Approved and recommended for acceptance as a thesis in partial fulfillment of the requirements for the degree of Master of Science.

Special committee directing the thesis work of Preeyaporn Songkiatisak

Michael Deaton Date

Thomas Benzing Date

Jeffrey Tang Date

Polly Cushman Date

Received by The Graduate School

Date

A Simulation Model for Triclosan Concentrations in the North and Middle Rivers, Virginia

Preeyaporn Songkiatisak

A thesis submitted to the Graduate Faculty of

JAMES MADISON UNIVERSITY

In

Partial Fulfillment of the Requirements

for the degree of

Master of Science

Department of Integrated Sciences and Technology

December 2009

Acknowledgement

I sincerely appreciate my thesis advisors, Michael Deaton and Thomas Benzing, for all of their inputs and guidance. Their support and assistance are valuable to the completion of this thesis.

I also would like to thank Jeffrey Tang for his guidance and thoughtful advice.

Lastly, I would like to thank my family for support and encouragement over the time of completing my thesis.

Table of Contents

Lists of Tables

List of Figures

Abstract

Incidences of fish kills and intersex phenomena have occurred extensively in the Shenandoah River since 2004. Pharmaceuticals including triclosan have been detected at low concentrations in the Shenandoah River. Scientists hypothesize that triclosan, an antibacterial agent, may be one of the pharmaceuticals that is responsible for fish kills and intersex phenomena. Methyl triclosan (MTS) were found in fish tissues at a significantly higher concentration in the part of the Shenandoah River where fish kills are present compared to a non-impact river.

Triclosan is widely used in personal care products, such as soaps, shampoos, and toothpastes and is rinsed down the drain. It enters the aquatic environment via wastewater discharges and can accumulate in the surface waters since waters and wastewater treatment technologies do not completely remove triclosan from treated wastewater.

This thesis explores an application of the system dynamics problem solving and modeling methodology to predict triclosan concentration levels in parts of the North and Middle Rivers, main tributaries of the South Fork Shenandoah River. A simulation model calculate triclosan concentrations in the North and Middle River based on numerous factors including watershed characteristics, streamflow, and removal efficiency of triclosan in wastewater treatment plants.

The effect of removal efficiency in WWTPs is the most sensitive factor to the triclosan concentration levels regarding simulated results. Concentrations significantly change whether treatment systems are improved or deteriorated. Treatment technology improvement would be a significant approach to reduce triclosan concentrations in the North and Middle Rivers.

For further research, the model platform could be applied to predict concentrations of triclosan or other pollutants in other rivers. However, a number of variables are needed to be modified to fulfill this purpose.

Chapter 1

Introduction

Incidences of fish kills and intersex phenomena, which are immature female eggs in the testes, have occurred extensively in the Shenandoah River since 2004. The fish kills in the North Fork and South Fork Shenandoah River caused ecological and financial impacts since the incidences resulted in an estimated loss of 80% of the adult smallmouth bass, an economically important sport fish (Garman & Orth, 2007). To date, the causes of the fish kills remain unknown due to a significant gap of information available and the complexity of the ecological system. However, cumulative effects of organic chemicals and pharmaceuticals in surface waters have been considered as a high priority factor that may contribute to fish kills and intersex phenomena.

Pharmaceuticals have been detected at low concentrations in U.S. surface waters including the Shenandoah River. Some pharmaceuticals present in surface waters are suspected to disrupt normal endocrine function (Garman & Orth, 2007; Friends of the North Fork of the Shenandoah River, 2008) and scientists have found pharmaceuticals in dead and dying fish tissues (Ramirez, Mottaleb, Brooks, & Chambliss, 2007;Luellen, 2009). This evidence has led to a hypothesis that pharmaceuticals at low concentrations might be interfering with the normal functions of the endocrine system of fish.

Although some evidence supports the assumption that pharmaceutical contamination in the aquatic environment may affect aquatic organisms, to date the U.S. Environmental Protection Agency (EPA) and the Virginia Department of Environmental Quality (VA DEQ) have not regulated pharmaceuticals as water pollutants. None of the pharmaceuticals have been controlled for in the discharge of treated wastewater into surface waters.

Triclosan, 2-(2, 4-dichlorophenoxy)-5- chlorophenol, is a broad-spectrum antimicrobial agent that may be one of the pharmaceutical compounds responsible for the fish kills and intersex phenomena. Triclosan is widely used in personal care products, such as soaps, shampoos, and toothpastes (Glaser, 2004; Morrall et al., 2004; McAvoy, Schatowitz, Jacob, Hauk, & Eckhoff, 2002). The market of antimicrobial cleaning products is growing. Global sales of biocide products are forecasted at $350 – 400 million per year and rise at 3-7 % annually (Jagger, 2008). Several studies found that over 75% of liquid soaps and about 30% of bar soaps, which combined comprise 45% of all soaps in the market, contain antibacterial agents (Glaser, 2004). Nearly half of the commercial antibacterial soaps contain triclosan generally at about 0.2-0.3% concentration (Glaser, 2004; Jagger, 2008). Even though total sale volume of triclosan-containing products has not been reported, it could be presumed that massive quantities of triclosan have been produced and consumed every year.

The ubiquitous triclosan-containing products are typically rinsed and disposed of down the drain after use. Wastewater is transported to wastewater treatment plants (WWTPs), which mostly treat wastewater with conventional activated sludge treatment technology. This technology does not completely remove triclosan from treated wastewater. Consequently, triclosan enters the aquatic environment via wastewater effluents and continually accumulates in the surface water. Triclosan is likely to accrue in surface waters since the triclosan-containing products have profoundly increased and the triclosan usage per capita has increased.

Scientists believe that triclosan is harmful to fish because they found methyl triclosan (MTS) in fish tissues at a significantly higher concentration in the part of the Shenandoah River where fish kills are present compared to a non-impact river (Luellen, 2009). In addition, several research papers have reported that triclosan is toxic to aquatic biota (Capdevielle et al., 2008). For instance, triclosan has been found to disrupt development in frogs and cause endocrine disruption in mussels (Bennett, 2008). This is possibly because triclosan in water converts to more lipophillic compounds which can be absorbed and accumulated in aquatic organism tissues via bio-methylation and photolysis (Canosa et al., 2005).

So far, reported triclosan concentrations in the Shenandoah River and its tributaries are limited. Factors that significantly contribute to triclosan concentration levels in the rivers, such as triclosan usage or removal efficiency in WWTPs, have not been identified. This thesis will create a simulation model of triclosan concentrations in the North and Middle Rivers which are main tributaries of the South Fork Shenandoah River. A purpose of the simulation model is to help quantify and predict triclosan concentrations over time, based on known factors such as river discharge volume and average triclosan usage per capita. In this way, the dynamic effects of those factors which are most important in determining triclosan concentrations can be evaluated. The effects of such significant factors as the efficiency of wastewater treatment plants to remove triclosan prior to discharge of treated wastewater to surface waters, precipitation, and the amount of used triclosan will be explored. Ultimately, the understanding of the system behaviors and the results of the simulation model may deepen our understanding of the possible sources and pathways of this substance in the North and the Middle River watershed and may eventually provide a basis for reducing the amount of triclosan in the rivers.

Note that this thesis is the first attempt to predict triclosan concentration over time, and to evaluate the most significant factors contributing to the accumulation of triclosan concentrations by exploring an application of the system dynamics problem solving and modeling methodology. This “first generation” model, referred to hereafter as TCNMR, accounts for only parts of the North and Middle Rivers watersheds, not for the entire South Fork Shenandoah watershed. However, our model will provide a simulation platform that could be enhanced in future studies.

