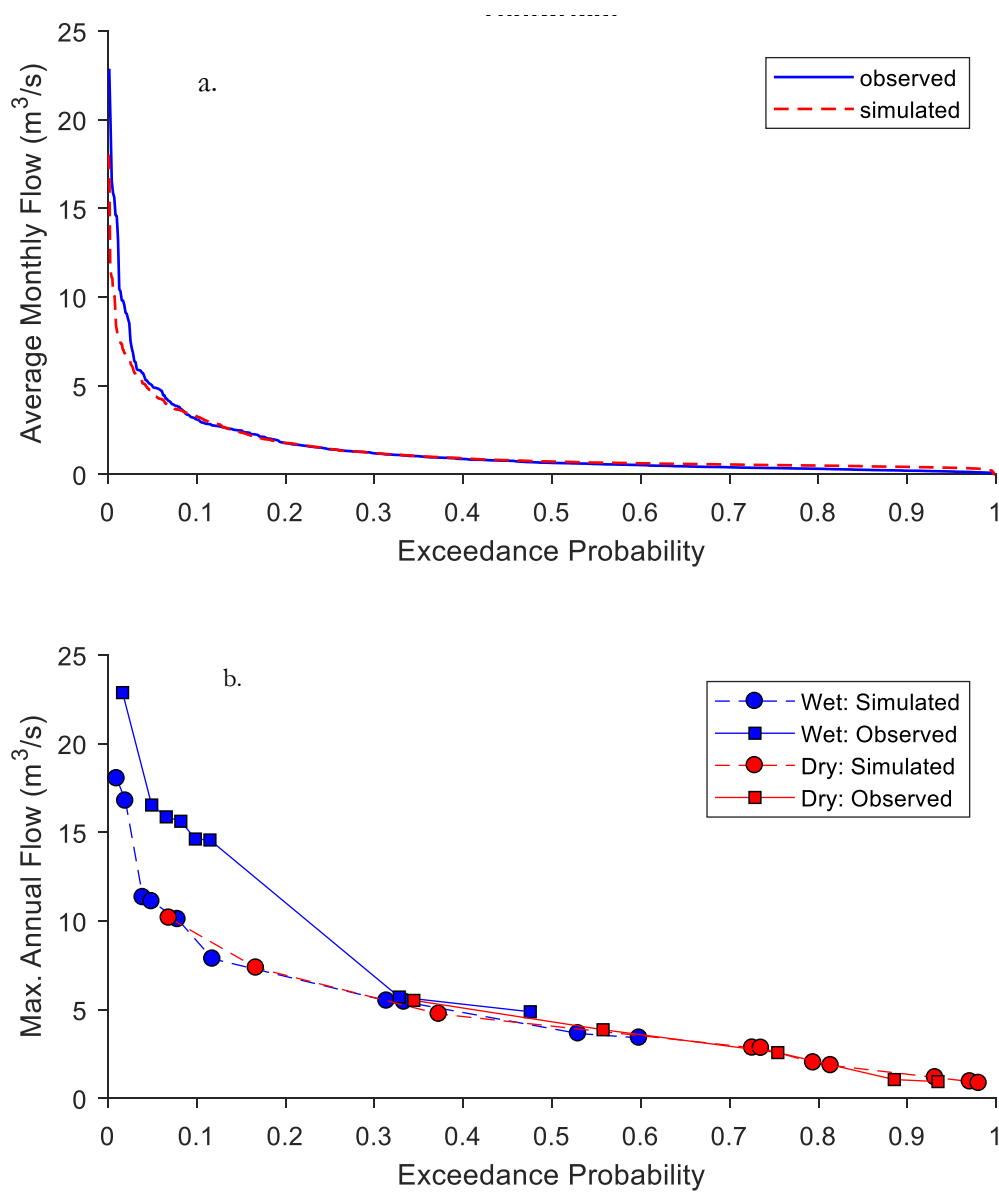


Figure 3.11 Exceedance probability of (a) monthly and (b) maximum annual flows

3.4 Discussion

A Shell Creek hydrological model was forced using rain gage and radar forcings. Radar and rain gage models displayed similar sensitivity results. The most sensitive parameter was CN2, followed by FFCB, CH_K2, and CH_S1. Radar was also sensitive to ESCO. The generated runoff volume strongly depends on the method for calculation. Since we chose the SCS curve number method, one could expect CN2 to be very sensitive. Studies using rain gage and radar forcings have also reported CN2 as the most sensitive parameter in flow generation (Kalin and Hantush 2006; Price et al. 2014). The sensitivity to ESCO by radar might indicate differences in precipitation inputs. Errors in small and large precipitation events are corrected in the calibration step to match simulated outcomes and observed flows (Price et al. 2014). Thus, calibration of the ESCO, which reflects the water evaporated from bare soils and cropland, could balance the evaporative demands from deeper soil layers. Differences were evident in the non-calibrated radar model that showed annual ET lower than rain gage (Figure 3.7). Studies have shown infiltration and subsurface storage parameters as sensitive parameters to calibrate and allow adjusting water budgets (Price et al. 2012). Nevertheless, the sensitivity analysis suggests a similar physical representation of water processes in both rain gage- and radar-forced models.

For the entire calibration-validation period (2002-13), radar displayed a better performance than the rain gage model. It was evident by a greater NSE, lower RSR and smaller PBIAS of 0.75, 0.50 and 3%, respectively, in comparison with rain gage, which had 0.71, 0.54, and -12.1% for the same statistics (Table 3.3). Studies in watersheds smaller than 3,200 km² have found that model performance improved using radar forcings with NSE of 0.57-0.84, although, rain gage showed lower values of 0.48-0.78 (Golden et al. 2010; Moon,

Srinivasan, and Jacobs 2004; Kalin and Hantush 2006; Chintalapudi et al. 2012). In watersheds of 7,700 and 8,900 km², the performance of radar (0.62-0.90) was better than rain gages in the calibration period (0.19-0.30), and differences reduced in validation (0.69-0.69, 0.98-0.95) (Tobin and Bennett 2009). A rain gage-forced model could even perform better than radar and exhibit NSE values of 0.66-0.87 and 0.49-0.73, respectively (Beeson et al. 2011). In this study, radar model was slightly better than rain gage in the calibration period (0.6 vs. 0.58) but quite similar in the validation with NSE equal to 0.92 (Table 3.3).

Studies have found similar performance using NEXRAD and rain gage forcings with NSE of 0.51-0.98 and 0.49-0.86, respectively (H. Zhang et al. 2012; Tuppad et al. 2010; Sexton et al. 2010). Our results confirmed the SWAT ability to simulate Shell Creek flows using both radar and rain gage forcing. The similar performances of the radar- and rain gage-forced models suggested that precipitation was likely corrected to match the precipitation estimates. Also, that rain gages preserve its spatial distribution. Then, rain gage around Shell Creek seemed reliable data for the streamflow simulations.

The integration of both techniques rain gage and radar contribute to high-quality precipitation data in rain-ungaged watersheds. Moreover, the performance of hydrologic simulations at watershed scale can improve (e.g. Price et al. (2014), Sexton et al. (2010), Tobin and Bennet (2009), Kalin and Hantush (2006). Thus, a model able to predict maximum extreme conditions becomes relevant for watershed management. More accurate flow estimations under limiting water conditions bring pertinent information for water users to make decisions. For instance, increasing water subtractions from the stream in very dry conditions would affect water supply downstream, while putting on risk its ecology. Understanding the flow responses under extreme precipitation would help farmers to plan accordingly and reduce crop losses.

The rain gage model better reproduced extreme and medium flow regimes ($> 20^{\text{th}}$ percentile) than low flows (Figure 3.10). It better reproduced flows within the 50^{th} and 80^{th} percentiles since the best-simulated flow matches the observed value. The model overestimated low-flow conditions below the 10^{th} percentile, while underestimated higher flows (90^{th} - 99^{th} percentiles). A few hydrologic modeling studies have reported the analysis of flow regimes distribution. In a self-contained four sub-basins of a forest-agricultural (89%) watershed, a rain gage-forced model underestimated low, medium, and high flows at the 5^{th} , 50^{th} , and 95^{th} percentiles, respectively (Price et al. 2014). On the other hand, radar led to more accurate high-flows predictions (95^{th} percentile). The distribution of the simulated flows captured the observed flows, but the model failed to reproduce medium and low flows (50^{th} and 5^{th} percentiles, respectively) with even greater underestimates by rain gage (Price et al. 2014).

Influence of rain gage and radar forcings in model performance under extreme climate conditions have been reported. An NEXRAD model showed better performance (NSE=0.55) than rain gage (NSE=0.39) for the highest 10% of flows (Moon, Srinivasan, and Jacobs 2004). However, rain gage displayed a slightly better performance (NSE=0.64-0.73) than radar (NSE=0.51-0.71) under extreme wet conditions (Biggs and Atkinson 2011).

3.5 Conclusions

The main goal was to evaluate the sensitivity of flow responses to extreme hydrometeorological and climate conditions in a rain-ungaged watershed. First, rain gage and radar precipitation estimates were validated as forcing of the hydrologic model for Shell Creek, Nebraska. Two similar models were set-up in the SWAT with same watershed characteristics (topography, land use, and soil types), but differ only by precipitation data. Observed and simulated flows were compared using the NSE coefficient. The sensitivity analysis and model performances of the models indicated that rain gage offered a reliable precipitation data, preserve its spatial distribution, and was suitable for Shell Creek flow simulations. The rain gage-forced model performance in a long-term flow simulation (1950-2010) showed NSE of 0.40, RSR of 0.78 and PBIAS of -1.73. The model reproduced seasonal flows variation in very wet summers, accounting for the peaks. It also overestimated low flows in years with very wet and dry summers by 1-2 m³/s.

Second, long-term simulated flows were fitted to a gamma distribution. Low, medium and high regimes were evaluated at 1-10th, 20-80th and 90-99th percentiles, respectively. The rain gage-forced model reproduced medium flows closer to the observations. However, it overestimated low-flows below the 20th percentile and underestimated high-flow above the 80th percentile, both by 0.1 and 1 m³/s, respectively. The approach presented shows that rain gage and radar data set are suitable forcings for hydrologic modeling of the small (1,200 km²) rain-ungaged watershed of Shell Creek using SWAT. Their integration can support hydrologic modeling and bring quantitative information to watershed managers. Users of the Shell Creek model should be cautious under extreme climate conditions. In low-flow regimes, one could get less water than predicted. In contrast, high-flow regimes can produce larger amounts than simulated.

Chapter 4 Water Quality Response to Extreme Hydrometeorological and Climate Conditions and Modeling Emerging Contaminants in Surface Waters of an Agricultural Watershed

This chapter is in preparation to submit:

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4.1 Introduction

Agricultural runoff is a significant non-point source (NPS) of contaminants to water bodies. Rainfall-runoff events mobilize sediments, nutrients, and organic matter from croplands and facilitate transport of chemicals. For instance, a Swiss agricultural watershed generated sediments, total nitrogen and total phosphorus of 4.6 t ha^{-1} , 42 and 2.7 kg ha^{-1} , respectively (Abbaspour, Yang, et al. 2007). Water contamination affects aquatic biota and flora, as high loads of nutrients and organic matter can reduce dissolved oxygen and lead to eutrophication, which introduces impairment for uses like water supply, animal feeding, fishing, and recreation.

Pesticides transport and fate is a water quality concern in agricultural watersheds. Atrazine, a synthetic herbicide to control broadleaf and grassy weeds in corn, sorghum, and sugarcane crops, is mostly detected in the US agricultural watersheds (Wu et al. 2010; Gilliom et al. 2006). Application rates range from 60-70 million pounds per year (USGS 2012). Studies have documented adverse effects of atrazine to aquatic life including bioaccumulation, reduction in reproduction, tissue abnormalities (Tillitt et al. 2010), and sex changes (Hayes et al. 2003). Also, it inhibits photosynthesis, alters community structure, and destroys aquatic flora (U.S. EPA 2006). A human health concern of pesticides use relates to their carcinogenic potential. However, studies have found that atrazine does not promote breast cancer (Mills and Yang 2006; Hopenhayn-Rich, Stump, and Browning 2002). Atrazine exposure could induce reproductive cancers in animals, although, it might not be the causal agent (Alavanja, Hoppin, and Kamel 2004). The European Union banned its use more than a decade ago, although, it is still commercialized in many countries.

Veterinary antibiotics are used worldwide and commonly prescribed for prevention and treatment of disease in animals. Their global estimates used in livestock production were 63,151 ($\pm$ 1,560) tons in 2010 with projections of 67% increase by 2030 (Van Boeckel et al. 2015). China (23%) and USA (13%) are the largest consumers of antimicrobials (Van Boeckel et al. 2015). Antibiotic sales have increased 17% in recent years (2009-2013) with 14,800 tons distributed in 2013 (Food and Drug Administration (FDA) - Center for Veterinary Medicine 2015).

Excreted unmetabolized, veterinary pharmaceuticals enter surface waters following rainfall-runoff events over crop fields fertilized with manure from animals (Burkholder et al. 2007; Davis et al. 2006; Kim et al. 2010; Joy et al. 2013). Once in the environment, processes such as degradation (from a few days up to months), adsorption, transport, and plant uptake drive their spatiotemporal fate, depending on crop type, soil microorganisms, water, and human activities. Their occurrence in the environment favors the development of antibiotic resistant bacteria (Jjemba 2006; Hughes and Andersson 2012; Truszczyński and Pejsak 2013)

The occurrence of emerging contaminants in the environment may pose a risk to non-target organisms. Moreover, their fate and transport are poorly understood. To date, no models have simulated veterinary pharmaceuticals at watershed scales. It might be due to the lack of monitoring data needed for calibration. Considering that chemical structures of some veterinary pharmaceuticals are similar to pesticides (e.g. fluconazole vs. azaconazole, sulfanilamide vs. asulam) (Swanton et al. 2011), I hypothesize that veterinary antibiotics can be simulated using the subroutine of pesticide modeling in SWAT.

Changes in hydro-meteorological and climate drive flow generation. Runoff determines the amount of sediment carried from landscapes into surface waters. Furthermore, sediments influence loading of nutrients as they can be dissolved (mobilized in the water) or sorbed by the soil particles. Floods increase the dilution of pollutants in waters, and runoff from agricultural land carries a larger amount of sediments. In contrast, drought can worsen the water quality due to low flow conditions. A Nebraska reservoir had lower water quality under low-flow conditions (Olds, 2011 cited by Peterson et al. (2014)). Drought also decreases the amount of agricultural runoff, and fewer nutrients and organic compounds remain in the soil. For instance, a wet year generated from 2.4 to 3 times larger loads of sediments, nitrogen, and phosphorus than a dry year (Abbaspour, Yang, et al. 2007).

There is a lack of information to quantify the impacts of changes (increase or decrease) in extreme climate events on water quality (Peterson et al. 2014). A common issue is the lack of records, which limits modeling attempts. Previous water quality modeling studies have faced shortages of observed water quality data (Gollamudi, A. Madramootoo, and Enright 2007; Jha, Gassman, and Arnold 2007; Santhi et al. 2006; Santhi et al. 2001). The lack of monitoring data limits our ability to analyze fate and transport of water pollutants and their responses to climate variations.

The aim of this chapter is to validate a water quality model for an agricultural watershed. Then, characterize the influence of extreme hydrometeorological and climate conditions on the loading pollutants in surface waters. Additionally, the pesticide sub-routine of the Soil and Water Assessment Tool (SWAT) was tested to model veterinary antibiotics.

4.2 Methods

4.2.1 Study area

The Shell Creek is a 1,200 km² watershed in the east-central Nebraska with 78.2% of land in cultivated crops, 14.6% herbaceous, and 4.4% urban (Figure 2.1a). The soils are mostly sandy clay loam with low infiltration rates and high runoff. Topography is mostly flat with elevations between 400 and 640 m.a.s.l. Since the Shell Creek is a rain-ungaged area, rain gage data from stations near the watershed (Figure 2.1b) were validated against radar estimates and found to represent the spatiotemporal distribution of precipitation adequately. Precipitation in summer range 2.5-4 mm/day while in winter it averages less than 1.5 mm/day.

4.2.2 Surface water quality

Spalding and Snow (1989) monitored a rainfall-runoff event in spring 1989 in the Shell Creek watershed. Streamflow ranged between 19 and 781 m³/s with a maximum level of atrazine of 89 µg/L prior the streamflow peak. Other agrichemicals measured include cyanazine, alachlor, and metolachlor. They found high correlations between suspended sediments (19 g/L) and pesticides levels, although nitrate-N (6.3 mg/L) did not. This records might be used in modeling of single precipitation events at hourly or daily time steps. Since the present study focuses in the analysis of extreme hydrometeorological and climate conditions, alternative data set was searched.

The National Water Information System (NWIS) repository of the USGS (2012) was accessed using the R package “dataRetrieval” (Hirsch and De Cicco 2015) to retrieve records at the Shell Creek stream gage No. 06795500 (Figure 2.1b). Streamflow averages 1.40 ± 5.13 m³/s with a median of 0.5 m³/s since 1947. The highest peak flow in records was 218 m³/s.

On the other hand, water quality data measured as sediments, nutrients, and atrazine are scarce and discontinuous. These are the main pollutants of waters in agricultural watersheds, and pesticides might be a threat to aquatic life. Unfortunately, this has been only monitored in 1992-94 and 2008-09 in Shell Creek with less than 60 observations while streamflow has constantly been monitored (Table 4.1).