Introduction to System Dynamics

This thesis employs the System Dynamics problem solving and modeling methodology. System dynamics is a modeling methodology developed by Jay Forester at Massachusetts Institute of Technology in the 1950’s. This method enhances learning and understanding of complex systems. An important assumption in system dynamics is that system behavior is governed by the system structures and interaction of the system components through feedback loops (Sterman, 2000). Systems structure is represented and modeled using stocks (system states) and flows. (rates at which system states change). To illustrate, the TCNMR model includes a streamflow sub-model. This tracks the quantity of water in a given section of a river as the contents of a stock; meanwhile, the flows affecting that stock are the rate at which water flows into that section of the river (from upstream sources, precipitation, etc); and the outflows the rate at which water flows out of that river section and into the next section (or into a reservoir, etc). Hence, the entire length of a river can be represented as a series of stocks (sections of river) connected by flows representing the flow rates (discharge rates) from each section into the next. The residence time for water in any given section of the river (any stock) is a function of the length of the river and the discharge (flow) rate out of that section. The volume stored in the North and Middle Rivers at any time “t” is the integral of the difference between inflows and outflows and the value of the stock at the beginning (time t_0). The following mathematical equation describes the content of the stock (section of river) over time

$$\text{stock}(t) = \int_0^t [(\text{inflows} - \text{outflows})]ds + \text{stock}(t_0) \qquad (1)$$

In the modeling software used in this thesis (STELLA©, v 9.0), the stocks and flow structure is represented schematically as follows:

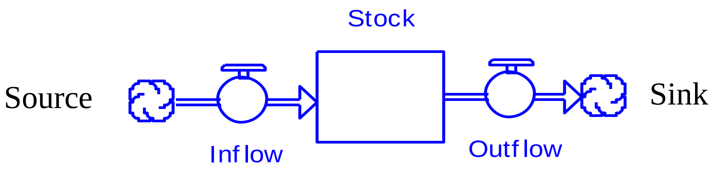


Figure1.Example of stock and flow structure in STELLA©

- A stock is represented by a rectangle.
- An inflow is represented by a pipe pointing to the stock and an outflow is represented by a pipe pointing out the stock.
- Valves control the flows
- Clouds represent the source and the sink of the flows. A source represents the stock from outside the model boundary that contributes to the system inflow. Hence, a sink represents the stock which flows leaving the model boundary.

Sources and sinks are assumed to have indefinite capacity (at least over the time horizon covered by the model) (Sterman, 2000).

Chapter 2

Overview of the Model and Model Development

The Study Area: The South Fork Shenandoah River Basin

The South Fork Shenandoah basin is comprised of 1.1million acres. The majority of the watershed locates within Augusta, Rockingham, Page, and Warren Counties (Mizel, Papadakis, Degner, Shepard, & Havinga, 2008). The South Fork Shenandoah River has three main tributaries which are the North, Middle, and South Rivers. The North River first joins the Middle River and then joins the South River to form the South Fork Shenandoah River as illustrated in Figure 2.

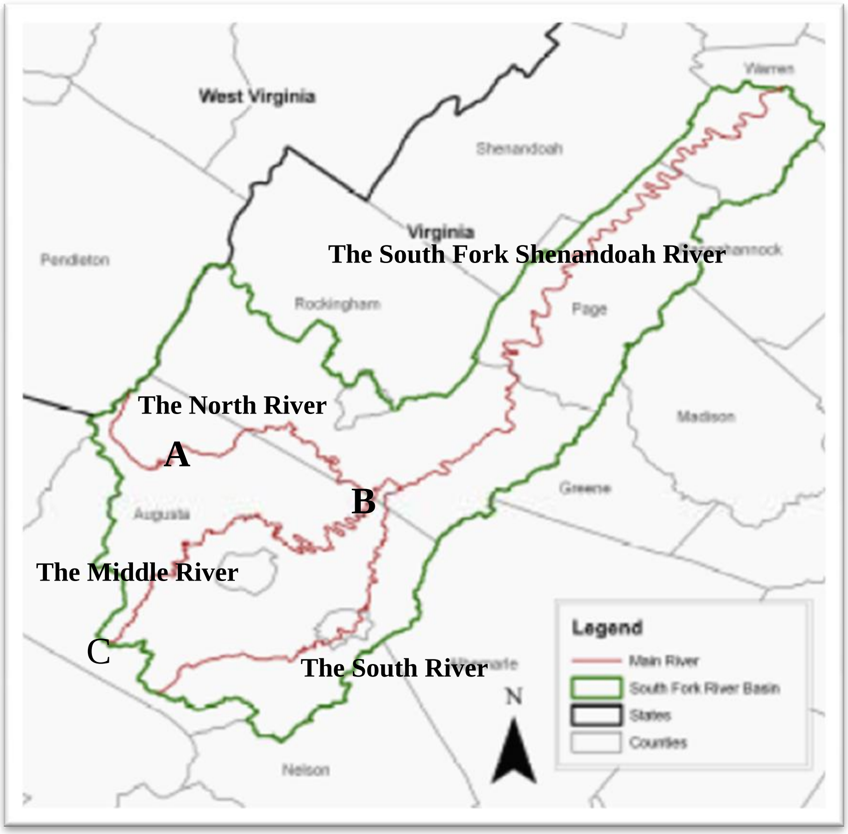


Figure 2. Main tributaries of the South Fork Shenandoah River (Modified from Mizel et al., 2008).

The North River sub basin has a drainage area of about 430 square miles. The total length of the river is of about 56 miles according to the VA DEQ. Its basin lies across the Shenandoah Valley, north of the Middle River basin, and contains a similar bed rock and topography to the Middle River basin (Hack, 1957). The Middle River, the main stream in the South Fork Shenandoah basin, is about 71 miles long (Virginia Department of Environmental Quality, 2009). At its confluence, where it joins the North River, the Middle River has a drainage area of about 380 square miles (Hack, 1957).

Area covered by the simulation model

The area covered by the simulation model is illustrated in Figure 3. The simulation model is constructed to estimate triclosan concentrations in the segments of the North and Middle Rivers, parts of the South Fork Shenandoah watershed. For the North River, the 46.38 –mile stream segment begins at the USGS 01620500 gage station near Stokesville and extends downstream to its confluence with the Middle River (A to B segment shown in Figure2). The watershed area includes 428 square miles. The delineation of the Middle River stream segment is located from its confluence with the North River to its mouth (B to C segment shown in Figure2). The segment is 71 miles long and provides 380 square miles of watershed area.

The study area falls within Rockingham County, Augusta County, Harrisonburg City, and Stanton City. There are two major and one minor municipal wastewater treatment plants serving the population who lives in the North and Middle River sub basins. The major plant, the Harrisonburg-Rockingham Regional SA Sewer treatment plant (STP) (HRSA) and the minor plant, the ACSA Weyers Cave STP (WC), discharge treated wastewater into the North River. Along the Middle River, the Middle River

Regional STP (MRR) is the only one considered municipal WWTP discharging effluent into the river. These three treatment facilities employ two different treatment technologies, and have various capacity as well as discharge volume loading to the rivers. Details about the treatment plants will be discussed in the triclosan section.

A schematic diagram of the modeled rivers (see Figure 3) presents the branch-model network. The main constructions include the South Fork Shenandoah Rivers; its tributaries, the North, Middle, and South Rivers; USGS gage stations; WWTPs. The double headed arrow AB indicates the north River segment A to B in Figure2, and the double headed arrow BC indicates the Middle River segment B to C in Figure2. The network is composed of ten river segments identified by Roman numerals. The blue solid arrows indicate river flow directions. A legend describing the symbols' in Figure 3 is provided in Table 1. The next section will describe the stock and flow structure for tracking the water and pollution flows through this region.

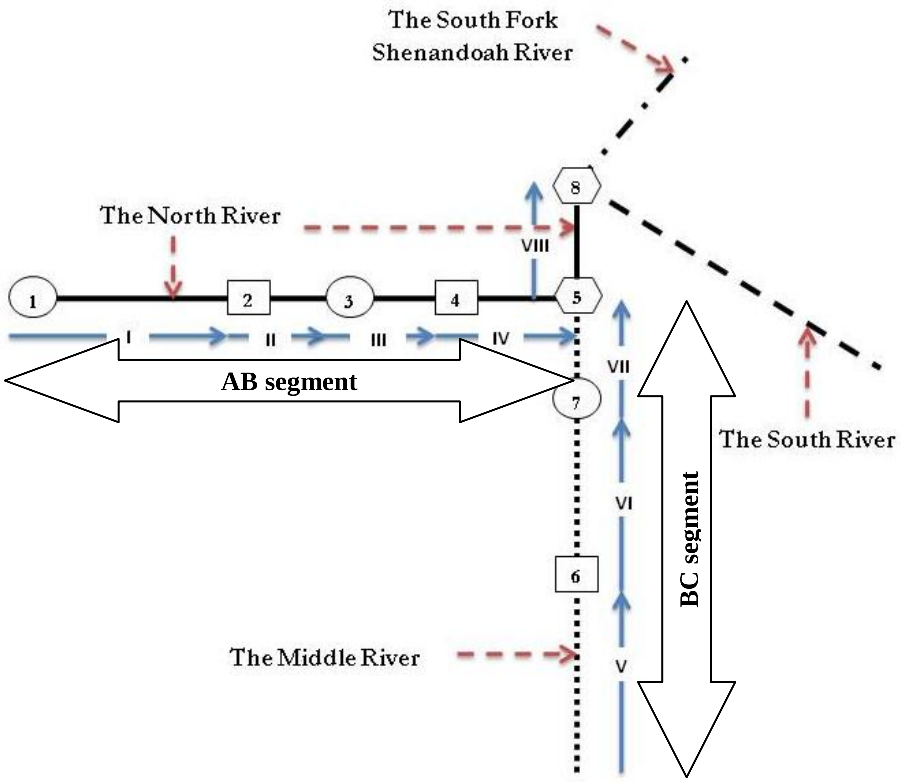


Figure 3. Schematic diagram of the South Fork Shenandoah, North, Middle, and South River system. **Note**: Solid lines represent the North River, dotted line represents to the Middle River, long dashes line represents the South River, and dash dots line represents the South Fork Shenandoah River. The "AB segment" and "BC segment" double headed arrows refer to the A to B section and the B to C section in Figure 2 respectively.

Table 1. Model Symbol Legend for Figure 3.

Sign	Descriptions
①	USGS 01620500 North River near Stokesville gage station
2	The Harrisonburg-Rockingham Regional SA Sewer treatment plant (STP) (HRSA)
③	USGS 01622000 North River near Burketown gage station
4	The ACSA Weyers Cave STP (WC)
5	The confluence of the North and Middle Rivers
6	The Middle River Regional STP (MRR)
⑦	USGS 01625000 Middle River near Grottoes gage station
8	The confluence of the North, South, and South Fork Shenandoah Rivers

Overview of Model Structure: Three Sectors

Implementation of TCNMR model was organized into three sub-models or sectors: the streamflow sector, the triclosan sector, and the triclosan concentration sector.

- **The streamflow sector** models the movement of water down the North and Middle rivers. Therefore, core stock and flow structure consists of the stocks of sectional river channels and their inflows and outflows. Fundamentally, the rivers are filled through baseline flows from upstream sections, and run-off from precipitation. Water is then discharged to downstream river sections.
- **The triclosan sector** models the transport of triclosan along the North and Middle Rivers. Wastewater treatment plants are the only source of triclosan loading that is represented in the model. Triclosan progresses down the river via water mixing and transport. A simplifying assumption in the model is that the triclosan is uniformly distributed as soon as it enters each section of the river (each stock of water). In addition, this sub model accounts for chemical decay of triclosan over time.
- **The triclosan concentration sector** provides a dynamic accounting of triclosan concentrations through time and along each section of the rivers. This concentration can vary over time based on the dynamic behavior of the streamflow and triclosan sectors. For example, triclosan concentrations in a given river segment change in response to the volume of water and the amount of triclosan in that segment. In order to calculate triclosan concentrations in a given river segment at any point in time, the amount of triclosan in that segment (from

the triclosan model sector) is divided by the volume of the water in that segment (from the streamflow sector) at the same time instant.

Description of the Streamflow Sector

A simplified version of the stock and flow structures in this sector is constructed based on stream hydrology. Generally, a river flows downstream at its baseflow rate, which is augmented by groundwater which gradually flows down slope towards a stream (Gordon, 2004). When precipitation falls on a watershed, some water is lost via evapotranspiration which is the combination of water evaporation from the soil matrix and transpiration by plants. The remaining water will flow towards the stream by runoff mechanisms: interflow and surface flow as shown in Figure 4. Some water seeps into the ground and moves through the soil which is defined as subsurface interflow; meanwhile, some water flows overland to the stream by the surface flow mechanism.

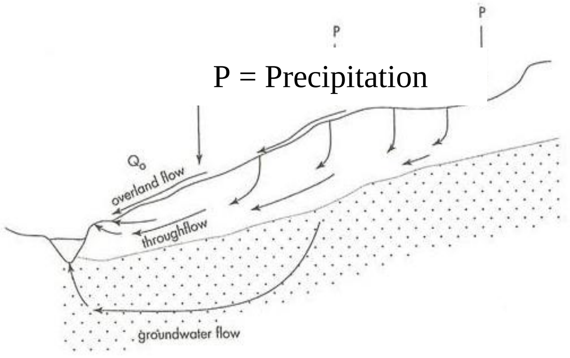


Figure 4. Runoff processes (Davie, 2008).

The TCNMR streamflow sector models the North and Middle Rivers by dividing them into several stocks corresponding to different segments of the rivers. These stocks are called N1 and N2 for the North River, M1and M2 for the Middle River, and NM for the section representing the combined segment of the North and Middle Rivers (see Figure 5). Each of these stocks is connected by a flow, representing the discharge of water from one segment to the next. The simple stock an flow diagram of the streamflow sector is shown in Figure 6. Note that the stocks represent sections of each river, while the flows to do not represent sections of the river, but rather represent physical points on the river at the junction between two river segments (between two stocks). Hence, the flows between the segments are expressed as rates at which water flows past that point and moves from one segment to the next.

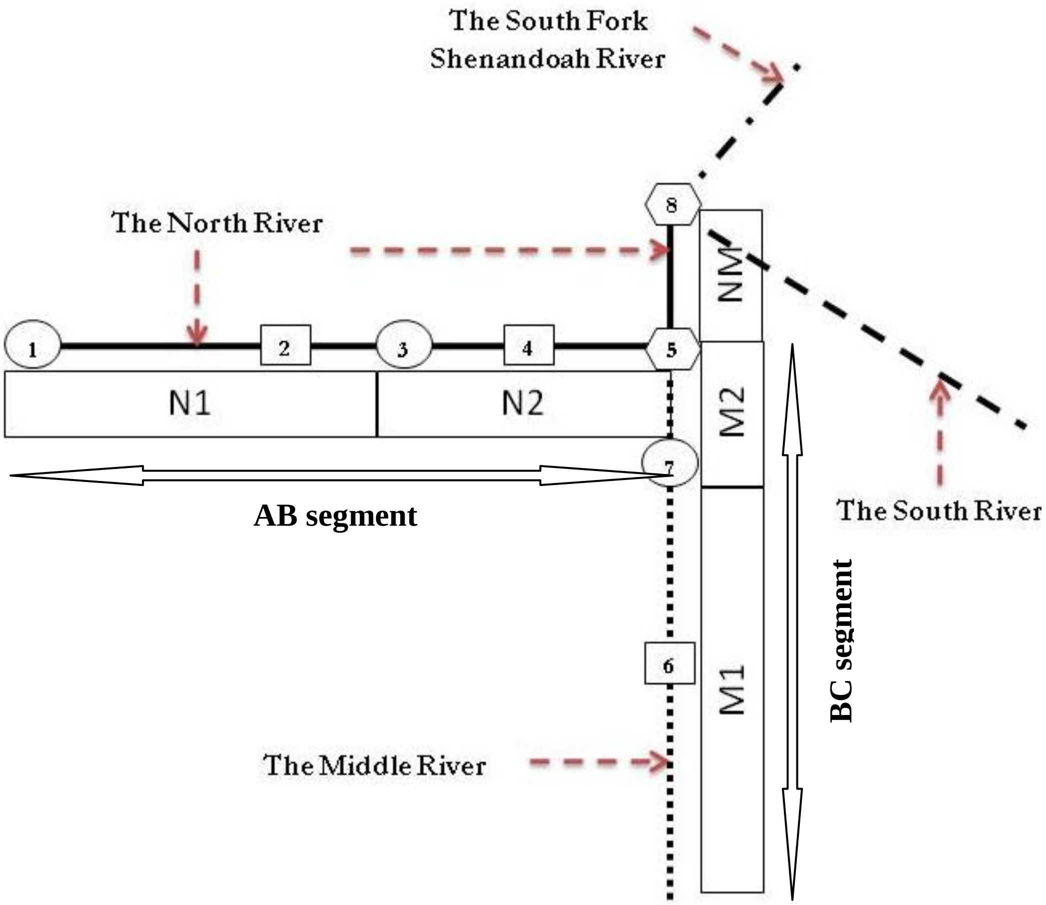


Figure 5. The stock regions in the streamflow sector. Note: The “AB segment” and “BC segment” double headed arrows refer to the A to B section and the B to C section in Figure 2 respectively.