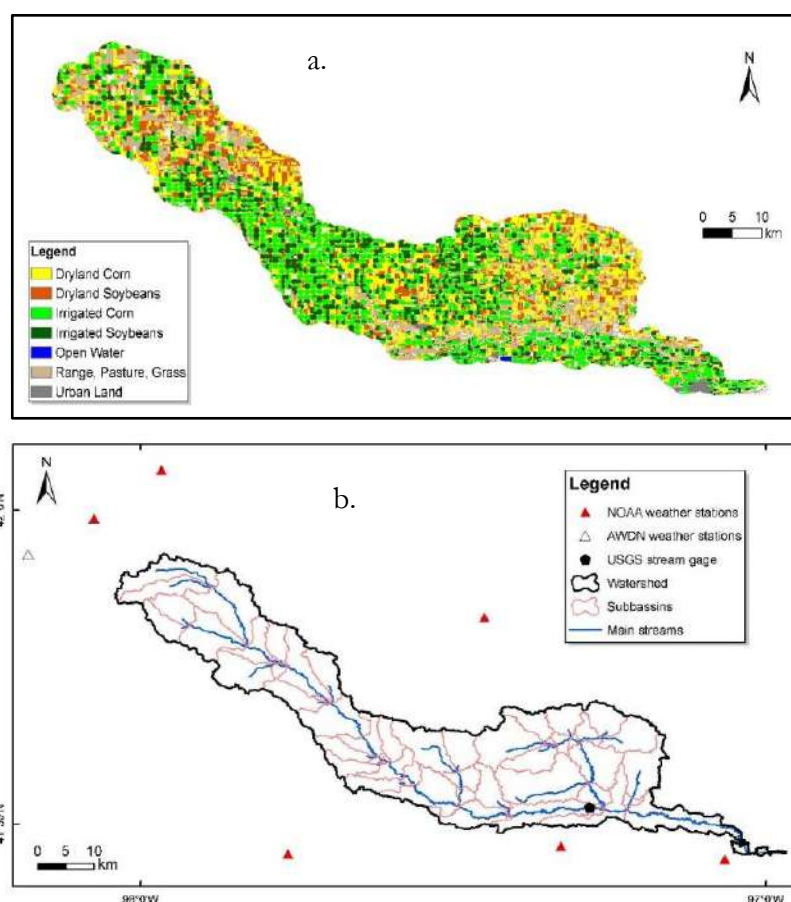


Figure 4.1 Shell Creek (a) major land uses (b) stream network and rain gage stations. Source: (b) 30 m cell size resolution. Source: Census of Agriculture (USDA-NASS 2012) distributed by CALMIT (2016).

Table 4.1 Shell Creek water quality data

Variable	Units	1992-94		2008-09	
		No. observations	Max. value	No. observations	Max. value
Flow	m ³ /s	1096	96.56	738	218.04
Sediments	mg/L	26	20,150	26	4,090
Total Nitrogen	mg/L	28	13	13	12
Total Phosphorus	mg/L	28	8.7	27	3.25
Atrazine	mg/L	28	0.055	24	0.015

Source: NWIS-USGS (2012)

That lack of data limits a further statistical analysis, although, a general comparison can be made. Pollutants concentration peak in summer months (Figure 4.3 and Figure 4.4), driven likely by higher monthly precipitation (Figure 3.2). There are blanks in monthly estimates due to lack of daily records. Sediment concentration increased to 12,000 and 15,000 mg/L in 1992-94 whereas it decreased to 4,000 mg/L in 2008-09. The difference between the frame records could be due to smaller but repeatedly flow peaks in the first period (Figure 4.2) that increase the sediments being wash-out crop fields.

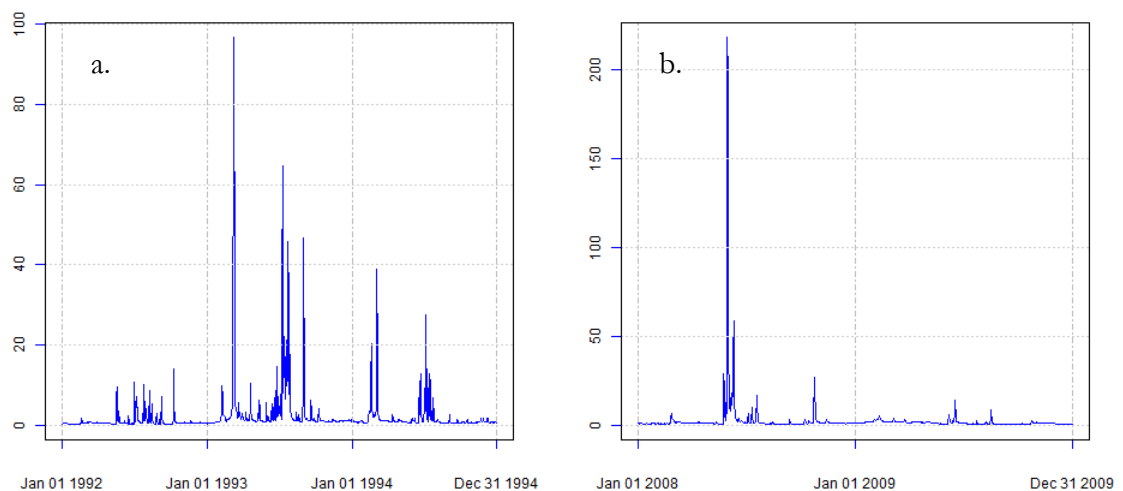


Figure 4.2 Shell Creek daily streamflow in (a) 1992-94 (b) 2008-09. Flow units in m³/s.

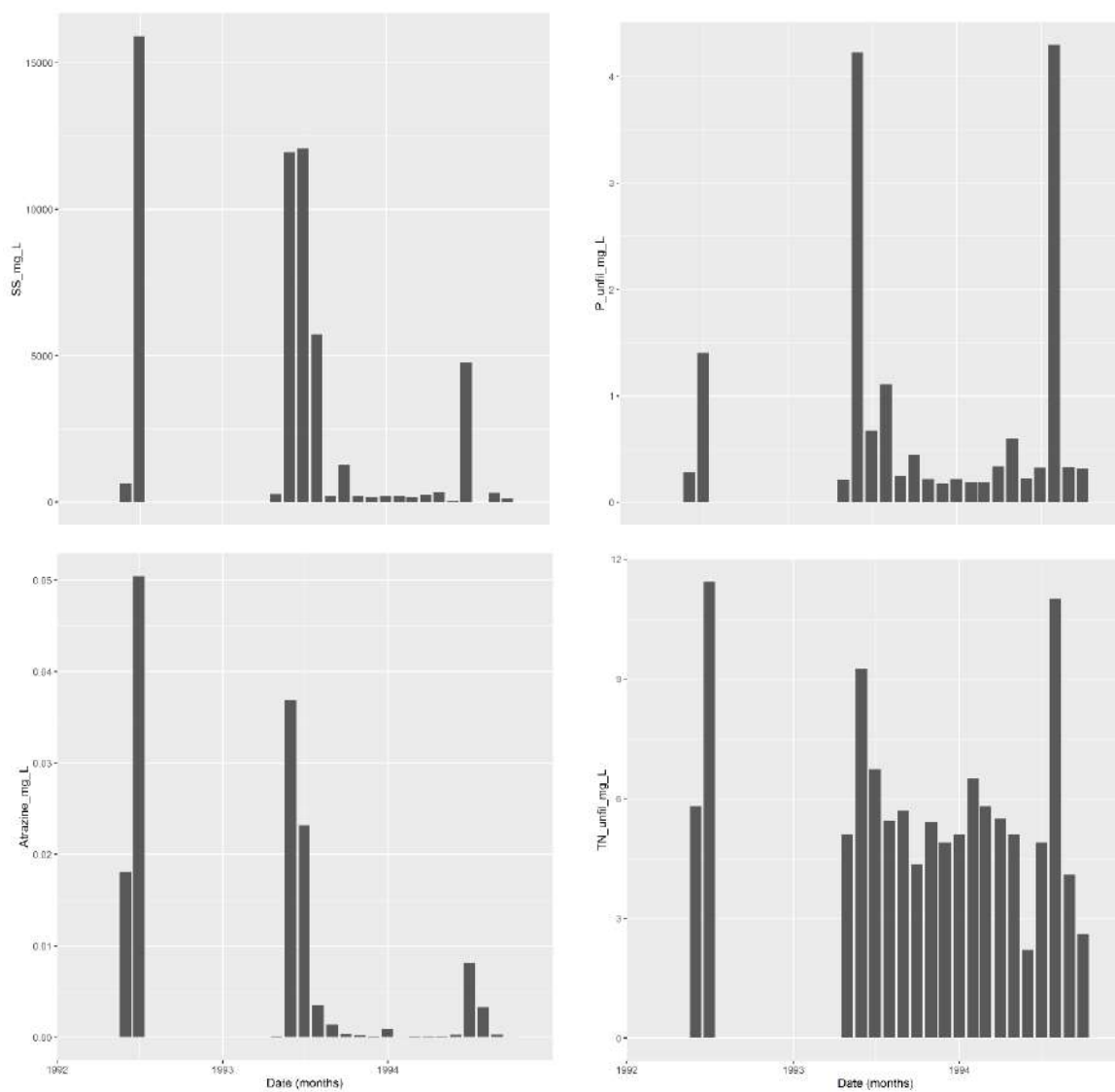


Figure 4.3 Mean concentrations of water quality variables in Shell Creek, 1992-94. SS: suspended sediments, P: total phosphorus, TN: total nitrogen

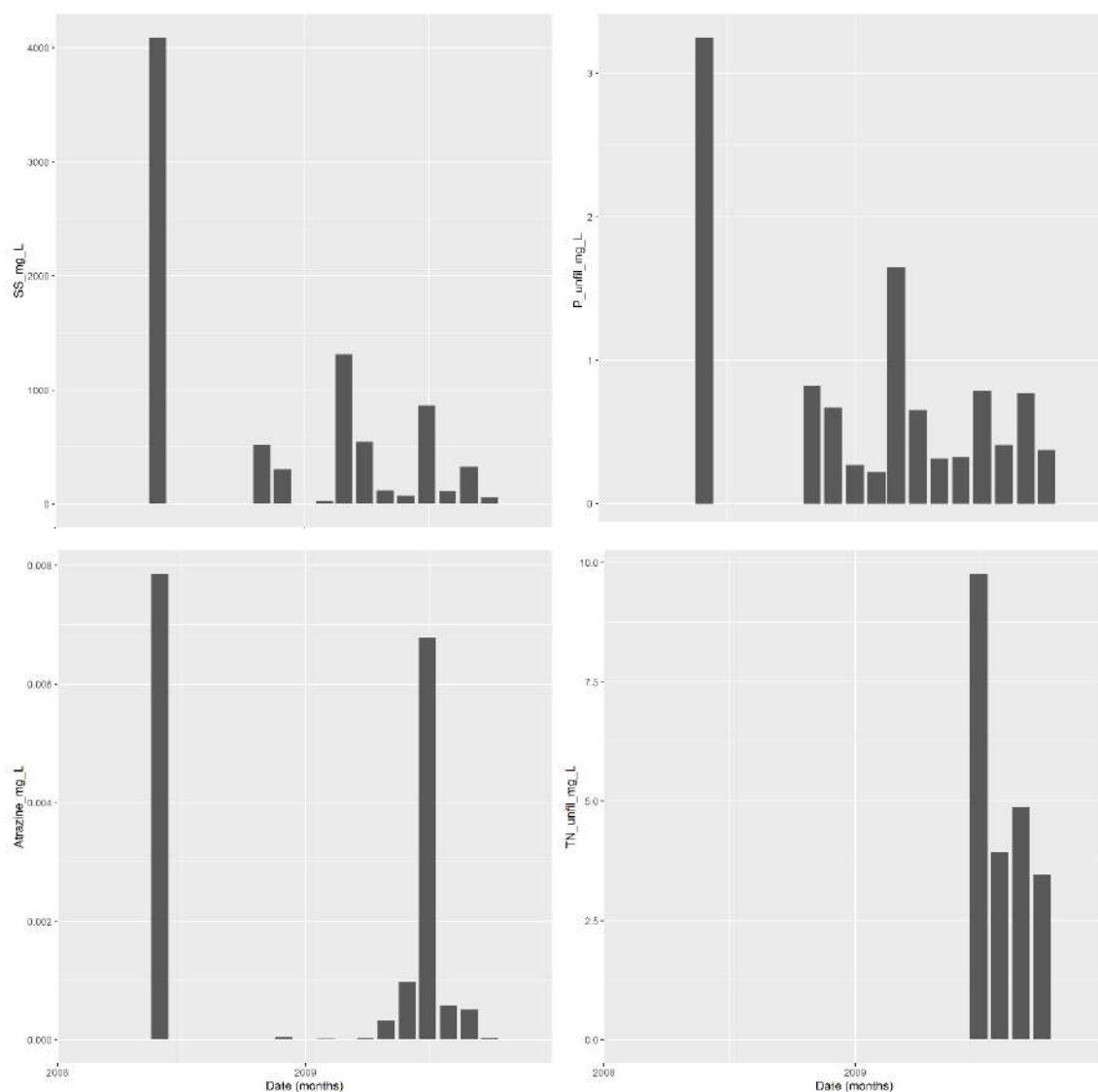


Figure 4.4 Mean concentrations of water quality variables in Shell Creek, 2008-09. SS: suspended sediments, P: total phosphorus, TN: total nitrogen

4.2.2.1 *Fitting a linear model to observed data*

Using a few observations (< 60) would constrain the model performance because it might not be calibrated for a broader range of conditions (e.g. higher and lower loads of pollutants). Researchers highlight that watershed models cannot be calibrated properly for sediments and nutrients, especially when watershed lacks monitoring data (Santhi et al. 2006; Gollamudi, A. Madramootoo, and Enright 2007; Santhi et al. 2001). Since Shell Creek has limited water quality data, a continuous time series of loading pollutants were computed by fitting a linear regression, or statistical model. The observed loads were calculated as the product of streamflow times the pollutant concentration, when available.

Initially, correlations between the predictor variable (streamflow) and response ones (e.g. sediments load) for loads in 1992-94 and 2008-09, were explored. A logarithmic transformation was identified to describe the correlation (Equation 4-1). Lately, a linear model was fit to the Log_{10} of sediments, nutrients, and atrazine loads. The multiple R^2 and the p-value of F-statistics evaluated the performance of the regression. With multivariate regression, each response variable follows its regression equation, but it takes into account the covariance that exists among each pairwise response variables. For instance, multivariate regression would consider the relationship between the nitrogen and phosphorus levels in the water, if one exists. The flows observed in the monitoring periods of water quality (Table 4.1) were assumed randomly selected and a representative sample of streamflows in Shell Creek, as it widely ranges from 0.23 to 200 m^3/s (Figure 4.2). Finally, a computed loads were generated by replacing observed flows and coefficients into the Equation 4-1 for each of contaminant.

$$\text{Log}_{10}(Y) = B_0 + B_1 * \text{Log}_{10}(X)$$

Equation 4-1 Multivariate regression with a logarithmic transformation

4.2.2.2 Occurrence of emerging contaminants

A few studies have evaluated the occurrence of veterinary pharmaceuticals in agricultural watersheds (e.g. (Kurwadkar et al. 2013; Xian Zhang et al. 2012; Arikan, Rice, and Codling 2008)). Tetracyclines, sulfonamides, and monensin have been detected at concentrations from hundreds of ng/L to tens of µg/L. Peak concentrations are observed in summer months (Bernot, Smith, and Frey 2013; Lissemore et al. 2006), but may occur in winter or low-flow conditions (Xian Zhang et al. 2012; Arikan, Rice, and Codling 2008).

The occurrence of veterinary pharmaceuticals in the Shell Creek watershed has been documented, as described in Chapter 2 (Jaimes-Correa, Snow, and Bartelt-Hunt 2015). Most pharmaceuticals were detected at concentrations below 10 ng/L while monensin and lincomycin showed the highest values of 49 and 68 ng/L, respectively (Figure 4.5). Tylosin, tiamulin, and sulfamethazine had the highest detection frequency between 52% and 94% of samples.

Results indicated that tiamulin and sulfadimethoxine displayed differences between 2008 and 2009. Tiamulin and lincomycin were significantly higher in summer as similar as peaks of dissolved contaminants. The study confirmed the land application of manure containing veterinary pharmaceuticals from livestock production in Shell Creek. It suggests that occurrence of these emerging contaminants in the watershed is affected by hydrological conditions.

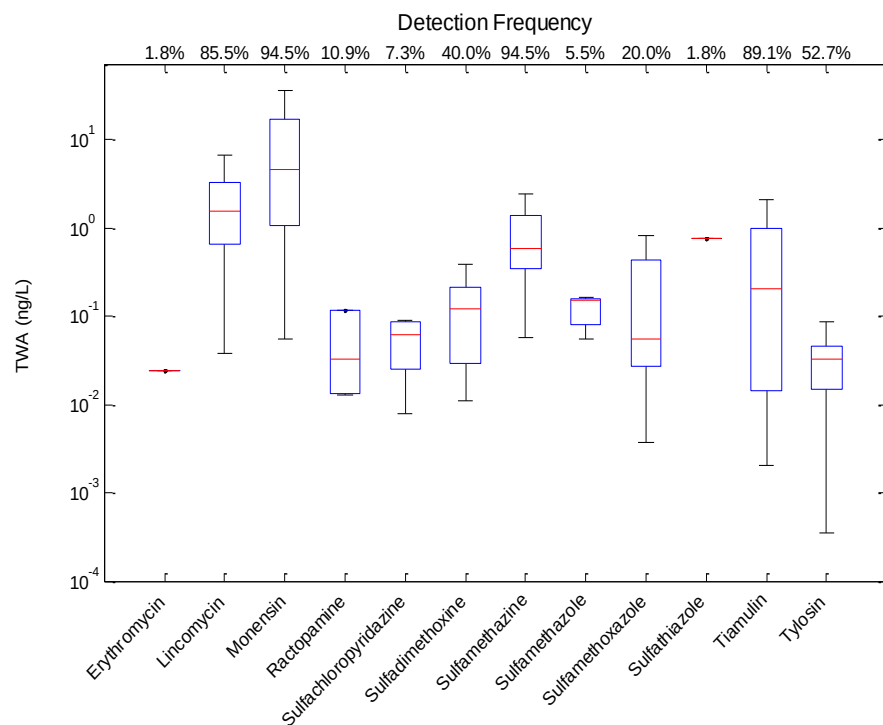


Figure 4.5 Occurrence of veterinary pharmaceuticals in Shell Creek, 2008-09. The split box shows the 25th, 50th, and 75th, whereas whiskers show the 5th and 95th percentiles.

4.2.3 The Soil and Water Assessment Tool

The Soil and Water Assessment Tool (SWAT) (Arnold et al. 1998; Neitsch et al. 2011) is a semi-distributed, physically-based, and open-source program that simulates hydrological processes, weather, sedimentation, soil temperature, crop growth, nutrients, pesticides, and agricultural practices of watersheds. It operates on daily time steps and discretizes the watershed into Hydrological Response Units (HRUs) overlapping soil type, land use, and slope. The HRU is the unit for routing water, sediments, nutrients, and contaminants fate and transport from landscapes.

4.2.3.1 *Input data*

Input data of hydrologic simulations included digital elevation model, land uses, and soil types. The configuration of the Shell Creek hydrologic model is presented in Chapter 3. Daily precipitation data were obtained from the National Oceanic and Atmospheric Administration (NOAA)'s National Climatic Data Center (NCDC) in the Global Historical Climatology Network (GHCN)-Daily database (Menne et al. 2012). Meteorological data such as relative humidity, solar radiation, air temperatures, and wind speed were accessed from the High Plains Regional Climate Center (HPRCC)'s Automated Weather Data Network (AWDN) (<http://www.hprcc.unl.edu>).

4.2.3.2 *Crop management and management practices*

Terracing was the selected management practice in Shell Creek and set through the operations option (.Ops) in SWAT. Irrigated crops and dryland are distributed equally in Shell Creek with 38% of the land area each (Table 4.2). Since the watershed model has 54 subbasins, the auto-irrigation was assigned randomly to the croplands in half of the subbasins. The other half of the subbasins were assumed drylands. The water source for irrigation was assumed from a deep aquifer, after Van Liew et al. (2012).

A common conservation practice in the US corn-belt is crop rotation that might involve corn-soybean or wheat-corn (Arabi et al. 2008). In Shell Creek, corn and soybean cover 49% and 27%, respectively (Table 4.2). Then, management operations shown in Table 4.3 were scheduled in SWAT. It preserved the spatial distribution of corn and soybean as follows. Corn was allocated randomly to 24 subbasins ($24/54 = 22\%$) while corn-soybean rotation was implemented in 30 subbasins (27%), and soybean exclusively was rotated to corn (27%).

Table 4.2 Distribution of irrigated and dryland areas, corn and soybean land use in Shell Creek

Land use	(%)	Irrigated	Dryland	Corn	Soybean
Irrigated Corn	24	✓		✓	
Irrigated Soybeans	14	✓			✓
Range, Pasture, Grass	18				
Dryland Corn	25		✓	✓	
Dryland Soybeans	13		✓		✓
Subtotal (%)	94	38	38	49	27

Source: Estimates from the 2005 Nebraska land use patterns map at 30 m cell size resolution distributed by CALMITT (2016).

Table 4.3 Scheduled management operations

Year	Month	Day	Operation	Description	Crop
1	4	10	Tillage operation	Tandem Disk, Plw Lc 13 ft.	CORN
1	4	28	Plant/begin growing season		
1	5	1	Pesticide application	Atrazine, 1 kg/ha	
1	6	28	Auto irrigation initialization*		
1	10	18	Harvest and kill operation		
1	10	25	Fertilizer application	Swine-fresh manure, 50 kg/ha	
1	11	1	Fertilizer application	Anhydrous Ammonia, 90 kg/ha	
1	11	15	Fertilizer application	Elemental Phosphorus, 15 kg/ha	
2	4	10	Tillage operation	Tandem Disk, Plw Lc 13 ft.	SOYBEAN
2	5	1	Pesticide application	Atrazine, 1 kg/ha	
2	5	10	Plant/begin growing season		
2	7	10	Auto irrigation initialization*		
2	9	20	Harvest and kill operation		
2	10	15	Fertilizer application	Swine-fresh manure, 50 kg/ha	
2	11	15	Fertilizer application	Elemental Phosphorus, 15 kg/ha	

* Water stress threshold = 0.95. Irrigation efficiency = 0.85. Water applied = 25 mm.

In the region, liquid manure that comes from feeding animal lots (CAFO) is commonly applied to cultivated land. The USDA (2012) reports about 1,550 farms with

1,050,000 head of swine, cattle, and poultry within the Shell Creek counties. From reviewed literature (Arabi et al. 2008; Van Liew, Feng, and Pathak 2012; Jha, Gassman, and Arnold 2007), the fertilization application rates for corn and soybean were assumed between 15 and 90 kg/ha (Table 4.3) and were the main source of nutrients into the watershed.

Pesticide routing for atrazine was activated in the soil chemistry module (.Chm) in SWAT. The atrazine application rate was assumed to 1 kg/ha, after reviewed literature (Van Liew, Feng, and Pathak 2012; Arabi et al. 2008). Pesticide application was also assumed homogeneous across the entire watershed since agriculture is the largest landuse.

4.2.3.3 Sediment, nutrients and pesticide modeling

SWAT simulates the physicochemical processes that might occur before water runoff from landscapes and routes through the sub-basins channels. Nitrogen and phosphorus cycles (Figure 4.6) are represented in SWAT like soil processes where elements are moving in and out pools (Figure 4.7). Nutrients processes include nitrification, mineralization of nitrogen or adsorption and fixation of phosphorus, and plant uptake. Soil erosion is estimated using the Modified Universal Soil Loss Equation (MUSLE) (Williams 1975), which is a modification of the Universal Soil Loss Equation (USLE) (Wischmeier and Smith 1978). Nutrients cycle are simulated after the Environmental Policy Integrated Climate (EPIC) model (J. R. Williams et al. 1989; Williams, Jones, and Dyke 1984). Nutrient inputs can include point and non-point sources.

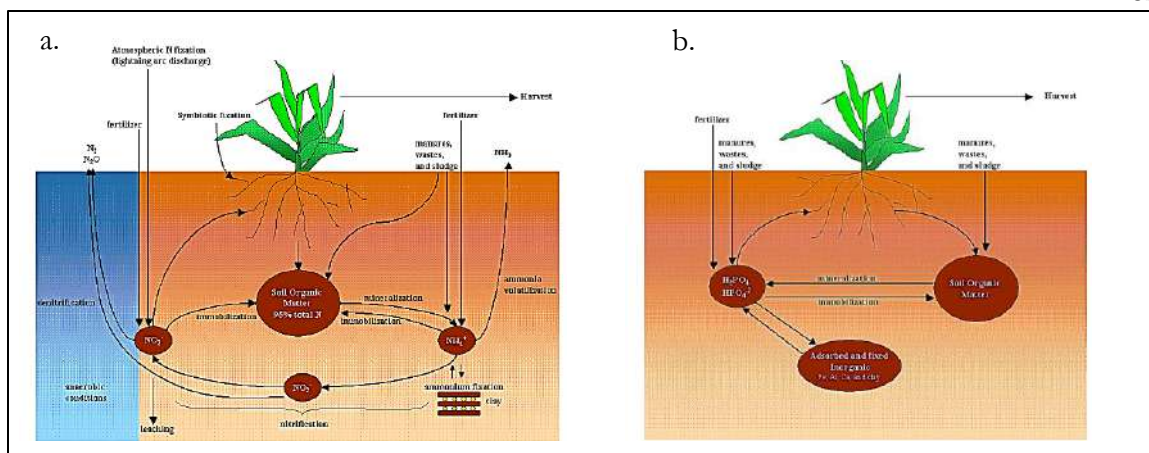


Figure 4.6 Cycles of (a) nitrogen and (b) phosphorus in SWAT. Adapted from Neitsch et al. (2011)

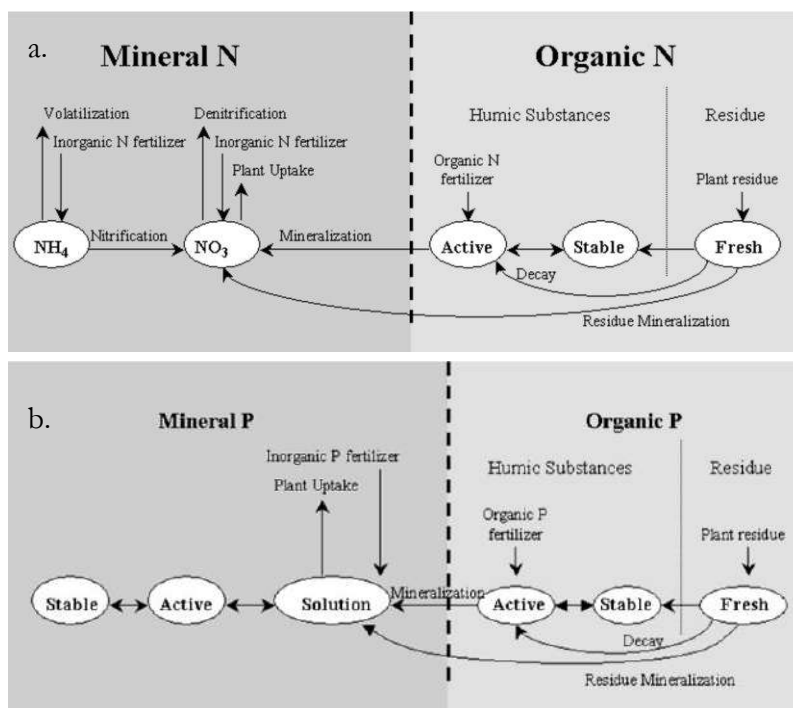


Figure 4.7 SWAT processes and pools of (a) nitrogen and (b) phosphorus in soil. Adapted from Neitsch et al. (2011).

Pesticide fate and transport involve degradation, infiltration, and volatilization processes (Figure 4.8). Algorithms in SWAT are also taken from EPIC model (J. R. Williams et al. 1989; Williams, Jones, and Dyke 1984). Pesticide can be moved in the solid (soil phase) or dissolved in the solution (liquid phase). Soluble pesticide can be transported via surface runoff, lateral flow, or infiltration, whereas surface runoff can transport sorbed pesticide to the main channel. Moreover, crop rotation and best management practices to reduce pollutants yield can be simulated in SWAT.

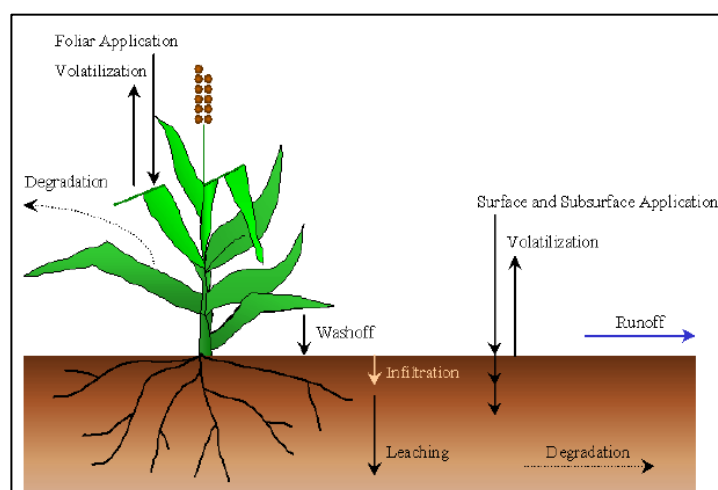


Figure 4.8 Fate and transport of pesticides in SWAT. Source: Neitsch et al. (2011).

SWAT also simulates the in-stream process of nutrients, pesticides, bacteria, and heavy metal using the Enhanced Stream Water Quality Model (QUAL2E) model (L. C. Brown and Barnwell Jr. 1987). The algorithm estimates 1-D longitudinal and temporal variation of water quality in-stream. SWAT algorithms for simulation of agricultural chemicals were adapted from GLEAMS (R. A. Leonard, W. G. Knisel, and D. A. Still 1987). For a more detailed description of process and equations of water quality modeling in

SWAT, refer to its software documentation (Neitsch et al. 2011). Previous works also summarize sediment and nutrient cycles modeling in SWAT (Abbaspour, Yang, et al. 2007; Santhi et al. 2006).

4.2.4 Water quality modeling

A watershed model of Shell Creek was built in SWAT following the procedure described in Chapter 3 and forced with rain gage precipitation data. Previous works suggest that a proper streamflow calibration ensures better water quality simulations (Gollamudi, A. Madramootoo, and Enright 2007; Santhi et al. 2001). Since runoff directly influences fate and transport of sediments, streamflow was calibrated first followed by sediments, nutrients, and atrazine loads.

The water quality model was calibrated in years 1992-94 through the Sequential Uncertainty Fitting ver. 2 (SUFI-2) procedure in SWAT-CUP (Abbaspour, Vejdani, et al. 2007). In SUFI-2, the P-factor represents the percentage of observed data within the 95% prediction uncertainty (95PPU), and R-factor equals the mean thickness of 95PPU band divided by the standard deviation of observed data (Abbaspour, Vejdani, et al. 2007). A single objective function evaluated the model performance, the Nash-Sutcliffe efficiency (NSE) coefficient (Nash and Sutcliffe 1970) shown in Equation 3-3, which compares simulated and observed data. Here, the fitted loadings from the statistical regression were assumed true observations. Implementing a multi-objective function to calibrate multiple water quality variables (e.g. (Abbaspour, Yang, et al. 2007; White and Chaubey 2005) can be challenging for novice modelers, require a higher level of expertise on setting calibration algorithms and use longer computational time.

For any variable (e.g. sediments), a 2,000-runs iteration was performed to identify the most sensitive parameters ($p\text{-value} < 0.1$) in its generation, and narrow their initial range.

Once parameters of a given output (e.g. flow) were calibrated, their ranges were fixed to the best simulation (i.e. the run that had the highest NSE). Later, parameters associated to the next variable (e.g. sediments) were calibrated and steps repeated until last variable.

Parameters were selected after literature and SWAT documentation (Van Liew, Feng, and Pathak 2012; Abbaspour, Yang, et al. 2007; Jha, Gassman, and Arnold 2007; Gollamudi, A. Madramootoo, and Enright 2007; Arabi et al. 2008; Santhi et al. 2006; White and Chaubey 2005; Santhi et al. 2001; Arnold et al. 2012).

Lastly, the water quality model was validated using another precipitation data set (2008-09) while the best parameters values from calibration remained fixed. The model performance was compared at daily and monthly simulation steps.

4.2.5 Extreme hydrometeorological and climate conditions

The 3-month Standardized Precipitation Index (SPI) was assessed to identify extreme hydrometeorological and climate conditions in Shell Creek (Table 4.4). The SPI in summer and winter was averaged in June-August and December-February, respectively. Precipitation data were obtained at the rain gage near Columbus, NE located closer to the stream gage station (Figure 2.1b). A large absolute SPI value indicates a very extreme condition. In this study, an index above 1 or below -1 indicated a very wet and very dry condition, respectively.

Additionally, precipitation anomalies along the 20th century in Shell Creek were estimated (Figure 4.9). Although the annual amount of precipitation seems to increase (Figure 4.9a), the trend is not significant as evaluated by a fitted least-squares regression with

a p-value of 0.11. Similarly, change in monthly anomalies (Figure 4.9b) is not significant (p-values = 0.08).

First, the watershed model of Shell Creek was calibrated for flow and water quality variables in 2002-13. The observed data generated using the fitted statistical model was assumed as actual observations. An iteration of 2,000-runs identified the most sensitive parameters to each variable and their calibrated ranges. Then, the parameters values from the “best” run (highest NSE) in calibration were fixed. Lastly, a long-term rain gage data forced the model in 1910-2010.

Table 4.4 Years with extreme climate conditions in summer and winter

Summer				Winter			
Dry		Wet		Dry		Wet	
Year	SPI	Year	SPI	Year	SPI	Year	SPI
1912	-1.03	1924	1.33	1923	-1.11	1914	1.52
1931	-1.21	1948	1.12	1931	-1.05	1915	2.02
1934	-1.10	1951	1.02	1933	-1.21	1925	1.22
1936	-2.90	1967	1.57	1951	-1.27	1932	2.09
1974	-1.21	1982	1.55	1955	-1.22	1936	1.68
1976	-1.96	1993	1.52	1957	-1.64	1941	1.06
1989	-1.42	1996	1.11	1968	-1.36	1949	1.51
1997	-1.06	1999	1.30	1971	-1.01	1982	1.15
2002	-1.06	2008	1.12	1977	-2.12	1983	1.14
2006	-1.45	2010	1.75	1978	-1.06	1984	1.02
2012	-1.12			1981	-2.08	1989	1.31
				1987	-1.48	1992	1.1
				1998	-1.38	1997	1.57
				2000	-1.41	2007	1.42
				2003	-1.18		
				2014	-1.05		

Finally, the distribution of monthly flows and pollutant loads in extreme climate conditions were calculated, and their exceedance probabilities plotted. A multiple

comparisons was performed using a Tukey-Kramer honest significant difference criterion.

Here, a p-value (0.05) tests the hypothesis that the true difference of means for the corresponding groups (e.g. wet summer, dry winter) was equal to zero.