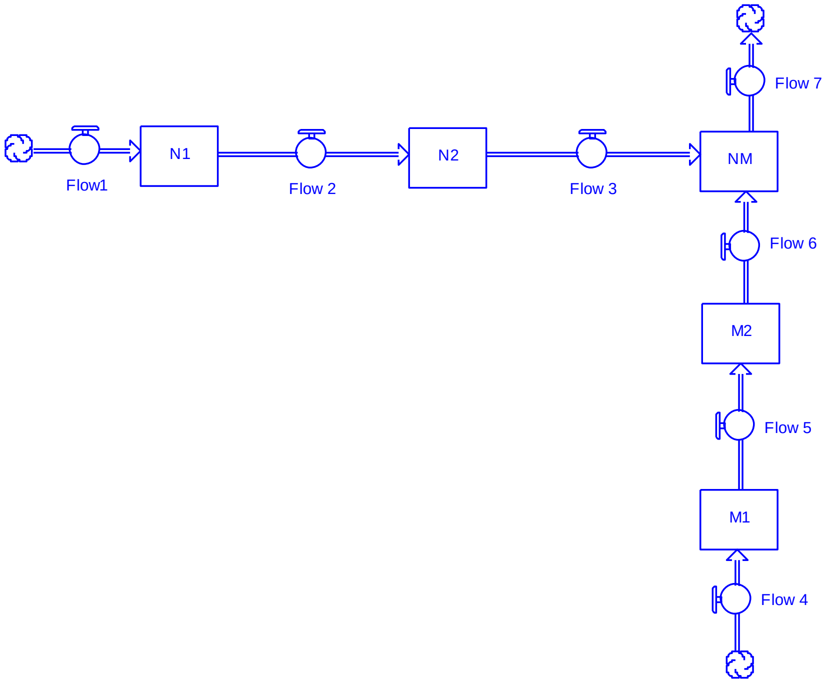


Figure 6. Simple stock and flow structure of the TCNMR streamflow sector.

The stocks in Figure 6 represent the quantity of water in the corresponding river segments, expressed in cubic feet. Regarding our study area map (Figure 2), the N1 and N2 stocks represent the volume of water in the A to B segment, and the M1 and M2 stocks represent the volume of water B to C segment. Rates at which water flows to the next stocks are represented by flows (Flow1to Flow7 in Figure 6). Water flows into the N1 stock at the USGS 01620500 gage station (point A in Figure 2) with the Inflow1 rate and then flows into the N2. Water leaves the N2 stock flowing into the NM stock at the confluence of the North and Middle Rivers (point B in Figure 2). For the Middle River, water flows into the M1 stock at its mouth (point C in Figure 2) with the Flow4 rate. Water moves to the next segment (M2 stock) and then combines the North River at point C in Figure 2. The NM stock represents the volume of water flowing from the N2 stock and the M2 stock. Water flows downstream out off the NM stock to the South Fork Shenandoah River with the Flow 7 rate (see Figure 6).

As the rivers are divided into several segments with different length, each segment contains a diverse amount of water depending on its length and drainage area. For example, the N1 stock, represented the North River segment from the USGS 01620500 gage station to the USGS 01622000 gage station, is 31.28 miles long. Its drainage area is 177.24 square miles. This means water from any source, such as precipitation and ground water, in the N1 drainage area would contribute to the volume of water in the N1 segment. More details on the specific river segments and watersheds associated with each stock are explained in Appendix A.

In order to illustrate how the streamflow sector accounts for the movement of water, we will explain in some detail how this is done with the first segment of the North River, represented by stock N1 in Figure 6. Refer to Figure 7 below as this explanation unfolds.

During “average flow” conditions, the flow in the river is at a constant level. During this time, water flows into the N1 stock at a constant baseflow rate (N1 Baseflow in Figure 7). As baseflow rates fluctuate through the seasons, we use an average baseflow during July to September in 2007 and 2008. This is because the TCNMR model is developed and tested in that time period, and seasonal average baseflows are requied to adjust the model so that the model fulfills the behavior reproduction criteria (details will be discussed in chapter 4). Moreover, because the dynamic behavior of triclosan concentrations in the river is expected to play out over hours and days, the model runs on an hour-by-hour time unit. Hence, we convert the flows from the USGS gage stations to be expressed in cubic feet/hr. We make the simplifying assumption that water flows into the N1 section at a constant baseflow rate. This inflow is then augmented with rain events, and it can also be reduced to represent drought conditions. The outflow from the N1 stock (Discharge N1 in Figure 7) can be thought of as the point on the river corresponding to the USGS gage station 01622000 near Burketown, VA. Hence, the baseflow rate was chosen so that, under steady state conditions with no rain, the N1 Discharge matched the average flow during July to September (2007-2008) from the USGS gage corresponding to that point on the river.

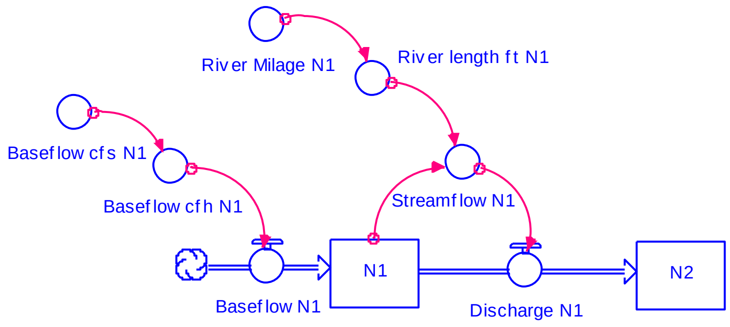


Figure 7. Stock and flow structure of the river segment N1 at a steady state.

Notice that Figure 7 has connector arrows (single lines with arrowheads) showing which variables determine the numeric values of which. For example, the Baseflow cfs N1 gives the baseflow into the N1 river section in cubic feet per second. This quantity then determines the Baseflow cfh for that segment (flow in cubic feet per hour). This in turn establishes the value of the inflow named Baseflow N1.

The most complicated part of the model involves the dynamic computation of the discharge rate in the flow Discharge N1. The following explains how these calculations are done.

<u>Explanation of Baseflow N1</u>: The Baseflow N1 inflow in Figure 7 is assumed to be a constant value representing the average flow into this section of the river. It represents the time-integrated average rate at which water flows into the N1 section, apart

from rain or drought events. The actual value of the Baseflow N1 value is set by specifying the baseflow in ft^3/sec (cfs) and then converting it to ft^3/hr (cfh). Once Baseflow N1 is fixed, water will be simulated to run into and accumulate in the N1 segment.

<u>Explanation of Discharge N1</u>: This quantity represents the rate at which water leaves the N1 segment (in cfs) and flows into the next river segment (stock N2). As the volume of water in N1 stock increases, the cross-sectional of the river increases and stream velocity rises. The Discharge N1 is calculated by first determining the cross-sectional area (based on the water volume in Stock N1), and then using that cross-sectional area in an equation that related cross-sectional are to discharge volume, where the equation was empirically determined from historical data taken from the USGS gage corresponding to the discharge flow.

In order to determine the cross-sectional area at the river location corresponding to the N1 discharge point, we made two simplifying assumptions:

1. The topography of the river channel (slope, width, smoothness, etc) was relatively constant along the N1 river segment
2. The volume of water in the N1 segment was uniformly distributed along that segment of river.

These two assumptions imply that the cross sectional area of the river is constant along the entire length of N1. Hence, by dividing the volume of water in the N1 segment (i.e. the contents of the N1 stock) by the river length of that segment (in feet), we could get the cross-sectional area of the river. That is,

$$A = \frac{N1}{L} \qquad (2)$$

where N1 is the volume of water in stock N1 (cubic feet), L is the length of river represented by N1 (feet), and A is the cross-sectional area of the river at the point represented by the Discharge N1 flow.

Once the cross-sectional area is determined at any given point in time, we can use historical data from the corresponding USGS gage to determine the streamflow discharge rate (Discharge N1). Figure 8 shows this relationship between cross-sectional area and discharge rate at the gage near Burktown from 1946 to 2009 (listed in Appendix B). This graph uses a natural log-log scale and shows a pronounced linear relationship. The least squares line for this relationship is given as follows:

$\ln(A) = \ln(13.777) + 0.4621*\ln(Q)$, where

A = cross-sectional area (ft^2), and

Q = discharge rate (ft^3/sec)

Solving for the discharge rate (Q) as a function of cross-sectional area (A), and re-expressing A as the ratio of water volume divided by river length (L), we have the following empirically determined equation for calculating the Discharge N1 flow in Figure 7 at each point in time, based on the volume of water in the stock N1.

$$Q = \left(\frac{A}{13.777}\right)^{\frac{1}{0.4621}} = \left(\frac{N1}{13.777 * L}\right)^{\frac{1}{0.4621}} \tag{3}$$

This is the equation used to calculate the Streamflow N1 and Discharge N1 in Figure 7.