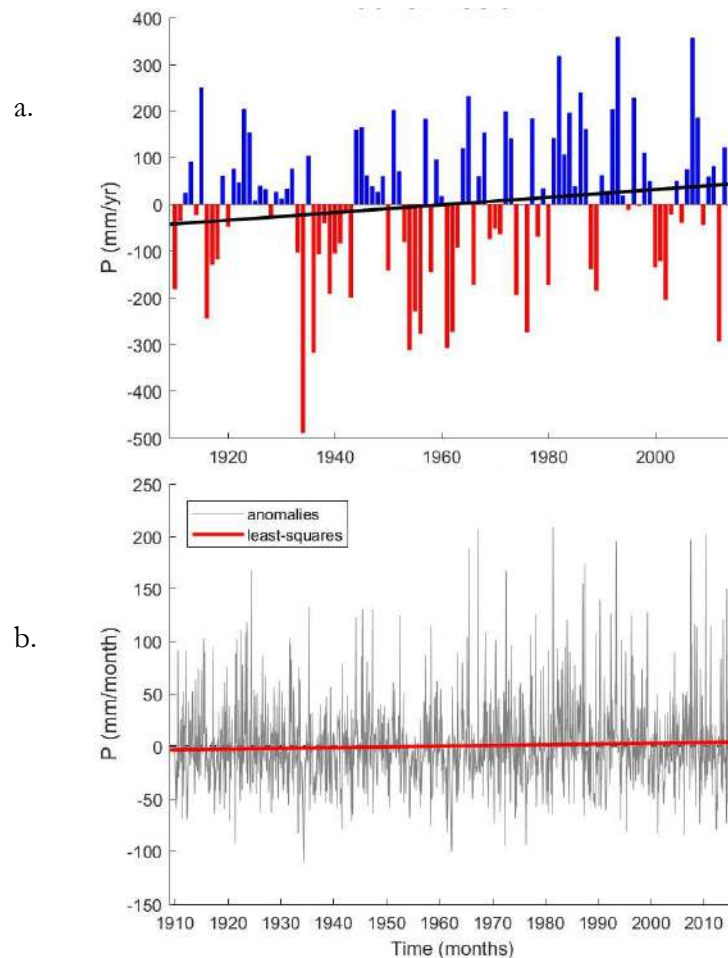


Figure 4.9 Shell Creek (a) annual and (b) monthly precipitation anomalies. Source: Daily precipitation of the NCDC-NOAA rain gage COLUMBUS 3 NE USC00251825.

4.2.6 Modeling veterinary antibiotics

The pesticide sub-routine of the Soil and Water Assessment Tool (SWAT) was used to simulate veterinary antibiotics in the Shell Creek watershed. Figure 4.10 shows possible

pathways in soils where manure is applied. A previous study in Shell Creek provides monthly concentrations of 12 veterinary antibiotics in 2008-09 (Jaimes-Correa, Snow, and Bartelt-Hunt 2015). Monensin, sulfamethazine, and tylosin had high occurrences and therefore selected for modeling. The monthly time-weighted average concentrations were obtained from POCIS (Chapter 2), and loads were calculated as the product of flow times the concentration.

Calibration of antibiotics loads was performed in SWAT-CUP for years 2008-09. Model was not validated due to the limited records. NSE evaluated the model performance and observed loads. Since SWAT can handle one pesticide at a time, each antibiotic was simulated individually. The water quality model validated for Shell Creek was used to simulate the monthly loads of veterinary antibiotics.

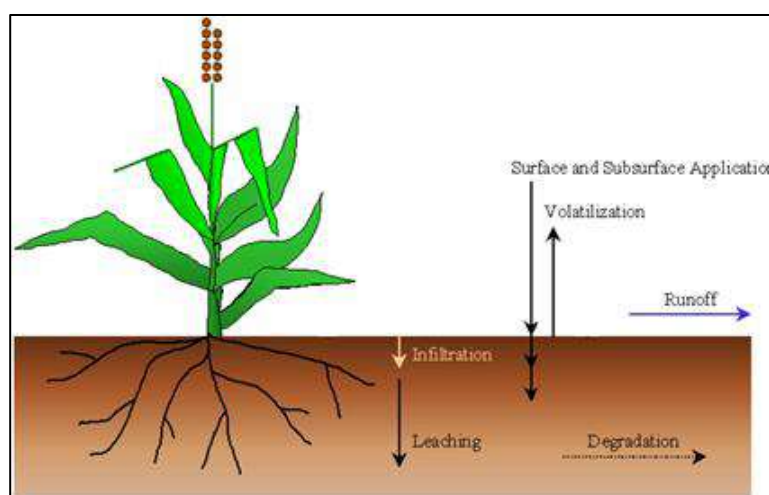


Figure 4.10 Fate and transport of emerging contaminants. Adapted from Neitsch et al. (2011).

The most sensitive parameters to atrazine included soil adsorption coefficient normalized for soil organic carbon content (SKOC) and wash-off fraction (WOF). The SKOC takes into account that partitioning of pesticides depend on the organic matter in soil and the WOF is the portion of pesticide on plant leave that can be washed off after precipitation events (Neitsch et al. 2011).

From reviewed literature, some values were changed for each veterinary antibiotic while others kept the default of atrazine (Table 4.5). When different values were reported (e.g. solubility in water, concentration in manure), their average was used instead. Initially, a single run with fixed parameters values was performed i.e. uncalibrated model. Lately, the model was calibrated by running 1,000 parameter-values combinations generated by SUFI-2 in SWAT-CUP, within a range $\pm 25\%$ from their initial values.

Table 4.5 Parameters values for atrazine and veterinary antibiotics modeling

SWAT parameters		Pesticide		Veterinary antibiotics	
Description	Units	Atrazine	Monensin	Sulfamethazine	Tylosin
Class			Antiprotozoal	Sulfonamide	
Chemical Abstract Number			17090-79-8	57-68-1	1401-69-0
Pesticide percolation coefficient		0.5	5E-1	5E-1	5E-1
Application efficiency	fraction	0.99	9.90E-1	9.90E-1	9.90E-1
Degradation half-life on the foliage	days	5	5E+0	5E+0	5E+0
Degradation half-life in the soil	days	61	8.64E+3 (e)	1.8E+3 (e)	0.553E+3 to 7.99E+3 (e)
Soil adsorption coefficient normalized for soil organic carbon content	(mg/kg) / (mg/L)	171	62.05E+0 (e)	35.23E+0 (e)	16.03E-1 (e)
Wash-off fraction	fraction	0.45	4.50E-1	4.50E-1	4.50E-1
Solubility of the chemical in water	mg/L	33	2.2E-6 to 3.1E-3 (c); Slightly soluble in water (d); 3.12E-3 (e)	7.5E+0 to 1.5E+3 (c); 1.50E+3 to 1.92E+3 (d); 1.127E+4 (e); 3.1E-1 g/L (f)	5E+0 § (d)
Amount of pesticide applied to HRU	kg/ha	1	2.50E-4	3.60E-4	3.95E-4
Depth of pesticide incorporation in the soil	mm	0	0	0	0

Sources: (a) Aga et al., 2016. (b) Brown et al., 2015. (c) Thiele-Brun, 2003 (d) PubChem. (e) EPIWEB 4.1. US EPA. 2012. Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.11. The United States Environmental Protection Agency, Washington, DC, USA. (f) Sallach et al., 2015. (g) Soni et al., 2015. (h) Joy et al., 2013. (i) Song and Guo, book chapter in Z. He and H. Zhang (eds.).

4.3 Results

4.3.1 Fitted linear model to observed data

Table 4.6 and Figure 4.11 illustrate the regression analysis performed for water quality variables as a function of monthly flows. Results indicate that after accounting for the relationships among the response variables, between 75% and 89% of the variation seen in the Log_{10} of nutrients and sediments is explained by the $\text{Log}_{10}(\text{Q})$. Moreover, the p-value of $< 3.8 \times 10^{-8}$ confirmed it is useful in predicting the Log_{10} of loading pollutants. However, atrazine displayed the lowest variation (56%) explained by the $\text{Log}_{10}(\text{Q})$, which suggests that other processes rather than hydrological (e.g. biochemical) might influence the fate and transport of atrazine. Figure 4.11 shows that the statistical model for sediments and nutrients has a narrow confidence interval at lower $\text{Log}_{10}(\text{Q})$, but there is a larger uncertainty for atrazine estimates.

Using streamflows and replacing in the Equation 4-1 the respective coefficients from Table 4.6 for each water quality variable, a dataset of daily loads was generated in both periods 1992-94 and 2008-09. Figure 4.12 and Figure 4.13 show the generated daily and monthly series of loading pollutants. Monthly estimates were calculated as averages of daily values.

Table 4.6 Multivariate regression results

Water quality variable	B_0	B_1	Multiple R-squared	p-value
Sediments	1.41	2.22	0.84	2.5×10^{-16}
Nitrogen	2.64	1.09	0.89	$< 2.2 \times 10^{-16}$
Phosphorus	1.57	1.22	0.75	1.36×10^{-12}
Atrazine	1.78	1.85	0.56	3.73×10^{-8}

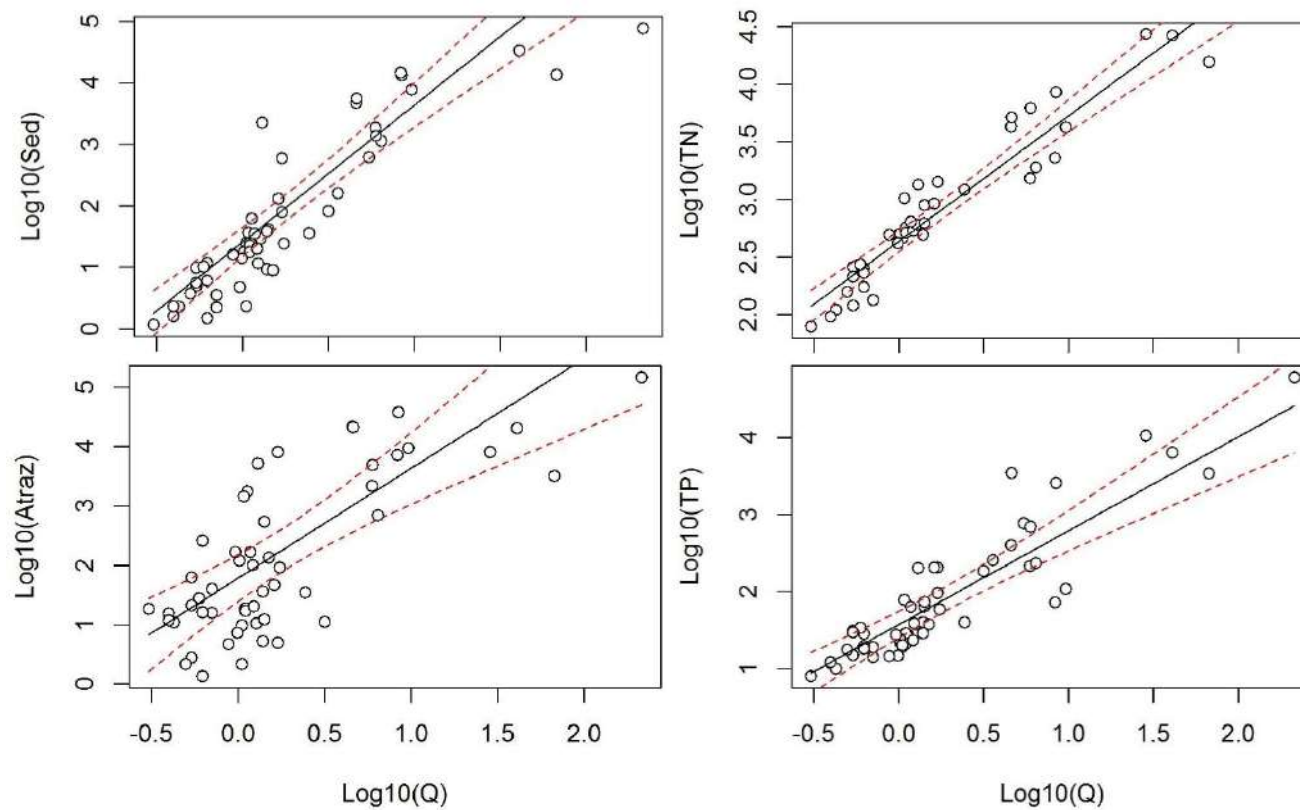


Figure 4.11 Logarithmic regression between sediments, nutrients, atrazine, and flow in Shell Creek. The black line is the fitted regression. Red dashed lines display the 95% confidence band. Sed: sediments; Atraz: atrazine; TN: total nitrogen; TP: total phosphorus; Q: flow.

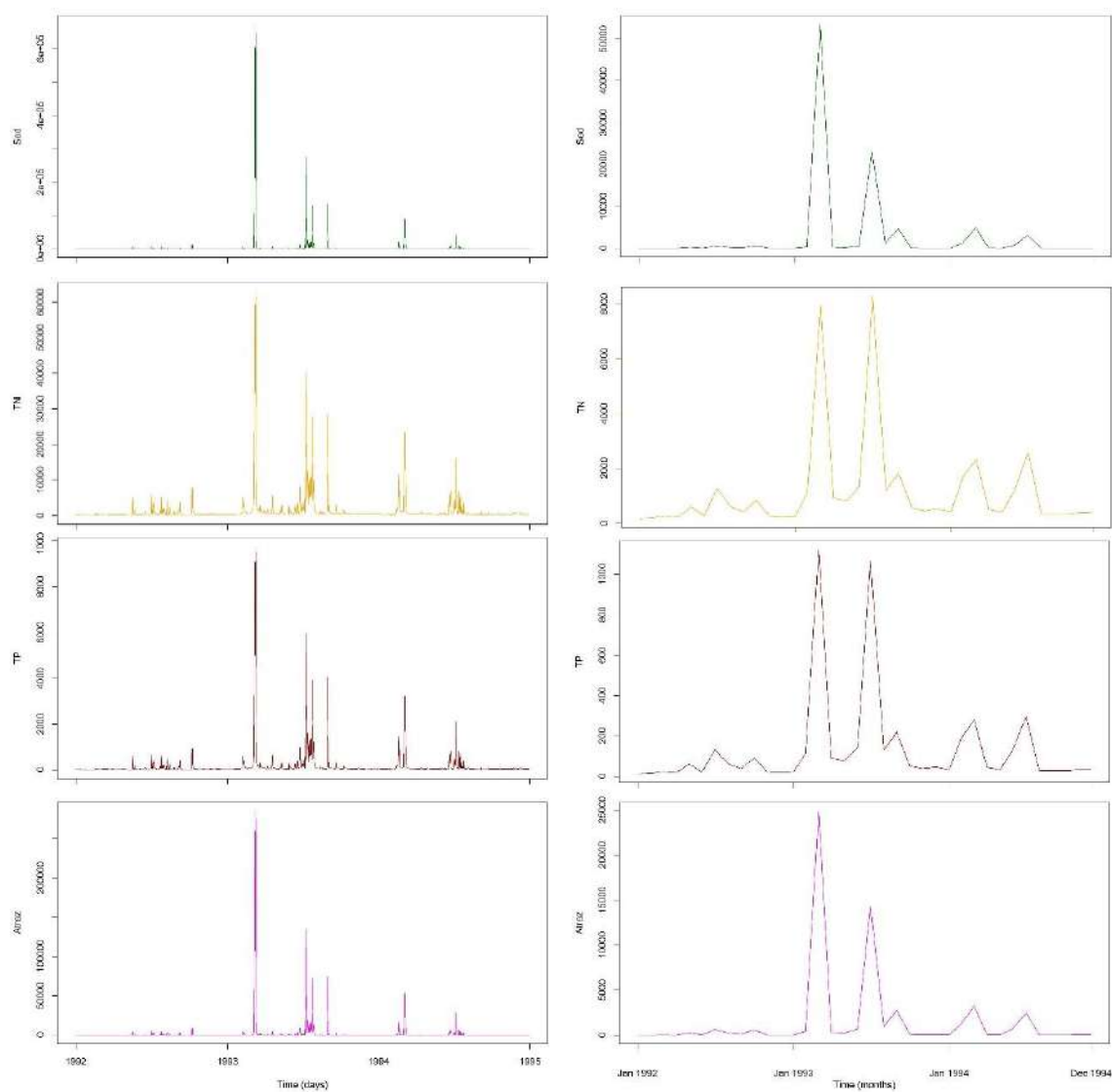


Figure 4.12 Computed daily and monthly loading pollutants, 1992-94. Sed: sediments (ton), TN: total nitrogen (kg), TP: total phosphorus (kg), Atraz: atrazine (mg)

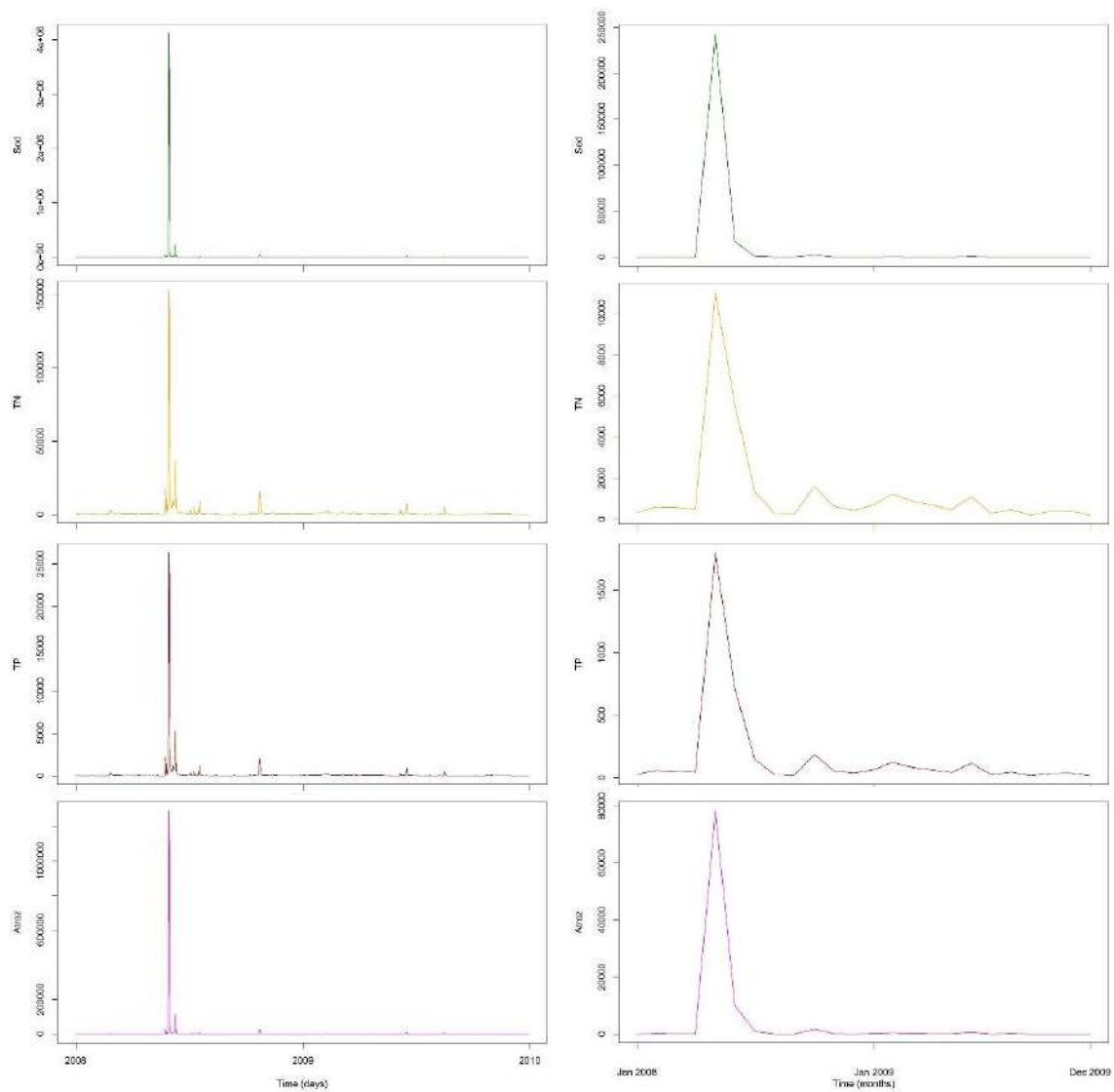


Figure 4.13 Computed daily and monthly loading pollutants, 2008-09. Sed: sediments (ton), TN: total nitrogen (kg), TP: total phosphorus (kg), Atraz: atrazine (mg)

4.3.2 Water quality modeling

4.3.2.1 Calibration using observed data

Figure 4.14a presents the model performance in calibration and validation periods.

Output flow and loads were compared against the available observations in Shell Creek. The

model performed better during calibration with NSE of 0.26-0.45 for streamflow, sediments, and nutrients. In validation, NSE of flow and pollutants decreased below 0.2. Lower performance in validation can be expected since parameters values were fixed to the best simulation in calibration and the model forced with another precipitation dataset. Nevertheless, SWAT poorly reproduced atrazine loads since it displayed negative NSE. In Figure 4.14b, numerical and linear models are compared using R^2 statistics. Both models similarly reproduced variance of sediments and phosphorus loads, although, the linear one showed a better atrazine variance ($R^2 = 0.56$).

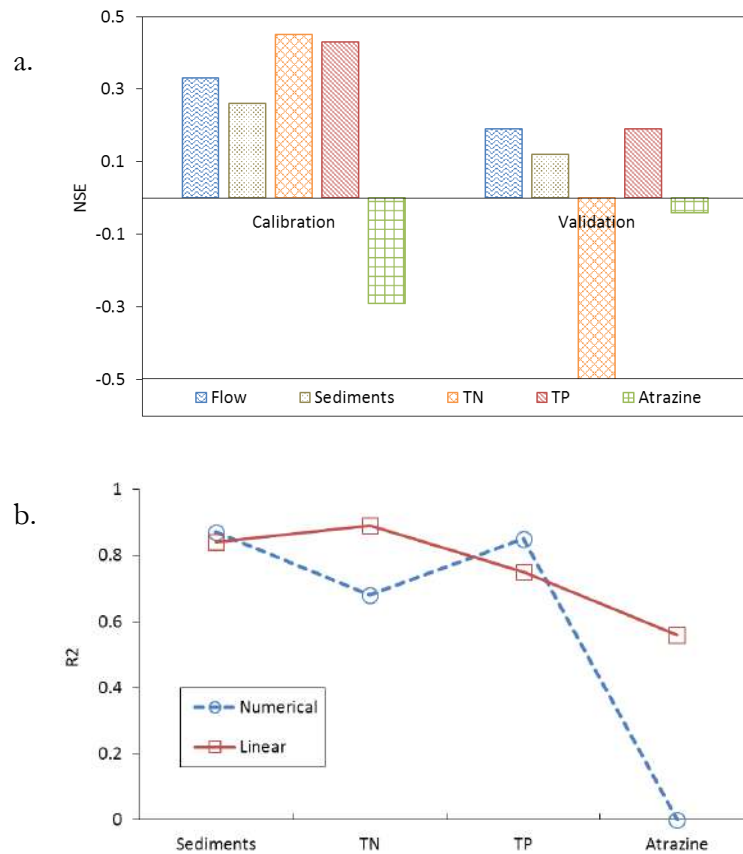


Figure 4.14 Performance of water quality (a) numerical and (b) linear regression models. Calibration (1992-94). Validation (2008-09). TN: total nitrogen, TP: total phosphorus. NSE of validated TN was -2.96.

4.3.2.2 Calibration using fitted observations

Table 4.7 and Figure 4.15 showed the model performance when the fitted loads calibrated and validated the water quality model outputs. Results compared outputs at daily and monthly time steps. Monthly flows and sediments are better reproduced than daily values as judged by greater NSE of 0.65-0.79 and 0.47-0.69, respectively. Model performance decreases for daily simulations with NSE of 0.19-0.43 for flows and near zero for sediments. Similarly, the model displayed a poor performance for atrazine with NSE below 0.25. In general, the model shows an NSE of streamflow better than it does for sediments and atrazine loads.

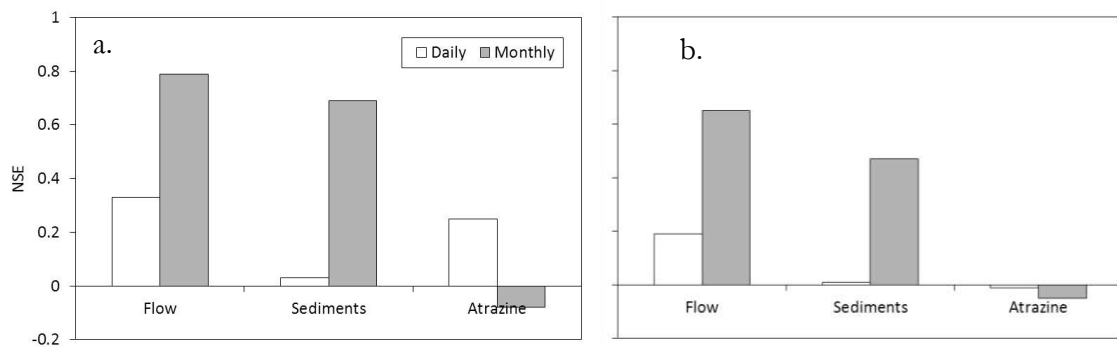


Figure 4.15 Model performance for daily and monthly flow and water quality in (a) calibration and (b) validation periods

Table 4.7 Daily and monthly performances of the water quality model for Shell Creek

SWAT output time-step	Target variable	Iteration [#]	No. parameters [§]	P [‡]	R [‡]	NSE [†] Flow	NSE Sediments	NSE Atrazine
Daily	Flow	S	31	0.94	0.79	0.29	-	-
		C	9	0.91	0.5	0.33	-	-
		V	-	-	-	0.19	-	-
	Sediments	S	9	0.37	0.01	0.36	0.02	-
		C	5	0.11	0.01	0.37	0.03	-
		V	-	-	-	0.43	0.01	-
	Atrazine	S	10	0.01	1365	0.37	0.03	0.23
		C	5	0.18	181.67	0.37	0.03	0.25
		V	-	-	-	0.43	0.01	-0.01
Monthly	Flow	S	31	0.94	1.91	0.63	-	-
		C	13	0.89	1.71	0.79	-	-
		V	-	-	-	0.65	-	-
	Sediments	S	9	0.33	1.21	0.77	0.69	-
		C	5	0.39	0.84	0.77	0.69	-
		V	-	-	-	0.69	0.47	-
	Atrazine	S	10	0	117141	0.77	0.69	-0.09
		C	4	0.61	12.19	0.77	0.69	-0.08
		V	-	-	-	0.69	0.47	-0.05

[#] S: Sensitivity analysis and C: Calibration (1992-94) used a 2,000-runs iteration total, V: Validation (2008-09) used a 1-run with the best parameters from calibration. [†] Nash-Sutcliffe efficiency coefficient. [§] Number of parameters allowed changing their values in a given iteration. [‡] P-factor: percentage of observations within 95PPU, and R-factor: mean thickness of 95PPU band divided by the standard deviation of observed data.

The best parameters range from the sensitivity and calibration are presented in Table 4.9. The sensitivity analysis revealed that similar parameters influence daily and monthly estimates of sediments and atrazine loads. However, parameters associated to flow generation varied between monthly and daily simulations. As shown in Chapter 3, the most sensitive parameter to streamflow was also CN2 since the curve number method was chosen in SWAT for flow generation.

4.3.3 Water quality responses to extreme climate conditions

The calibrated model in 2002-10 simulated streamflow, sediments, nitrogen, and phosphorus with NSE of 0.78, 0.82, 0.61, and 0.72, respectively, while atrazine had an NSE of 0.01. Figure 4.16 displays the temporal variation of loading pollutants in calibration period. Later, a long-term simulation between 1910 and 2010 was performed. Figure 4.17 compares the distribution of loads in years with extreme climate conditions in summer and winter. Results from the multiple comparison tests evidenced a significant difference between streamflow, sediments, and nutrients in wet summer and other seasons (Table 4.8). Atrazine had no differences under extreme climate conditions.

4.3.4 Veterinary antibiotics modeling

Table 4.10 presents the calibration of veterinary antibiotics loads in Shell Creek. Figure 4.19 displays their temporal variation. The uncalibrated model using the parameters values from literature had a poor performance ($NSE < -613$). However, the model performed better after calibration. For instance, NSE of monensin loads increased from -613 to -0.23.

Table 4.8 presents multiple comparison tests of flow and pollutant loads under extreme climate conditions in Shell Creek. Different letters show significant differences between group means (e.g. wet summer, dry winter). Results indicate that monthly flows are significantly greater in wet summer followed by wet winter (Figure 4.17). The analysis also suggests that sediments and nutrients loads are significantly larger in wet summer than any other extreme conditions with higher monthly loads, as evidence in Figure 4.17. Nonetheless, atrazine does not show differences between extreme conditions.

Figure 4.18 illustrates the probability of exceedance for flows and pollutants in extreme hydrometeorological and climate conditions between 1910 and 2010. As expected, conditions of greater flow and loads have lower probabilities, i.e. these are more extreme and less likely to occur.

Table 4.8 Multiple comparisons of flow and pollutants under extreme climate conditions

	Summer		Winter	
	Wet	Dry	Wet	Dry
Flow	A	B	C	B
Sediments	A	B	B	B
Nitrogen	A	B	B	B
Phosphorus	A	B	B	B
Atrazine	A	A	A	A

Table 4.9 Calibrated streamflow and loads for Shell Creek water quality model

Output	Parameter	Range		Monthly				Daily		
				Rank¶	Calibrated range		Rank	Calibrated range		
					Min.	Max.		Min.	Max.	
	SWAT name †	Description	Min.	Max.		Min.	Max.		Min.	Max.
Flow	r__ALPHA_BF.gw	Baseflow alpha factor (days)	-0.1	0.1	10	-0.008	0.1	--	--	--
	r__CN2.mgt	SCS runoff curve number factor	-0.2	0.2	1	-0.028	0.2	7	-0.082	0.153
	v__CH_K2.rte	Effective hydraulic conductivity in main channel alluvium	0.1	150	6	0.1	75.247	6	0.1	75.917
	v__CH_N2.rte	Manning's "n" value for the main channel	0.01	0.3	12	0.01	0.167	--	--	--
	v__ESCO.hru	Soil evaporation compensation factor	0.001	1	4	0.301	0.902	5	0.001	0.515
	v__GW_DELAY.gw	Groundwater delay (days)	0	500	11	125.357	376.143	--	--	--
	v__GW_REVAP.gw	Groundwater "revap" coefficient	0.02	0.2	13	0.02	0.119	--	--	--
	v__GWQMN.gw	Threshold depth of water in the shallow aquifer required for return flow to occur (mm)	0	5000	8	1608.571	4826.429	2	1451.070	4353.930
	v__OV_N.hru	Manning's "n" value for overland flow	0.01	30	9	0.01	17.143	--	--	--
	v__SFTMP.bsn	Snowfall temperature	-5	5	3	-5	1.488	4	-4.563	1.813
	v__SMTMP.bsn	Snow melt base temperature	-2	20	5	-2	11.756	1	-2	5
	v__SNO50COV.bsn	Snow water equivalent that corresponds to 50% snow cover	0.2	0.8	2	0.02	0.540	3	0.466	0.8
	v__SNOCOVMX.bsn	Minimum snow water content that corresponds to 100% snow cover	0	500	7	0	315.393	--	--	--
	r__CH_S2.rte	Average slope of main channel	-0.005	0.01	--	--	--	9	-0.001	0.007
	v__REVAPMN.gw	Threshold depth of water in the shallow aquifer for "revap" to occur (mm)	0	500	--	--	--	8	0	297.143

Sediments	v__CH_COV1.rte	Channel erodibility factor	-0.05	0.6	1	-0.011	0.396	1	-0.05	0.306
	r__USLE_K(1).sol	USLE equation soil erodibility (K) factor	-0.2	0.2	2	-0.020	0.2	2	-0.052	0.2
	r__USLE_P.mgt	USLE equation support practice factor	-0.2	0.2	3	-0.050	0.2	3	-0.007	0.2
	v__USLE_C{19}.plant.dat	Min value of USLE C factor	0.001	0.5	4	0.001	0.303	4	0.240	0.5
	v__USLE_C{56}.plant.dat	applicable to the land cover/plant	0.001	0.5	5	0.001	0.312	5	0.201	0.5
Atrazine	v__PST_DEP{[1],4}.mgt	Depth of pesticide incorporation in the soil	0	500	1	207.854	500	1	154.605	463.895
	v__AP_EF{3}.pest.dat	Application efficiency	0	1	2	0	0.517	2	0	0.580
	r__SKOC{3}.pest.dat	Soil adsorption coefficient normalized for soil organic carbon	-0.05	0.05	3	-0.028	0.024	3	-2.25E-04	0.05
	r__WSOL{3}.pest.dat	Solubility of the chemical in water	-0.05	0.05	4	-0.050	0.008	5	-0.049	0.017
	v__PERCOP.bsn	Pesticide percolation coefficient	0	1	--	--	--	4	0	0.515

[†] Indicate whether the original value was (v) replaced by another value, or (r) multiplied by one (1) $\pm$ new value, in the given range. --: Not applicable. [¶] Rank from global sensitivity analysis using SUFI-2 after a 1000-runs iteration.

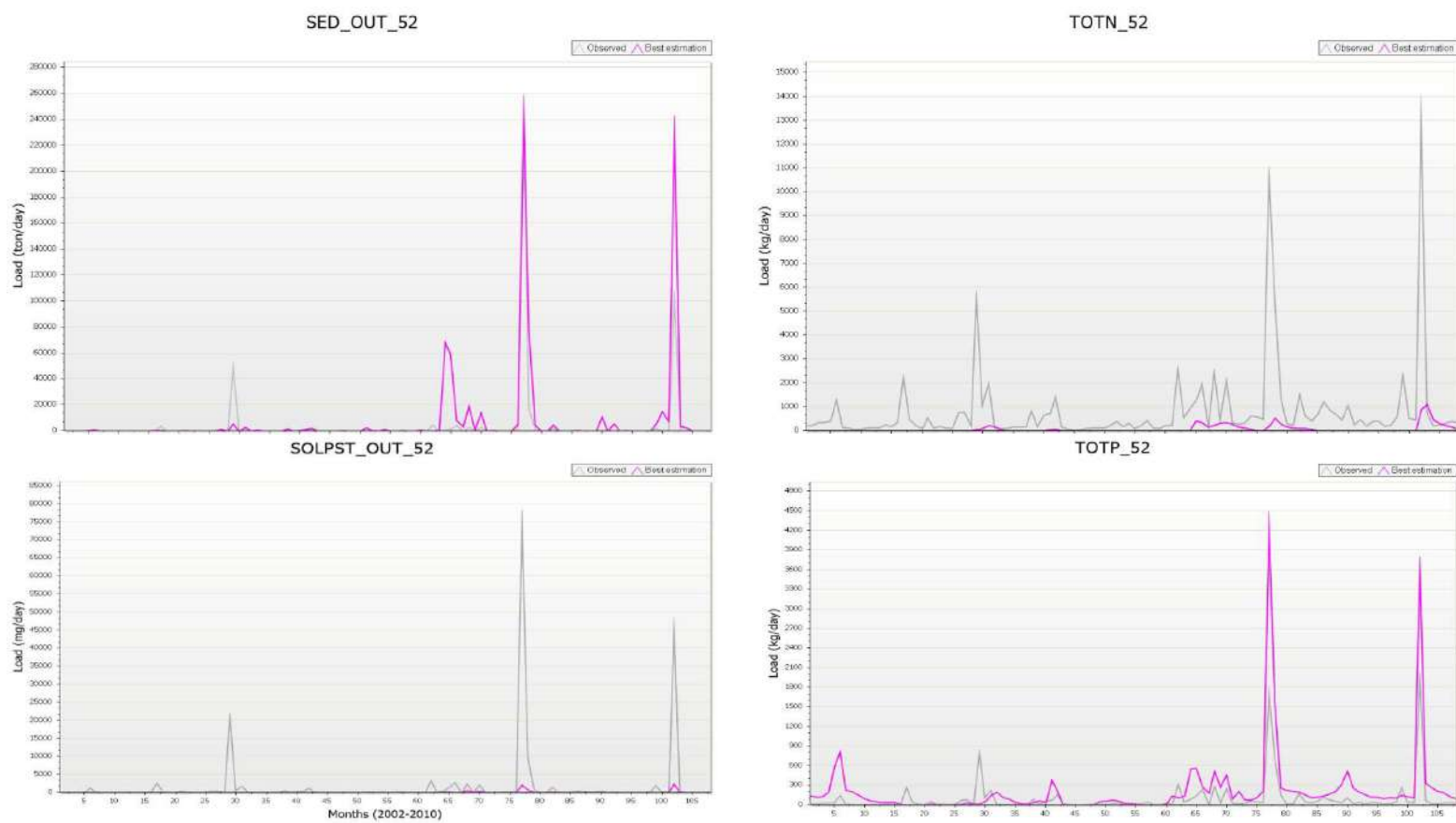


Figure 4.16 Calibrated monthly loads in Shell Creek in 2002-10. Observed data from the fitted model. FLOW_OUT: streamflow, SED_OUT: sediments, TOTN: total nitrogen, TOTP: total phosphorus, SOLPST_OUT: atrazine.