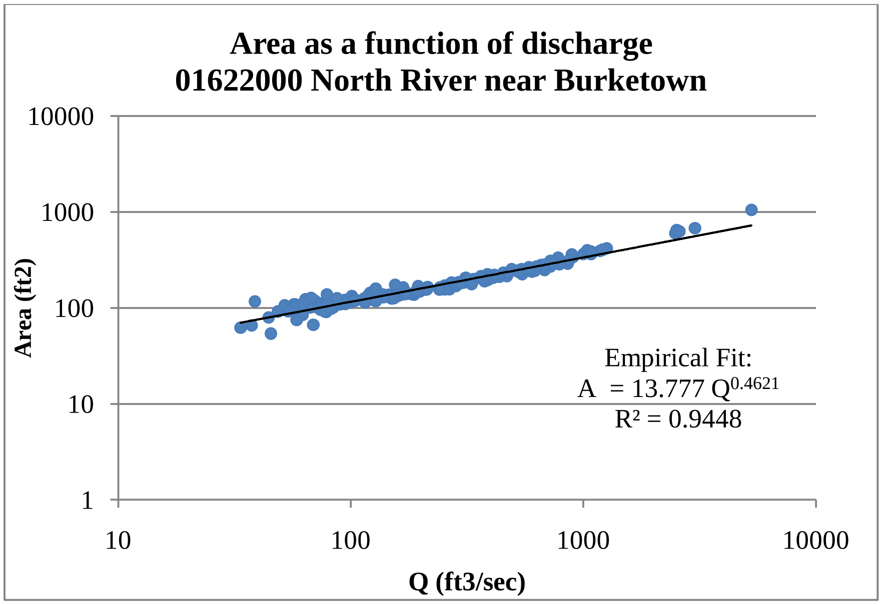


Figure8. Graph of the cross-sectional river area as a function of discharge.
Source: USGS surface water field measurement data (1946-2009)

The same model logic and the calculation method are applied for the other segments (N2, M1, and M2) in the stream flow sector. Figure 9 shows the main stock/flow structure for the streamflow sector. Table 2 shows which USGS gage corresponds to the various discharge flows in Figure 9.

Table 2. List of the USGS gage stations in the South Fork Shenandoah basin and their discharges on November 14, 2009

Gage Station	Station Name	Discharge (ft3/s)
1620500	NORTH RIVER NEAR STOKESVILLE, VA	104
1621050	MUDDY CREEK AT MOUNT CLINTON, VA	6.1
1622000	NORTH RIVER NEAR BURKETOWN, VA	686
1625000	MIDDLE RIVER NEAR GROTTOES, VA	508
1626000	SOUTH RIVER NEAR WAYNESBORO, VA	691
1626850	SOUTH RIVER NEAR DOOMS, VA	844
1627500	SOUTH RIVER AT HARRISTON, VA	1,160
1628500	S F SHENANDOAH RIVER NEAR LYNNWOOD, VA	2,430
1629500	S F SHENANDOAH RIVER NEAR LURAY, VA	4,020
1631000	S F SHENANDOAH RIVER AT FRONT ROYAL, VA	4,330

The equations used to calculate the discharges are listed in Appendix C. Note in Table 2 that there is no USGS gage station along the North River that can be used to determine relationship between the discharge and the cross-sectional area of the NM segment. Thus, we made the simplifying assumption that water flows into the NM stock with the combined outflow rates of the N2 and the M2 outflows and then flows out to the South Fork Shenandoah River immediately with the same rate as the inflow.

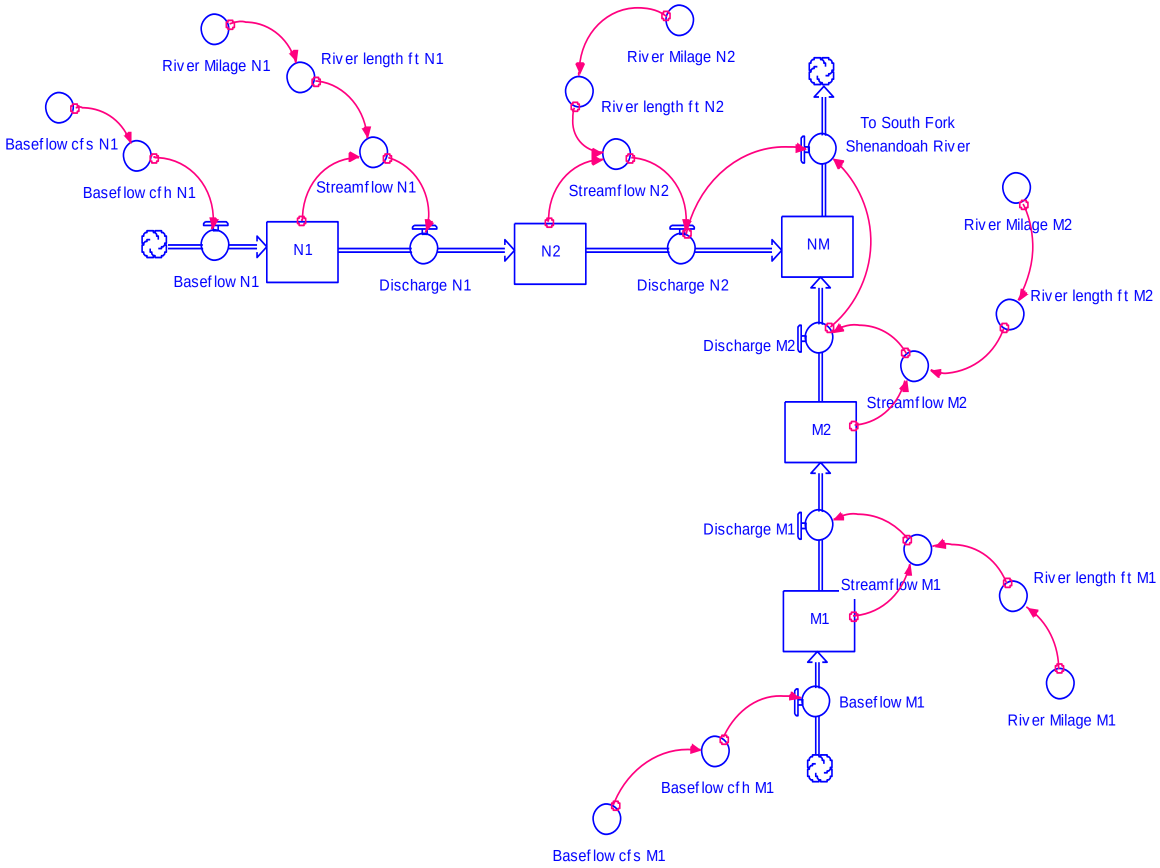


Figure 9. Intermediate model of the streamflow sector.

At this point the model in Figure 9 fails to account for tributaries that contributed to the flow in each river. It also does not account for the effects of precipitation. When precipitation falls on a watershed, some water is lost via evapotranspiration and the remaining water will flow to the stream by either interflow of surface flow pathways.

Figure 10 shows how the impact of precipitation is accounted for in the watershed corresponding to the N1 river segment from Figure 5. In this formulation, precipitation falls (Precipitation Rate N1 flow). Some of this water is lost due to evapotranspiration. The rest enters into the water shed in liquid form (N1 Watershed stock). From there the water travels to the river via two path, Interflow or Surface flow. This increased water contributes to the total water volume in stock N1, thereby affecting the discharge rate (Discharge N1).