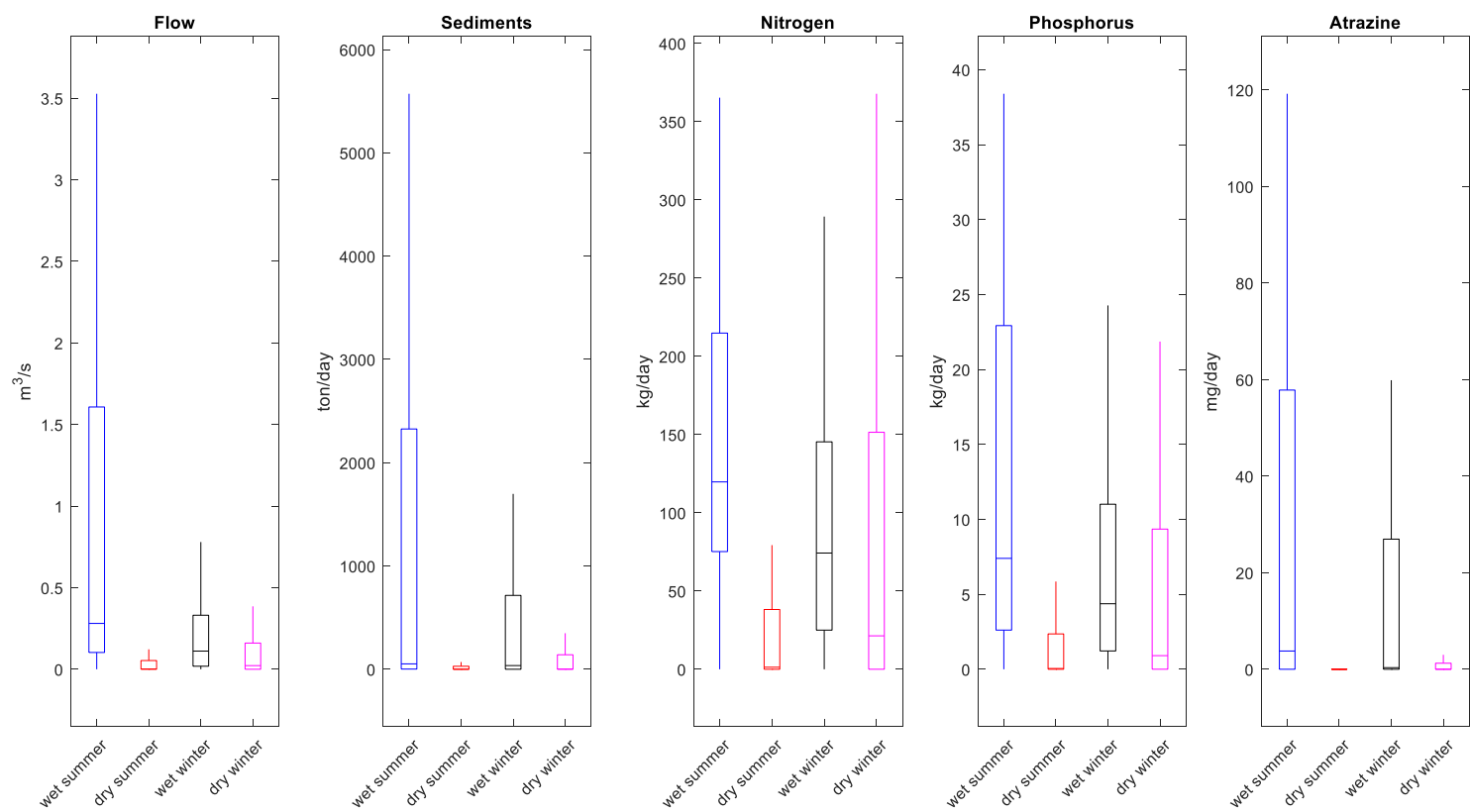


Figure 4.17 Monthly flows and loading pollutants in years of extreme climate conditions, 1910-2010

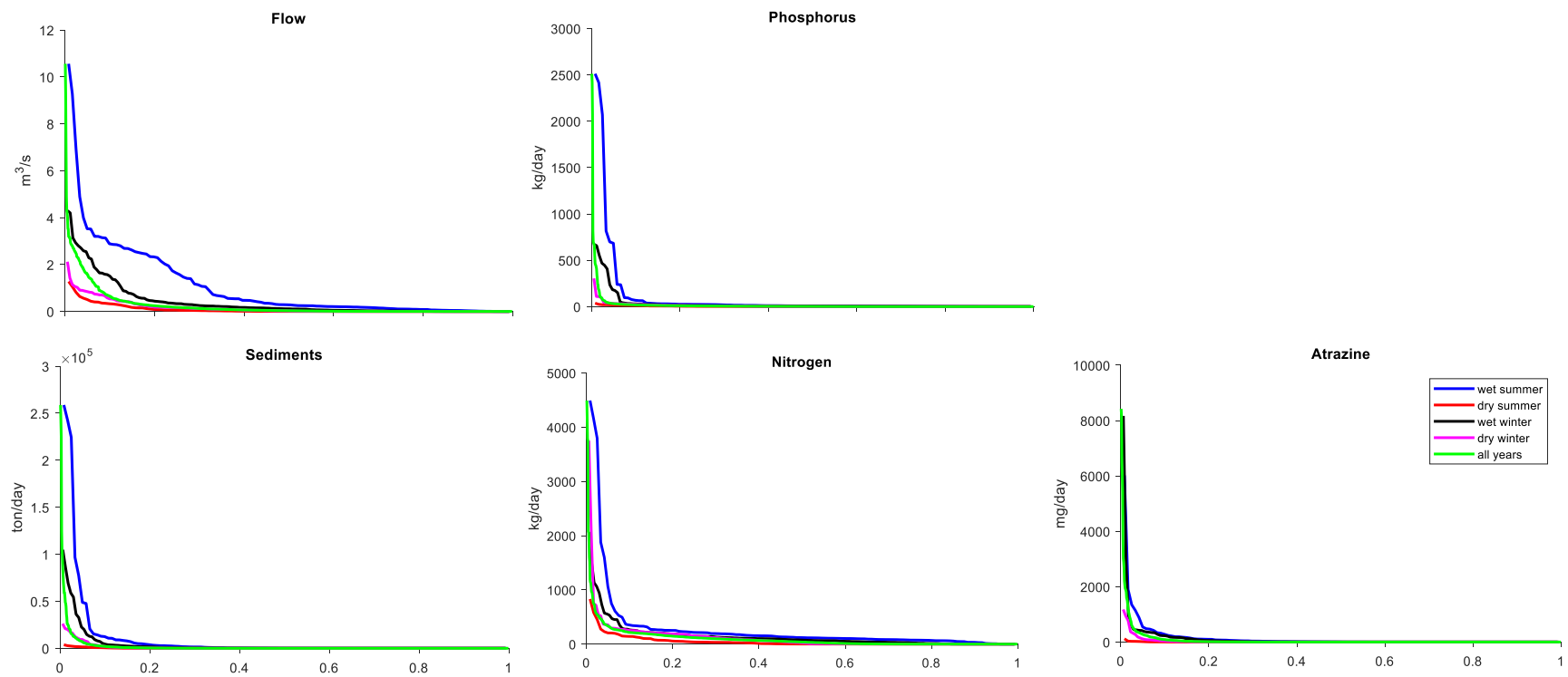


Figure 4.18 Probability of exceedance for monthly flows and pollutants in extreme hydrometeorological and climate conditions, 1910-2010

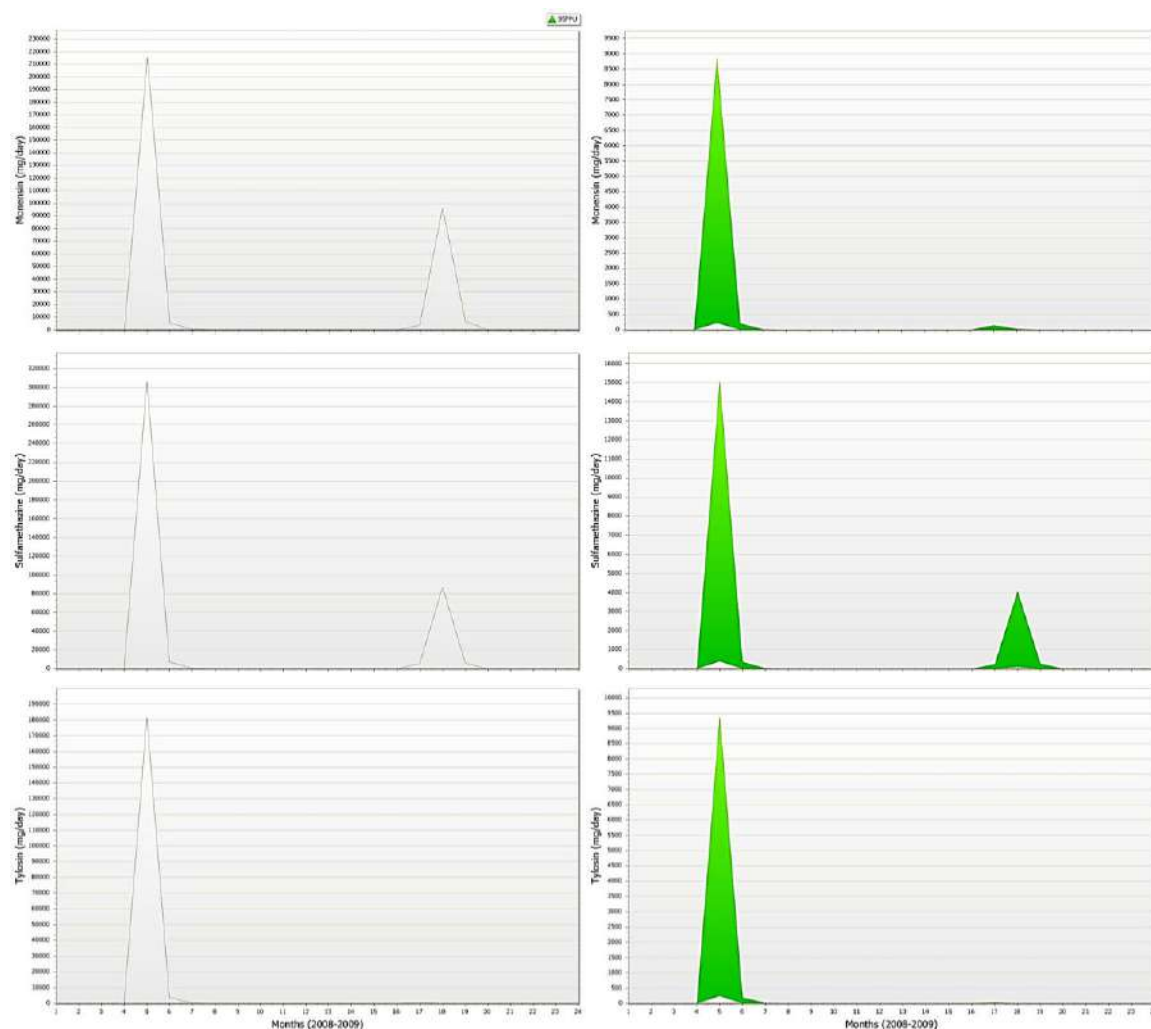


Figure 4.19 Simulated veterinary antibiotics loads in Shell Creek. Left: uncalibrated model. Right: calibrated model

Table 4.10 Uncalibrated and calibrated loads of veterinary antibiotics in SWAT

Parameter	Description	Monensin		Sulfamethazine		Tylosin	
		Uncalibrated	Calibrated	Uncalibrated	Calibrated	Uncalibrated	Calibrated
v__PST_DEP{[1],4}.mgt	Depth of pesticide incorporation in the soil	0	2.75	0	88.75	0	217.75
v__AP_EF{3}.pest.dat	Application efficiency	0.99	0.808335	0.99	0.958815	0.99	0.964755
v__SKOC{3}.pest.dat	Soil adsorption coefficient normalized for soil organic carbon content	62.05	54.829	35.23	26.25	1.603	1.306
v__WSOL{3}.pest.dat	Solubility of the chemical in water	0.0031	0.002421	1500	10574.04	5	5.54875
v__PST_KG{[1],4}.mgt	Amount of pesticide applied to Hydrologic Response Unit (HRU)	0.00025	0.000243	0.00036	0.000423	0.00028	0.000394
v__HLIFE_F{3}.pest.dat	Degradation half-life on the foliage	5	1.6975	5	4.8275	5	1.5025
v__HLIFE_S{3}.pest.dat	Degradation half-life in the soil	8640	7830	1800	2056.95	4270	7099.518
v__WOF{3}.pest.dat	Wash-off fraction	0.45	0.2565	0.45	0.2105	0.45	0.2045
NSE		-613.68	-0.23	-167,929	-1.21	-79.2	-0.07

4.4 Discussion

4.4.1 Water quality modeling

The sensitivity analysis displayed similarities in most of the parameters influencing daily and monthly loads of sediments and atrazine (Table 4.9). Simulations could have the same sensitive parameters since watershed physical characteristics and forcings remained identical. However, there were differences in the sensitivity to flow generation. Artifacts in automatic calibration to match simulated outputs with observations has been reported previously (Price et al. 2014).

The Shell Creek model displayed NSE for monthly flows and sediments of 0.65-0.79 and 0.47-0.69, respectively. A prior modeling of Shell Creek and Logan Creek, Nebraska reproduced monthly flows with NSE of 0.82-0.83 and 0.58-0.88, whereas sediments showed NSE of 0.90 and 0.84, respectively (Van Liew, Feng, and Pathak 2012). Simulated monthly flows in the North Bosque River, Texas had NSE between 0.62 and 0.87 (Santhi et al. 2001). The Shell Creek model performance in this study supports the modeling approach implemented, calibrating one variable at a time. First, flows followed by sediments, nutrients, and atrazine loads.

The model showed a better performance for monthly than daily flows and sediments. Previous works have reported that model performs better at larger time scales. For instance, the NSE of annual flows were 0.78-0.84 while monthly values had 0.12-0.72 (Santhi et al. 2006). In a 9,400 km² agricultural watershed in Iowa, Jha et al. (2007) reported NSE values of annual flows, sediments, and nitrates of 0.97, 0.93, and 0.78, respectively. The same variables had lower NSE at monthly time steps of 0.87, 0.53, and 0.73. Greater

streamflow regime generates smaller pollutant concentrations since it has a dilution effect of compounds, as illustrated by Hrdinka et al. (2012)

The Shell Creek model showed higher NSE for flows (0.65-0.79) than sediments and atrazine (< 0.25). Studies have reported similar results for monthly estimates with NSE of streamflows (0.5-0.89) greater than sediment (0.23-0.85) (White and Chaubey 2005). One reason for the better model performance for pollutants at monthly scales might be due to limitations in SWAT in reproducing the second storm effect at daily scales. For instance, it led to an overestimate of sediment loads of 92% in an agricultural watershed in Switzerland (Abbaspour, Yang, et al. 2007).

In another study, flow overestimates resulted in underestimation of sediments driven by a dilution effect (Jha, Gassman, and Arnold 2007). Gollamudi et al. (2007) determined that extreme events underestimated phosphorus loads due to limitations in model calibration. Unknown processes (e.g. chemical transport) and other events (e.g. landslides, irrigation and water diversion) represent uncertainties in modeling watersheds (Abbaspour, Yang, et al. 2007) that introduce error in model estimates. Sediments and nutrients processes might be disconnected in SWAT. Sensitivity analysis indicated that channel sedimentation does not affect total nitrogen or phosphorus estimates (Arabi et al. 2008).

The model poorly reproduced atrazine loads, as evidenced by negative NSE. The scarce water quality data available constrained the ability to conduct temporal analysis and modeling. NSE estimates can be biased when performance is judged using a few observed data (e.g. 1-3 years) as previous studies have used (Abbaspour, Yang, et al. 2007; Gollamudi, A. Madramootoo, and Enright 2007; White and Chaubey 2005).

4.4.2 Water quality response to extreme hydrometeorological and climate conditions

Results indicate that Shell Creek water quality measured as loads of sediments, nutrients, and atrazine is affected by extreme wet hydrological conditions. Peak flows in early spring (April) were commonly overestimated by 10-40 mm in Boyd watershed, Texas (Santhi et al. 2006). It might be due to overestimated precipitation. For instance, overestimated high flow conditions turned into larger loads of sediments and nutrients in the Pike River watershed, Canada (Gollamudi, A. Madramootoo, and Enright 2007)

Results evidence that years with wet summer in Shell Creek leads to significantly higher streamflow and loads of sediments, N, and P. However, atrazine is not affected significantly by climatic conditions. Similarly, Abbaspour et al. (2007) found that runoff from agricultural land use carries 1.4 to 2 times larger loads of sediments, and nutrients in a wet year in an agricultural watershed of 1,700 km². Surface runoff contributes to water generation in wet years, while lateral flow dominates the water yield from croplands in dry years. Then, very wet hydrometeorological and climate conditions drive streamflow and water quality responses, with larger flows and loads in periods of wet summers. Under climate change scenarios, Shell Creek flow will lead to 1.2-1.5 times greater sediment and N losses (Van Liew, Feng, and Pathak 2012). Soil types and landuse might influence contaminant losses into surface waters of agricultural watersheds.