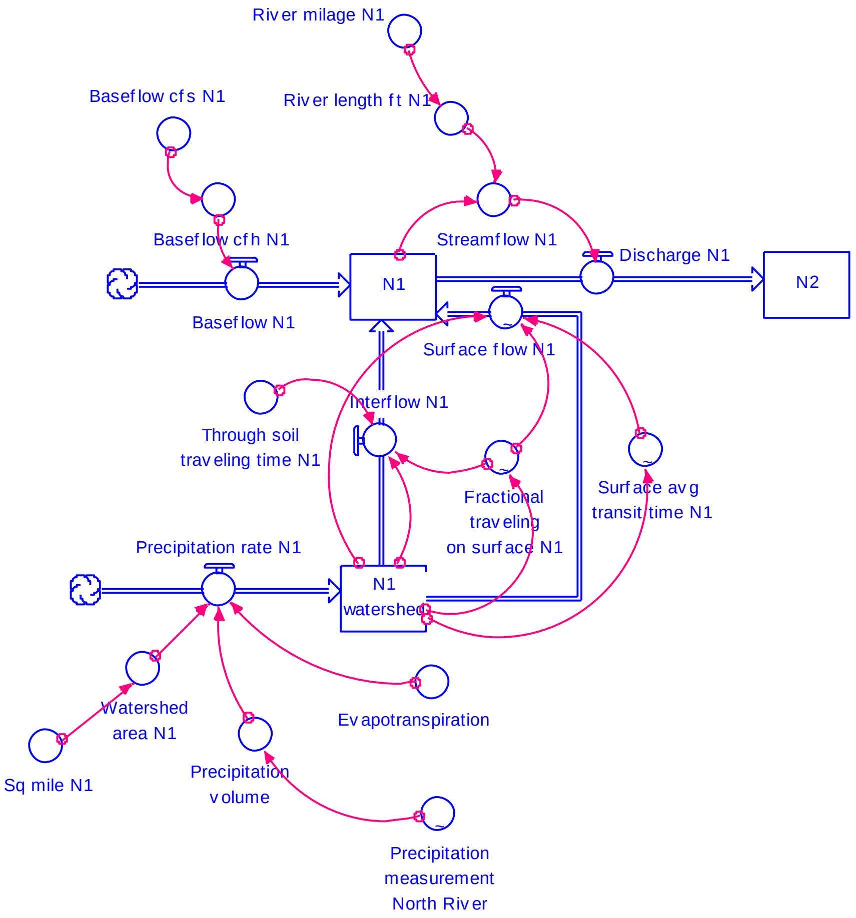


Figure 10. Stock and flow structure of the N1 stock and the N1 watershed stock.

We will illustrate and focus attention on water in the watershed N1 and how the model calculation works in order to predict the amount of water from precipitation adding to the volume of water in the river segment N1 (stock N1). The N1 watershed represents the land area where water contributes to the volume of water in the segment N1 by run-off mechanisms. Water flows into the N1 watershed stock from one inflow (Precipitation Rate N1) and leaves into the stock N1 by two outflows (Interflow N1 and Surface flow N1).

Explanation of Precipitation Rate N1**:** The precipitation measurement North River in Figure 10 represents the rainfall intensity, expressed in inches per hour. This value is converted into feet per hour, presented by the precipitation volume, since the volume of water in the stock N1 is stated in cubic feet units. Once rain falls into the watershed, water accumulates in the area (the bigger watershed area, the larger volume of water the watershed holds). However, most water from precipitation is lost via the evapotranspiration process. Therefore, the Precipitation Rate N1 at which water from precipitation flows into the N1 watershed stock is calculated as follows;

$$\text{Precipitation Rate N1 } (ft^3/hr) = \text{Precipitation volume } (ft/hr) * (1-\text{evapotranspiration fraction}) * \text{Watershed area N1 } (ft^2) \quad (4)$$

Explanation of Surface flow N1: This quantity represents the rate at which water leaves the N1 watershed stock (ft^3/hr) and flows into the N1 river segment (stock N1) via the surface flow mechanism. As watershed has limited ability to absorb water from precipitation, some water seeps into the soil and the remaining transits on the land surface towards the N1 segment. The average surface transit time decreases in nonlinear fashion as the volume of water in N1 watershed increases. When the watershed reaches its capacity, the more volume of water accumulates on land surface resulting in the greater flow velocity. We estimated the relationship between the Surface average transit time N1and the volume of water in the N1 watershed area in nonlinear graphical function (the values are listed in Appendix C). Moreover, we had to determine the portion of water that flows on land surface and that seeps into the soil. In fact, the infiltration rate declines rapidly after a certain time in an early part of a storm. As the soil becomes saturated, the hydraulic capillary force is reduced resulting in no more water is drawing into the soil and more water travels on land surface (Dunne & Leopold, 1995). Thus, when the volume of water in the watershed N1 reaches its capacity, the fraction of water traveling on the land surface exponentially increases. We determined the relationship between Fractional traveling on surface N1 (in Figure9) and the volume of water in the N1 watershed area as nonlinear graphical function (the values are listed in Appendix B). Regarding the above discussion, the Surface flow N1 is determined as the following equation:

$$\text{Surface flow N } (\text{ft}^3/\text{hr}) = (\text{N1 watershed (ft3)}/\text{Surface average transit time N1 (hr)})^* \\ \text{Fractional traveling on surface N1} \qquad (5)$$

<u>Explanation of Interflow N1:</u> This quantity represents the rate at which water leaves the N1 watershed stock (in ft^3/hr) and flows into the N1 river segment (stock N1) via the interflow mechanism. The Interflow N1 is determined by the volume of water from precipitation seeping into the soil and the time that the water takes to flow through the soil towards the N1 segment. Since we assumed that water from precipitation flows

towards the stream (N1 stock) by the Surface flow N1 and the Interflow N1, the fraction of water traveling through soil is calculated as follows:

$$\text{Fractional traveling through soil} = 1 - \text{Fractional traveling on surface} \quad (6)$$

Hence

$$\text{Interflow N1} = (\text{N1 watershed}/\text{Through soil traveling time N1}) * (1 - \text{Fractional traveling on surface N1}) \quad (7)$$

with regard to Figure 10, when there is a rainfall event, the volume of the N1 segment (stock N1) at any given time changes in response to the volume of water from three inflows (Baseflow N1, Surface flow N1, and Interflow N1) and one outflow (Discharge N1). Therefore, the volume of water in the N1 stock at any time t is calculated as:

$$\text{N1}(t) = \int_0^t [(\text{Baseflow N1} + \text{Surface flow N1} + \text{Interflow N1}) - \text{Discharge N1}]ds \quad (8)$$

With the similar assumption applied to the other river segments, the stock and flow structure (in Figure 9) is developed by adding the watershed stocks, precipitation rate inflow, surface flow, and interflow for the N2, M1, and M2 river segments. To build the whole streamflow sector, we combined the North River sub-sector (Figure11) and the Middle River sub-sector (Figure 12) by connecting them at the NM stock. In addition, we assumed that the rainfall intensity is the same for the whole North River watershed. Essentially, the interflow and surface flow rates vary depending on watershed characteristics, such as watershed elevation and soil characteristics. Since the N1, N2, M1, and M2 river segments are located in the area with the same topography, we assumed that each watershed of all river segments will receive rain in a consistent amount and respond to any rainfall event similarly.