4.4.3 Veterinary antibiotics modeling

The Shell Creek model does not reproduce well the observed loads of veterinary antibiotics. Using parameters values from literature, the model displayed an inferior performance with negative NSE (< -79.2). This poor performance might be due to the assumption that antibiotics in manure were homogeneously applied across the entire

watershed. The few observations could also limit a proper model calibration for a wider range of load variations.

Nevertheless, after calibration of sensitive parameters, NSE of the antibiotics loads increased to values near zero (-0.23, -1.21, -0.07). Uncertainty in initial parameters values (from literature or assumed), fertilizer, and pesticide applications rate also contributed to larger errors in simulated antibiotics loads. For instance, depth of pesticide incorporation in the soil was assumed zero. It might not be realistic as liquid manure is applied to the first layer (e.g. 100 mm). Calibrated values of depth incorporated of antibiotics were 2.75, 88, and 217 mm for monensin, sulfamethazine, and tylosin, respectively. Moreover, chemical properties might influence transport and dissipation of loading pollutants in waters. Soil adsorption coefficient normalized for soil organic carbon ranged 1.3-54.8 and wash-off fraction reduced to 0.20-0.25.

4.5 Conclusions

Understanding the hydrologic processes that influence the fate and transport of pollutants in surface waters support water management. Moreover, evaluation of the extreme climate effects on surface waters brings essential information to forecast climate change-driven events. Validation of a model that reproduces variations in loading pollutants is relevant to assess the effects of extreme hydro-meteorological and climate conditions on the streamflows and water quality of watersheds.

Continuous monitoring of water quality data is a need for an adequate implementation of hydrological models. Future studies might include improvement of SWAT code on antibiotics modeling including newly-discover processes that might occur in the environment. Also, evaluation of extreme climate conditions impacts on antibiotics occurrence in surface waters.

Chapter 5 Summary and Future Work

The occurrence of emerging contaminants in surface waters of an agricultural watershed, Shell Creek was demonstrated by using passive samplers (POCIS). This study demonstrates their utility for the evaluation of low concentration of veterinary pharmaceuticals in aquatic environments. The high frequencies of sampling between 40% and 94.5% for lincomycin, monensin, tiamulin, sulfadimethoxine, and sulfamethazine confirm that agricultural activities such as land application of manure and livestock production heavily influence Shell Creek. Increases in concentrations of veterinary pharmaceuticals were identified in summer driven by heavy precipitation events. Lincomycin, tiamulin, and sulfadimethoxine showed significant temporal variation, which is consistent with other studies that have observed a summer pulse of veterinary pharmaceuticals in agricultural watersheds.

An integrative monitoring of precipitation data from rain gages and radar adequately fed a hydrologic model to simulated streamflows of a rain-ungaged and agriculturally driven watershed. Once adequately calibrated and validated for a shorter time-frame, estimations were valid for longer time frames bypassing data needs. The rain gage-forced model reproduces more accurately medium-flow regimes. Nevertheless, streamflow responses to extreme climate conditions in the past might not be captured by the model outputs. The low- and high-flow conditions were over- and under- estimated, respectively.

The lack of water quality records in small watersheds like Shell Creek should call the attention of watershed managers, environmental agencies, and policy makers. A continuous monitoring plan for Shell Creek is highly recommended to support future modeling studies. While the academia can offer short field works to assess the occurrence of water pollutants,

longer term monitoring programs should be established by the states. The longer the continuous water quality data becomes available, the more robust watershed models can be built.

How changing climate will impact water availability is more noticeable at global scales. However, streamflow responses at smaller scales differed within regions. Thus, studies on the influence of extreme hydrometeorological and climate extremes are highly recommended, especially in agricultural watersheds.

REFERENCES

- Abbaspour, Karim C., M. Vejdani, S. Haghighat, and J. Yang. 2007. "SWAT-CUP Calibration and Uncertainty Programs for SWAT." In *The Fourth International SWAT Conference*, 1596–1602. doi:10.1007/s00402-009-1032-4.
- Abbaspour, Karim C., Jing Yang, Ivan Maximov, Rosi Siber, Konrad Bogner, Johanna Mieleitner, Juerg Zobrist, and Raghavan Srinivasan. 2007. "Modelling Hydrology and Water Quality in the Pre-Alpine/alpine Thur Watershed Using SWAT." *Journal of Hydrology* 333 (2–4): 413–30. doi:10.1016/j.jhydrol.2006.09.014.
- Alavanja, Michael C R, Jane A Hoppin, and Freya Kamel. 2004. "Health Effects of Chronic Pesticide Exposure: Cancer and Neurotoxicity." *Annual Review of Public Health* 25 (1): 155–97. doi:10.1146/annurev.publhealth.25.101802.123020.
- Alder, Alfredo C., Christian Schaffner, Marius Majewsky, Jörg Klasmeier, and Kathrin Fenner. 2010. "Fate of β -Blocker Human Pharmaceuticals in Surface Water: Comparison of Measured and Simulated Concentrations in the Glatt Valley Watershed, Switzerland." *Water Research* 44 (3): 936–48. doi:10.1016/j.watres.2009.10.002.
- Alexander, L. V., X. Zhang, T. C. Peterson, J. Caesar, B. Gleason, A. M. G. Klein Tank, M. Haylock, et al. 2006. "Global Observed Changes in Daily Climate Extremes of Temperature and Precipitation." *Journal of Geophysical Research* 111 (D5): 1–22. doi:10.1029/2005JD006290.
- Alvarez, D A, P E Stackelberg, J D Petty, J N Huckins, E T Furlong, S D Zaugg, and M T Meyer. 2005. "Comparison of a Novel Passive Sampler to Standard Water-Column Sampling for Organic Contaminants Associated with Wastewater Effluents Entering a New Jersey Stream." *Chemosphere* 61 (5): 610–22. doi:10.1016/j.chemosphere.2005.03.023.
- Alvarez, David A, Jimmie D Petty, James N Huckins, Tammy L Jones-Lepp, Dominic T Getting, Jon P Goddard, and Stanley E Manahan. 2004. "Development of a Passive, in Situ, Integrative Sampler for Hydrophilic Organic Contaminants in Aquatic Environments." *Environmental Toxicology and Chemistry* 23 (7). Wiley Periodicals, Inc.: 1640–48. doi:10.1897/03-603.
- Arabi, Mazdak, Jane R Frankenberger, Bernie A Enge, and Jeff G Arnold. 2008. "Representation of Agricultural Conservation Practices with SWAT." *HYDROLOGICAL PROCESSES* 22 (16). COMMERCE PLACE, 350 MAIN ST, MALDEN 02148, MA USA: WILEY-BLACKWELL: 3042–55. doi:10.1002/hyp.6890.
- Arikan, Osman A., Clifford Rice, and Eaton Codling. 2008. "Occurrence of Antibiotics and Hormones in a Major Agricultural Watershed." *Desalination* 226 (1–3): 121–33. doi:10.1016/j.desal.2007.01.238.
- Arnold, J.G., J.R. Kiniry, R. Srinivasan, J.R. Williams, E.B. Haney, and S.L. Neitsch. 2012. *Soil and Water Assessment Tool Input/Output Documentation Version 2012*.
- Arnold, J G, R Srinivasan, R S Muttiah, and J R Williams. 1998. "Large Area Hydrologic Modeling and Assessment Part 1: Model Development." *JAWRA Journal of the American Water Resources Association*. doi:10.1111/j.1752-1688.1998.tb05961.x.

- Bartelt-Hunt, Shannon L, Daniel D Snow, Teyona Damon-Powell, DelShawn L Brown, Gyanendra Prasai, Matthew Schwarz, and Alan S Kolok. 2011. "Quantitative Evaluation of Laboratory Uptake Rates for Pesticides, Pharmaceuticals, and Steroid Hormones Using POCIS." *Environmental Toxicology and Chemistry / SETAC* 30 (6): 1412–20. doi:10.1002/etc.514.
- Bartelt-Hunt, Shannon L, Daniel D Snow, Teyona Damon, Johnette Shockley, and Kyle Hoagland. 2009. "The Occurrence of Illicit and Therapeutic Pharmaceuticals in Wastewater Effluent and Surface Waters in Nebraska." *Environmental Pollution* 157 (3). Elsevier Ltd: 786–91. doi:10.1016/j.envpol.2008.11.025.
- Bartelt-Hunt, Shannon, Daniel D Snow, Teyona Damon-Powell, and David Miesbach. 2011. "Occurrence of Steroid Hormones and Antibiotics in Shallow Groundwater Impacted by Livestock Waste Control Facilities." *Journal of Contaminant Hydrology* 123 (3–4): 94–103. doi:10.1016/j.jconhyd.2010.12.010.
- Beermann, D H. 2002. "Beta-Adrenergic Receptor Agonist Modulation of Skeletal Muscle Growth." *Journal of Animal Science* 80. Madison, WI: The American Society of Animal Science: E18–23. doi:10.2134/animalsci2002.00218812008000ES10004x.
- Beeson, P C, P C Doraiswamy, A M Sadeghi, M Di Luzio, M D Tomer, J G Arnold, and C S T Daughtry. 2011. "TREATMENTS OF PRECIPITATION INPUTS TO HYDROLOGIC MODELS." *TRANSACTIONS OF THE ASABE* 54 (6). 2950 NILES RD, ST JOSEPH, MI 49085-9659 USA: AMER SOC AGRICULTURAL & BIOLOGICAL ENGINEERS: 2011–20.
- Bernot, Melody J, Lora Smith, and Jeff Frey. 2013. "Human and Veterinary Pharmaceutical Abundance and Transport in a Rural Central Indiana Stream Influenced by Confined Animal Feeding Operations (CAFOs)." *Science of the Total Environment* 445–446 (February). Elsevier B.V.: 219–30. doi:10.1016/j.scitotenv.2012.12.039.
- Biggs, Eloise M., and Peter M. Atkinson. 2011. "A Comparison of Gauge and Radar Precipitation Data for Simulating an Extreme Hydrological Event in the Severn Uplands, UK." *Hydrological Processes* 25 (5): 795–810. doi:10.1002/hyp.7869.
- Brain, Richard A, David J Johnson, Sean M Richards, Hans Sanderson, Paul K Sibley, and Keith R Solomon. 2004. "Effects of 25 Pharmaceutical Compounds to Lemna Gibba Using a Seven-Day Static-Renewal Test." *Environmental Toxicology and Chemistry* 23 (2): 371–82.
- Brown, Linfield C., and Thomas O. Barnwell Jr. 1987. *The Enhanced Stream Water Quality Models QUAL2E and QUAL2E-UNCAS: Documentation and User Manual*. Athens, GA.
- Brown, Simon J., J. Caesar, and C. a T Ferro. 2008. "Global Changes in Extreme Daily Temperature since 1950." *Journal of Geophysical Research: Atmospheres* 113 (D5): 1–11. doi:10.1029/2006JD008091.
- Burkholder, Joann, Bob Libra, Peter Weyer, Susan Heathcote, Dana Kolpin, Peter S Thorne, and Michael Wichman. 2007. "Impacts of Waste from Concentrated Animal Feeding Operations on Water Quality." *Environmental Health Perspectives* 115 (2): 308–12. doi:10.1289/ehp.8839.

- Center for Advanced Land Management Information Technologies (CALMIT). 2016. "2005 Nebraska Land Use Patterns." <http://calmit.unl.edu/2005landuse/statewide.php>.
- Centner, T J, J C Alvey, and A M Stelzleni. 2014. "Beta Agonists in Livestock Feed: Status, Health Concerns, and International Trade." *Journal of Animal Science* 92 (9). PO BOX 7410, CHAMPAIGN, IL 61826-7410 USA: AMER SOC ANIMAL SCIENCE: 4234–40. doi:10.2527/jas2014-7932.
- Chintalapudi, Singaiah, Hatim O Sharif, Subash Yeggina, and Almoutaz Elhassan. 2012. "Physically Based, Hydrologic Model Results Based on Three Precipitation Products." *Journal of the American Water Resources Association* 48 (6): 1191–1203. doi:10.1111/j.1752-1688.2012.00679.x.
- Davis, J G, C C Truman, S C Kim, J C Ascough II, and K Carlson. 2006. "Antibiotic Transport via Runoff and Soil Loss." *Journal of Environmental Quality* 35 (6). 677 S SEGOE RD, MADISON, WI 53711 USA: AMER SOC AGRONOMY: 2250–60. doi:10.2134/jeq2005.0348.
- Dollison, Robert M. 2010. "The National Map: New Viewer, Services, and Data Download."
- Easterling, D. R., J. L. Evans, P. Ya. Groisman, T. R. Karl, K. E. Kunkel, and P. Ambenje. 2000. "Observed Variability and Trends in Extreme Climate Events: A Brief Review." *Bulletin of the American Meteorological Society* 81 (3): 417–25. doi:10.1175/1520-0477(2000)081<0417:OVATIE>2.3.CO;2.
- Easterling, D R, G A Meehl, C Parmesan, S A Changnon, T R Karl, and L O Mearns. 2000. "Climate Extremes: Observations, Modelling, and Impacts." *Science* 289 (5487): 2068–74. doi:10.1126/science.289.5487.2068.
- Food and Drug Administration (FDA) - Center for Veterinary Medicine. 2015. "2013 Summary Report on Antimicrobials Sold or Distributed for Use in Food-Producing Animals."
- Gali, R K, K R Douglas-Mankin, X Li, and T Xu. 2012. "Assessing NEXRAD P3 Data Effects on Stream-Flow Simulation Using SWAT Model in an Agricultural Watershed." *JOURNAL OF HYDROLOGIC ENGINEERING* 17 (11, SI). 1801 ALEXANDER BELL DR, RESTON, VA 20191-4400 USA: ASCE-AMER SOC CIVIL ENGINEERS: 1245–54. doi:10.1061/(ASCE)HE.1943-5584.0000618.
- Gesch, D B. 2007. "The National Elevation Dataset." In *Digital Elevation Model Technologies and Applications: The DEM Users Manual*, edited by David F Maune, 2nd ed., 99–118. Bethesda, Maryland: American Society for Photogrammetry and Remote Sensing.
- Gesch, D, M Oimoen, S Greenlee, C Nelson, M Steuck, and D Tyler. 2002. "The National Elevation Dataset." *Photogrammetric Engineering and Remote Sensing* 68 (1): 5–11.
- Gilliom, Robert J, Jack E Barbash, Charles G Crawford, Pixie A Hamilton, Jeffrey D Martin, Naomi Nakagaki, Lisa H Nowell, et al. 2006. "The Quality of Our Nation's Waters - Pesticides in the Nation's Streams and Ground Water, 1992–2001."
- Golden, Heather E., Christopher D. Knightes, Ellen J. Cooter, Robin L. Dennis, Robert C. Gilliam, and Kristen M. Foley. 2010. "Linking Air Quality and Watershed Models for

- Environmental Assessments: Analysis of the Effects of Model-Specific Precipitation Estimates on Calculated Water Flux.” *Environmental Modelling & Software* 25 (12): 1722–37. doi:10.1016/j.envsoft.2010.04.015.
- Gollamudi, A, C A. Madramootoo, and P Enright. 2007. “Water Quality Modeling of Two Agricultural Fields in Southern Quebec Using SWAT.” *Transactions of the ASABE* 50 (6): 1973–80.
- Hayes, Tyrone, Kelly Haston, Mable Tsui, Anhthu Hoang, Cathryn Haeffele, and Aaron Vonk. 2003. “Atrazine-Induced Hermaphroditism at 0.1 Ppb in American Leopard Frogs (*Rana Pipiens*): Laboratory and Field Evidence.” *Environmental Health Perspectives* 111 (4): 568–75.
- Hirsch, Robert M., and Laura De Cicco. 2015. “User Guide to Exploration and Graphics for RivEr Trends (EGRET) and dataRetrieval: R Packages for Hydrologic Data.” In *Techniques and Methods Book 4*, 93. U.S. Geological Survey. doi:http://dx.doi.org/10.3133/tm4A10.
- Hopenhayn-Rich, C, M L Stump, and S R Browning. 2002. “Regional Assessment of Atrazine Exposure and Incidence of Breast and Ovarian Cancers in Kentucky.” *Archives of Environmental Contamination and Toxicology* 42 (1): 127–36. doi:10.1007/s002440010300.
- Hrdinka, Tomáš, Oldřich Novický, Eduard Hanslík, and Mark Rieder. 2012. “Possible Impacts of Floods and Droughts on Water Quality.” *Journal of Hydro-Environment Research* 6 (2): 145–50. doi:10.1016/j.jher.2012.01.008.
- Hughes, Diarmaid, and Dan I Andersson. 2012. “Selection of Resistance at Lethal and Non-Lethal Antibiotic Concentrations.” *Current Opinion in Microbiology* 15 (5): 555–60. doi:http://dx.doi.org/10.1016/j.mib.2012.07.005.
- Huntington, Thomas G. 2006. “Evidence for Intensification of the Global Water Cycle: Review and Synthesis.” *Journal of Hydrology* 319 (1): 83–95. doi:10.1016/j.jhydrol.2005.07.003.
- J. R. Williams, J. R., C. A. C. A. Jones, J. R. J. R. Kiniry, and D. A. D. A. Spanel. 1989. “The EPIC Crop Growth Model.” *Transactions of the ASAE* 32 (2): 0497–0511. doi:10.13031/2013.31032.
- Jaimes-Correa, Juan C., Daniel D. Snow, and Shannon L. Bartelt-Hunt. 2015. “Seasonal Occurrence of Antibiotics and a Beta Agonist in an Agriculturally-Intensive Watershed.” *Environmental Pollution* 205 (October): 87–96. doi:10.1016/j.envpol.2015.05.023.
- Jha, M K, P W Gassman, and J G Arnold. 2007. “Water Quality Modeling for the Raccoon River Watershed Using SWAT.” *Transactions of the ASABE* 50 (2): 479–93.
- Ji, Xiuling, Qunhui Shen, Fang Liu, Jing Ma, Gang Xu, Yuanlong Wang, and Minghong Wu. 2012. “Antibiotic Resistance Gene Abundances Associated with Antibiotics and Heavy Metals in Animal Manures and Agricultural Soils Adjacent to Feedlots in Shanghai; China.” *Journal of Hazardous Materials* 235–236 (October): 178–85. doi:10.1016/j.jhazmat.2012.07.040.