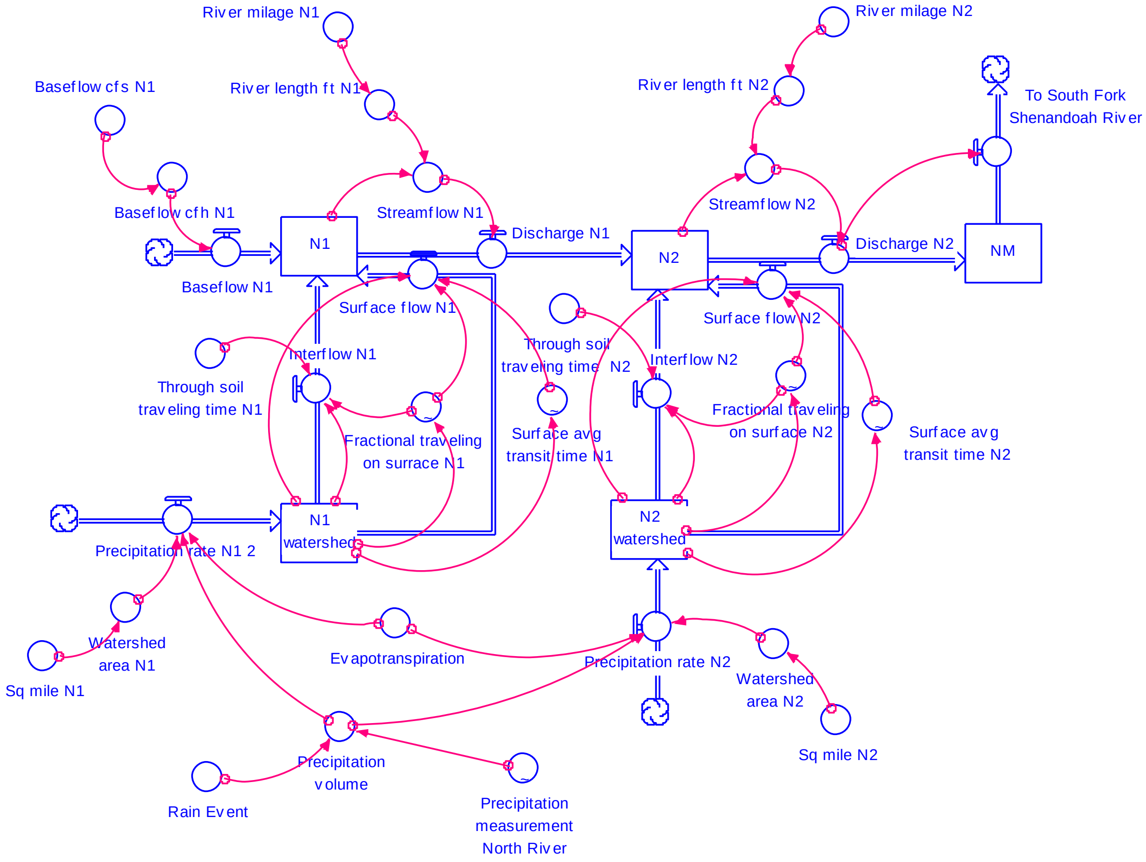


Figure 11. North River sub-sector of the stream flow sector.

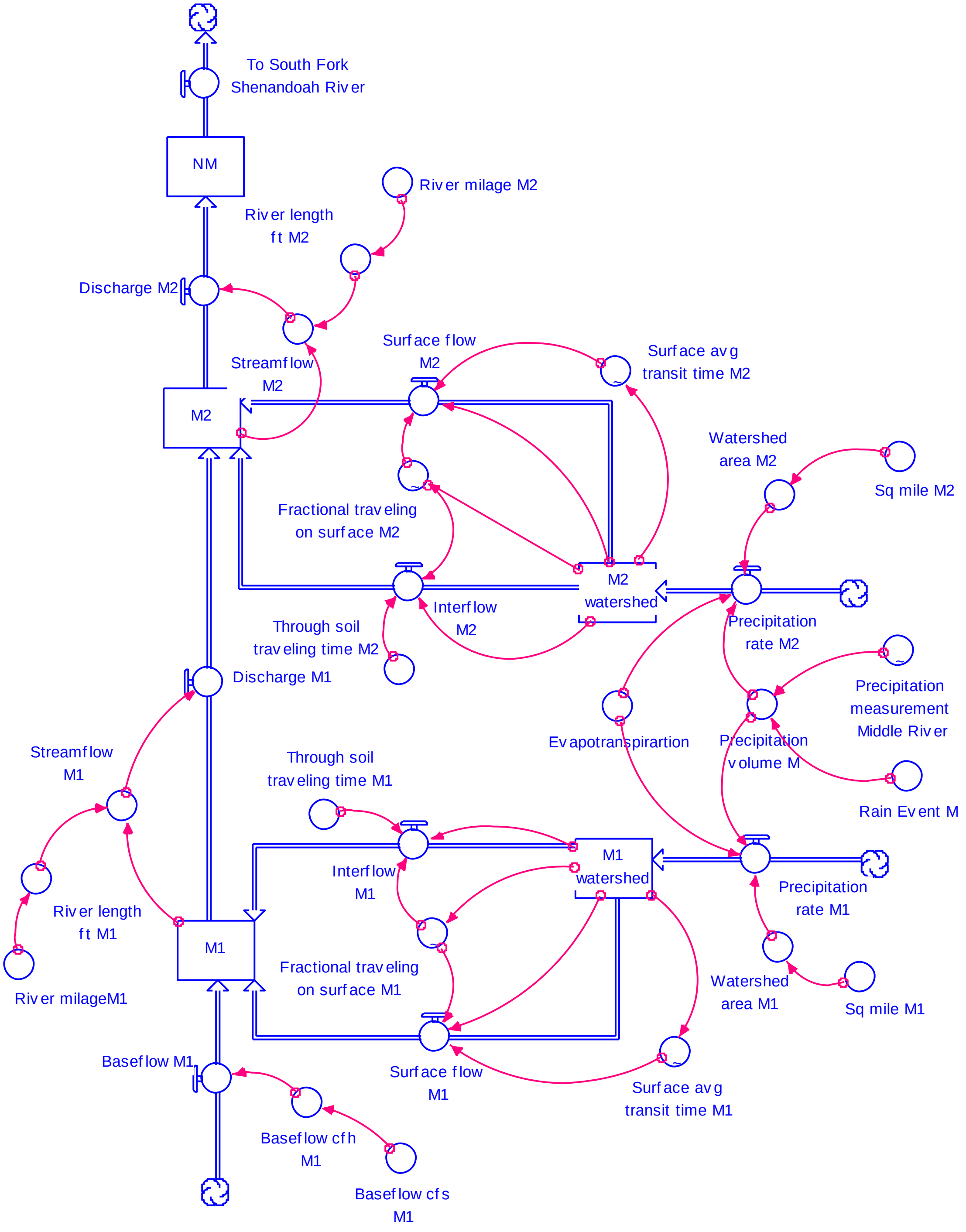


Figure 12. Middle River sub-sector of the streamflow sector.

After the whole streamflow sector is developed, we set values of variables at an initial steady state condition that matches the average discharge rates in the USGS gages (with precipitation set to zero). We then fine-tuned the rates affecting interflow and surface flow to match gage data during historical rain events. The details of this model validation are given in chapter 3. The values for the baseflows and initial water volumes in the stocks are listed in Appendix C.

Description of the Triclosan Sector

This sector simulates the flow of triclosan in the North and Middle Rivers. Triclosan, an emerging contaminant may enter the aquatic environment via the effluents from sewage treatment plants and via the disposal of unused triclosan-containing products. However, this model boundary defines municipal wastewater treatment plants as the only exogenous source of triclosan entering the aquatic environment. In order to select WWTPs to include in our model, we listed municipal wastewater facilities that discharge treated wastewater directly into the North and Middle Rivers (within our study river segments indicated in Figure 2). We compared the average daily discharges of the listed WWTPs with the average streamflow rate at the nearest USGS gage station. Three of WWTPs that have the most percentage in the comparison were selected. Based on the VA DEQ and USGS flow data, the Harrisonburg-Rockingham Regional SA Sewer treatment plant (HRSA) and the ACSA Weyers Cave STP (WC) are selected as a primary source of triclosan in the North River; meanwhile, the Middle River Regional (MRR) STP is defined as a source of triclosan in the Middle River. In addition, we made an assumption that the amount of triclosan loading to the treatment plants depends on the size of the population they serve and triclosan usage per capita per year. According to the EPA (2009), the HRSA, WC, and MRR were predicted to serve a resident population of about 78 thousand, 587, and 43 thousand people respectively (Environmental Protection Agency, 2009).

Treatment technologies used in WWTPs have different efficiencies to remove triclosan from effluents. The HRSA and the WC treat wastewater with conventional activated sludge processes (Environmental Protection Agency, 2009). This treatment process is able to reduce triclosan concentrations in influent by 93% on average (Bester, 2003; Bester, 2005; McAvoy et al., 2002;Ying & Kookana, 2007). Although the MRR employs the oxidation ditches technology (Virginia Department of Environmental Quality, 2007), triclosan removal efficiency is about 93 % (Winkler et al., 2007; Ying & Kookana, 2007), similar to the activated sludge process.

In order to construct the model's stock and flow structure, we primarily divided the North and Middle Rivers into a series of stocks (see Figure 13) and connected the stocks by flows. The simple stock and flow diagram of the triclosan sector is shown in Figure 14. The triclosan sector consists of six stocks, the T1, T2, T3, T4, T5, and T6 stocks. The North River is divided into three parts, the T1, T2, and T3 stocks; while, the Middle River is split into two segments, the T4 and T5 stocks. Both rivers join together at the T6 stock. For the triclosan sector, the rivers are split differently from that in the streamflow sector based on sources of triclosan and streamflow rate in river segments. For example, the HRSA is a starting point of the T1 stock because triclosan is firstly introduced into the North river via a WWTP. The North River segment upstream of the HRSA beyond the USGS 01620500 is assumed to have no triclosan contamination. Furthermore, we split apart river segments between USGS gage stations due to our concerns about stream velocity upstream as the gages may change corresponding to a rain event. The changes of stream velocity affect a decay rate of triclosan and the triclosan traveling time. More details will be discussed later in this chapter.