- Jjemba, Patrick K. 2006. "Excretion and Ecotoxicity of Pharmaceutical and Personal Care Products in the Environment." *Ecotoxicology and Environmental Safety* 63 (1): 113–30. doi:10.1016/j.ecoenv.2004.11.011.
- Jones-Lepp, T L, D A Alvarez, J D Petty, and J N Huckins. 2004. "Polar Organic Chemical Integrative Sampling and Liquid Chromatography–Electrospray/Ion-Trap Mass Spectrometry for Assessing Selected Prescription and Illicit Drugs in Treated Sewage Effluents." *Archives of Environmental Contamination and Toxicology* 47 (4). Springer-Verlag: 427–39. doi:10.1007/s00244-004-3146-6.
- Joy, Stacey R, Shannon L Bartelt-Hunt, Daniel D Snow, John E Gilley, Bryan L Woodbury, David B Parker, David B Marx, and Xu Li. 2013. "Fate and Transport of Antimicrobials and Antimicrobial Resistance Genes in Soil and Runoff Following Land Application of Swine Manure Slurry." *Environmental Science & Technology* 47 (21). American Chemical Society: 12081–88. doi:10.1021/es4026358.
- Kalin, Latif, and Mohamed M. Hantush. 2006. "Hydrologic Modeling of an Eastern Pennsylvania Watershed with NEXRAD and Rain Gauge Data." *Journal of Hydrologic Engineering* 11 (6): 555–69. doi:10.1061/(ASCE)1084-0699(2006)11:6(555).
- Karl, Thomas R., and Richard W. Knight. 1998. "Secular Trends of Precipitation Amount, Frequency, and Intensity in the United States." *Bulletin of the American Meteorological Society* 79 (2): 231–41. doi:10.1175/1520-0477(1998)079<0231:STOPAF>2.0.CO;2.
- Kim, Sung-Chul, Jessica G Davis, Clinton C Truman, James C Ascough, and Kenneth Carlson. 2010. "Simulated Rainfall Study for Transport of Veterinary Antibiotics--Mass Balance Analysis." *Journal of Hazardous Materials* 175 (1–3): 836–43. doi:10.1016/j.jhazmat.2009.10.086.
- Koontz, A F, S W El-Kadi, D L Harmon, E S Vanzant, J C Matthews, J A Boling, and K R McLeod. 2010. "Effect of Ractopamine on Whole Body and Splanchnic Energy Metabolism in Holstein Steers." *Canadian Journal of Animal Science* 90 (1): 77–85.
- Kumar, Kuldip, Satish C. Gupta, Yogesh Chander, and Ashok K. Singh. 2005. "Antibiotic Use in Agriculture and Its Impact on the Terrestrial Environment." In *Advances in Agronomy*, 87:1–54. Advances in Agronomy. Academic Press. doi:10.1016/S0065-2113(05)87001-4.
- Kurwadkar, Sudarshan, Victoria Sicking, Barry Lambert, Anne McFarland, and Forrest Mitchell. 2013. "Preliminary Studies on Occurrence of Monensin Antibiotic in Bosque River Watershed." *Journal of Environmental Sciences* 25 (2). The Research Centre for Eco-Environmental Sciences, Chinese Academy of Sciences: 268–73. doi:10.1016/S1001-0742(12)60041-2.
- Lin, Ying, and Kenneth E Mitchell. 2005. "The NCEP Stage II/IV Hourly Precipitation Analyses: Development and Applications." *Preprints, 19th Conf. on Hydrology, American Meteorological Society, San Diego, CA, 9-13 January 2005, Paper 1.2*, 2–5.
- Lissemore, Linda, Chunyan Hao, Paul Yang, Paul K Sibley, Scott Mabury, and Keith R Solomon. 2006. "An Exposure Assessment for Selected Pharmaceuticals within a Watershed in Southern Ontario." *Chemosphere* 64 (5): 717–29. doi:10.1016/j.chemosphere.2005.11.015.

- Martínez-Carballo, Elena, Carmen González-Barreiro, Sigrid Scharf, and Oliver Gans. 2007. "Environmental Monitoring Study of Selected Veterinary Antibiotics in Animal Manure and Soils in Austria." *Environmental Pollution* 148 (2): 570–79. doi:10.1016/j.envpol.2006.11.035.
- Matthiessen, P, D Arnold, A C Johnson, T J Pepper, T G Pottinger, and K G T Pulman. 2006. "Contamination of Headwater Streams in the United Kingdom by Oestrogenic Hormones from Livestock Farms." *Science of the Total Environment* 367 (2–3): 616–30. doi:10.1016/j.scitotenv.2006.02.007.
- Menne, Matthew J, Imke Durre, Russell S Vose, Byron E Gleason, and Tamara G Houston. 2012. "An Overview of the Global Historical Climatology Network-Daily Database." *Journal of Atmospheric and Oceanic Technology* 29 (7). American Meteorological Society: 897–910. doi:10.1175/JTECH-D-11-00103.1.
- Mills, Paul K, and Richard Yang. 2006. "Regression Analysis of Pesticide Use and Breast Cancer Incidence in California Latinas." *Journal of Environmental Health* 68 (6): 15–22.
- Milly, P. C. D., K. A. Dunne, and A. V. Vecchia. 2005. "Global Pattern of Trends in Streamflow and Water Availability in a Changing Climate." *Nature* 438 (7066). Nature Publishing Group: 347–50. doi:10.1038/nature04312.
- Moldovan, Zaharie. 2006. "Occurrences of Pharmaceutical and Personal Care Products as Micropollutants in Rivers from Romania." *Chemosphere* 64 (11): 1808–17. doi:10.1016/j.chemosphere.2006.02.003.
- Monteith, J L. 1965. "Evaporation and Environment. The State and Movement of Water in Living Organisms." In *Symposium of the Society of Experimental Biology, Vol. 19*, 205–34. New York, NY: Cambridge: Cambridge University Press.
- Moon, J, R Srinivasan, and J H Jacobs. 2004. "Streamflow Estimation Using Spatially Distributed Rainfall in the Trinity River Basin, Texas." *Transactions of the ASAE* 47 (5): 1445–51.
- Nash, J E, and J V Sutcliffe. 1970. "River Flow Forecasting through Conceptual Models Part I — A Discussion of Principles." *Journal of Hydrology* 10 (3): 282–90. doi:10.1016/0022-1694(70)90255-6.
- Nawaz, Mohamed S, Bruce D Erickson, Ashraf A Khan, Saeed A Khan, Jairaj V Pothuluri, Fatemeh Rafii, John B Sutherland, R Doug Wagner, and Carl E Cerniglia. 2001. "Health Human Health Impact and Regulatory Issues Involving Antimicrobial in the Food Animal Production Environment." *Regulatory Research Perspectives* 1 (1): 1–10.
- Neitsch, S.L., J.G. Arnold, J.R. Kiniry, and J.R. Williams. 2011. *Soil and Water Assessment Tool Theoretical Documentation Version 2009*. College Station, TX.
- Peterson, Thomas C., Thomas R. Karl, James P. Kossin, Kenneth E. Kunkel, Jay H. Lawrimore, James R. McMahon, Russell S. Vose, and Xungang Yin. 2014. "Changes in Weather and Climate Extremes: State of Knowledge Relevant to Air and Water Quality in the United States." *Journal of the Air & Waste Management Association* 64 (2). Taylor & Francis: 184–97. doi:10.1080/10962247.2013.851044.

- Price, Katie, S. Thomas Purucker, Stephen R. Kraemer, and Justin E. Babendreier. 2012. "Tradeoffs among Watershed Model Calibration Targets for Parameter Estimation." *Water Resources Research* 48 (10): 1–16. doi:10.1029/2012WR012005.
- Price, Katie, S. Thomas Purucker, Stephen R. Kraemer, Justin E. Babendreier, and Chris D. Knightes. 2014. "Comparison of Radar and Gauge Precipitation Data in Watershed Models across Varying Spatial and Temporal Scales." *Hydrological Processes* 28 (9): 3505–20. doi:10.1002/hyp.9890.
- R. A. Leonard, R. A., W. G. W. G. Knisel, and D. A. D. A. Still. 1987. "GLEAMS: Groundwater Loading Effects of Agricultural Management Systems." *Transactions of the ASAE* 30 (5). American Society of Agricultural and Biological Engineers: 1403–18. doi:10.13031/2013.30578.
- Retchless, David, Nathan Frey, Chongming Wang, Li-San Hung, and Brent Yarnal. 2014. "Climate Extremes in the United States: Recent Research by Physical Geographers." *Physical Geography* 35 (1). Taylor & Francis: 3–21. doi:10.1080/02723646.2013.871191.
- Santhi, C., R. Srinivasan, J.G. Arnold, and J.R. Williams. 2006. "A Modeling Approach to Evaluate the Impacts of Water Quality Management Plans Implemented in a Watershed in Texas." *Environmental Modelling & Software* 21 (8): 1141–57. doi:10.1016/j.envsoft.2005.05.013.
- Santhi, C, J G Arnold, J R Williams, W A Dugas, R Srinivasan, and L M Hauck. 2001. "Validation of the SWAT Model on a Large River Basin with Point and Nonpoint Sources." *JAWRA Journal of the American Water Resources Association* 37 (5). Blackwell Publishing Ltd: 1169–88. doi:10.1111/j.1752-1688.2001.tb03630.x.
- Sexton, A M, A M Sadeghi, X Zhang, R Srinivasan, and A Shirmohammadi. 2010. "Using Nexrad and Rain Gauge Precipitation Data for Hydrologic Calibration of Swat in a Northeastern Watershed." *Asabe* 53 (5): 1501–10.
- Soil Survey Staff. Natural Resources Conservation Service. United States Department of Agriculture. 2016. "Web Soil Survey." <http://websoilsurvey.nrcs.usda.gov/>.
- Song, Wenlu, Yunjie Ding, Cary T. Chiou, and Hui Li. 2010. "Selected Veterinary Pharmaceuticals in Agricultural Water and Soil from Land Application of Animal Manure." *Journal of Environmental Quality* 39 (4): 1211. doi:10.2134/jeq2009.0090.
- Spalding, Roy F, and Daniel D Snow. 1989. "STREAM LEVELS OF AGRICHEMICALS DURING A SPRING DISCHARGE EVENT." *Chemosphere* 19 (8–9): 1129–40. doi:10.1016/0045-6535(89)90061-1.
- Swanton, Clarence J., Hamid R. Mashhadi, Keith R. Solomon, Maha M. Afifi, and Stephen O. Duke. 2011. "Similarities between the Discovery and Regulation of Pharmaceuticals and Pesticides: In Support of a Better Understanding of the Risks and Benefits of Each." *Pest Management Science* 67 (7): 790–97. doi:10.1002/ps.2179.
- Tillitt, Donald E, Diana M Papoulias, Jeffrey J Whyte, and Catherine A Richter. 2010. "Atrazine Reduces Reproduction in Fathead Minnow (Pimephales Promelas)." *Aquatic Toxicology* 99 (2): 149–59. doi:10.1016/j.aquatox.2010.04.011.

- Tobin, Kenneth J., and Marvin E. Bennett. 2009. "Using SWAT to Model Streamflow in Two River Basins with Ground and Satellite Precipitation Data." *Journal of the American Water Resources Association* 45 (1): 253–71. doi:10.1111/j.1752-1688.2008.00276.x.
- Truszczyński, M., and Z. Pejsak. 2013. "Sources and routes of spread of antibiotic resistance of bacteria." *Medycyna Weterynaryjna* 69 (4). Lublin: Polskie Towarzystwo Nauk Weterynaryjnych: 203–7.
- Tuppad, P., K. R. Douglas- Mankin, J. K. Koelliker, and J. M. S. Hutchinson. 2010. "SWAT DISCHARGE RESPONSE TO SPATIAL RAINFALL VARIABILITY IN A KANSAS WATERSHED." *Transactions of the ASABE* 53 (1): 65–74.
- U.S. Census Bureau. 2010. "United States Census 2010." <http://www.census.gov/2010census/>.
- U.S. EPA. 2006. "Decision Documents for Atrazine." Washington D.C.
- U.S. Geological Survey. 2014. "National Hydrography Dataset." Accessed November 3. <http://nhd.usgs.gov>.
- . 2012. "National Water Information System." *USGS Water Data for the Nation*. http://waterdata.usgs.gov/ne/nwis/uv/?site_no=06795500.
- United States Department of Agriculture-Natural Resources Conservation Service (USDA-NRCS), United States Geological Survey (USGS), and Environmental Protection Agency (EPA). 2014. "Watershed Boundary Dataset for HUC10200201." Accessed November 3. <http://datagateway.nrcs.usda.gov>.
- USDA-Economic Research Service. 2017. "Corn and Other Feed Grains." <https://www.ers.usda.gov/topics/crops/corn/>.
- USDA-NASS. 2012. "Census of Agriculture." <http://nass.usda.gov/>.
- USDA-NRCS. 2004. "Chapter 10 Estimation of Direct Runoff from Storm Rainfall." In *National Engineering Handbook, Part 630, Hydrology*, 79.
- USGS. 2012. "Pesticide Use Maps - Atrazine." *Pesticide National Synthesis Project*. https://water.usgs.gov/nawqa/pnsp/usage/maps/show_map.php?year=2012&map=ATRAZINE&hilo=L&disp=Atrazine.
- Van Boeckel, Thomas P, Charles Brower, Marius Gilbert, Bryan T Grenfell, Simon a Levin, Timothy P Robinson, Aude Teillant, and Ramanan Laxminarayan. 2015. "Global Trends in Antimicrobial Use in Food Animals." *Proceedings of the National Academy of Sciences of the United States of America*, no. 16: 1–6. doi:10.1073/pnas.1503141112.
- Van Liew, M W, S Feng, and T B Pathak. 2012. "Climate Change Impacts on Streamflow, Water Quality, and Best Management Practices for the Shell and Logan Creek Watersheds in Nebraska, USA." *International Journal of Agricultural and Biological Engineering* 5 (1): 13–34. doi:10.3965/j.ijabe.20120501.003.
- Watkinson, A.J., E.J. Murby, D.W. Kolpin, and S.D. Costanzo. 2009. "The Occurrence of Antibiotics in an Urban Watershed: From Wastewater to Drinking Water." *Science of the Total Environment* 407 (8). Elsevier B.V.: 2711–23. doi:10.1016/j.scitotenv.2008.11.059.

- White, Kati L, and Indrajeet Chaubey. 2005. "Sensitivity Analysis, Calibration, and Validations for a Multisite and Multivariable SWAT Model." *Journal of the American Water Resources Association* 41 (5): 1077–89. doi:10.1111/j.1752-1688.2005.tb03786.x.
- Williams, J. R., C. A. Jones, and P. T. Dyke. 1984. "A Modeling Approach to Determining the Relationship Between Erosion and SoU Productivity." *TRANSACTIONS of the ASAE* 27 (1). American Society of Agricultural and Biological Engineers: 129–44. doi:10.13031/2013.32748.
- Williams, J R. 1969. "Flood Routing with Variable Travel Time or Variable Storage Coefficients." *Transactions of the ASAE* 12 (1): 100–103. doi:10.13031/2013.38772.
- . 1975. "Sediment-Yield Prediction with Universal Equation Using Runoff Energy Factor." In *Present and Prospective Technology for Predicting Sediment Yield and Sources*, ARS-S-40:244–52. U.S. Dept. Agric.
- Wischmeier, W.H., and D.D. Smith. 1978. "Predicting Rainfall Erosion Losses. A Guide to Conservation Planning." U.S. Department of Agriculture. doi:10.1029/TR039i002p00285.
- Wu, Mae, Mayra Quirindongo, Jennifer Sass, and Andrew Wetzler. 2010. *Still Poisoning the Well: Atrazine Continues to Contaminate Surface Water and Drinking Water in the United States*. Natural Resources Defense Council (NRDC).
- Xie, Hongjie, Xiaobing Zhou, Enrique R. Vivoni, Jan M.H. Hendrickx, and Eric E. Small. 2005. "GIS-Based NEXRAD Stage III Precipitation Database: Automated Approaches for Data Processing and Visualization." *Computers & Geosciences* 31 (1): 65–76. doi:10.1016/j.cageo.2004.09.009.
- Ying, Guang-Guo, Rai S Kookana, and Dana W Kolpin. 2009. "Occurrence and Removal of Pharmaceutically Active Compounds in Sewage Treatment Plants with Different Technologies." *Journal of Environmental Monitoring* 11 (8): 1498–1505. doi:10.1039/b904548a.
- Zhang, HuiLan, DanXun Li, XingKui Wang, and XiaoMing Jiang. 2012. "Quantitative Evaluation of NEXRAD Data and Its Application to the Distributed Hydrologic Model BPCC." *Science China Technological Sciences* 55 (9): 2617–24. doi:10.1007/s11431-012-4918-2.
- Zhang, Xian, Dandan Zhang, Han Zhang, Zhuanxi Luo, and Changzhou Yan. 2012. "Occurrence, Distribution, and Seasonal Variation of Estrogenic Compounds and Antibiotic Residues in Jiulongjiang River, South China." *Environmental Science and Pollution Research International* 19 (5): 1392–1404. doi:10.1007/s11356-012-0818-z.
- Zhang, Xuesong, and Raghavan Srinivasan. 2010. "GIS-Based Spatial Precipitation Estimation Using next Generation Radar and Raingauge Data." *Environmental Modelling and Software* 25 (12). Elsevier Ltd: 1781–88. doi:10.1016/j.envsoft.2010.05.012.
- Zhao, Ling, Yuan Hua Dong, and Hui Wang. 2010. "Residues of Veterinary Antibiotics in Manures from Feedlot Livestock in Eight Provinces of China." *The Science of the Total Environment* 408 (5): 1069–75. doi:10.1016/j.scitotenv.2009.11.014.