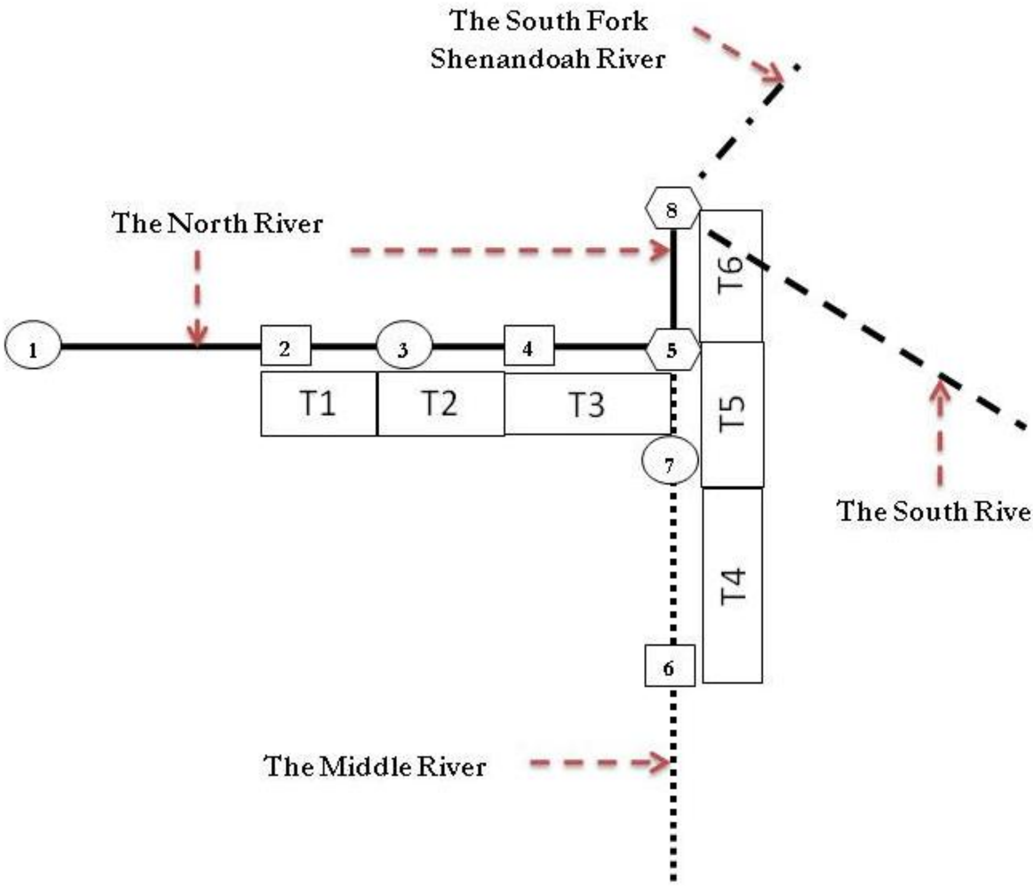


Figure 13. The stock legend in the triclosan sector. **Note:** the descriptions of the numbers are in Table1.

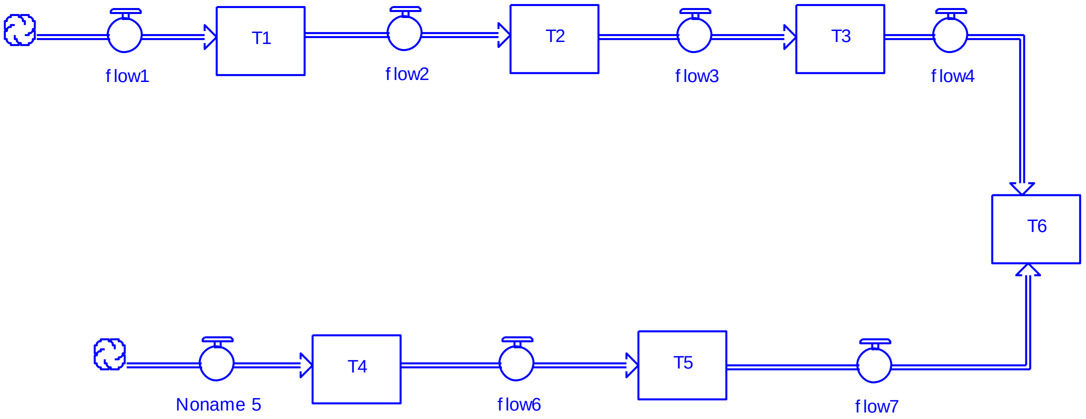


Figure 14. Simple stock and flow diagram of the triclosan sector

We will focus the first part of the triclosan sector (given in Figure 14) to explain how the model works and how we calculate the triclosan amount.

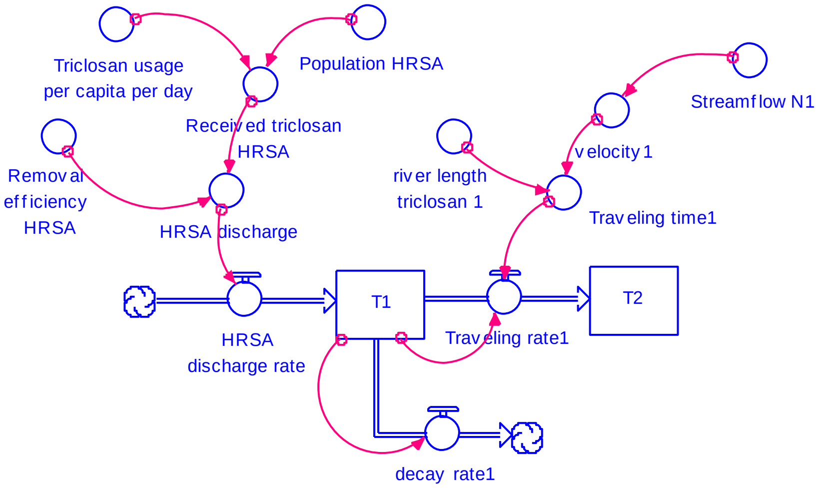


Figure 15. Preliminary model of the triclosan sector.

The T1 represents the mass of triclosan expressed in milligrams in the North River from the HRSA to the USGS 01625000 gage station. The stock accompanies inflow (HRSA discharge rate) and outflows (Traveling rate1 and Decay rate1). The HRSA discharge rate represents the rate at which triclosan enters the T1 stock (expressed in mg/hr). The Traveling rate1 represents the rate at which triclosan moves out of this river segment (T1 stock), expressed in mg/hr. The Decay rate1 represents the rate at which triclosan degrades (expressed in mg/hr).

Explanation of HRSA discharge: Based on our previous discussion, discharges from the WWTPs are the source of the amount of triclosan in the North and Middle Rivers. The triclosan amount depends upon size of population being served by the WWTPs (the more people, the more triclosan is used), the triclosan usage per capita per year, the efficiency of removal in the WWTPs (the more removal efficiency, the less triclosan is discharged into water). The amount of triclosan that the HRSA received is determined as follows:

Received triclosan HRSA (mg/hr) = Population (people) * Triclosan usage per capita per day (mg/d) /24 (hr/d) (9)

Some triclosan is removed through the treatment processes in the HRSA; hence, we can calculate the amount of triclosan in HRSA effluents by the following equation:

HRSA discharge rate (mg/hr) = Received triclosan HRSA (mg/hr) * (1-removal efficiency HRSA) (10)

Explanation of Traveling rate1: As triclosan presents in the water, it travels from a stock to the following stock with current flow. Residence time of triclosan in any stock depends on the length of the river segment and stream velocity. We calculated the Traveling rate 1by the following equation:

Traveling rate1 = length of the river segment (T1 stock) / velocity1 (11)

Since velocity is the discharge (Q) divided by river cross sectional area, stream velocity can be calculated by modifying equation (3) as shown below.

$$Velocity\ (\frac{ft2}{s}) = \frac{Q(cfs)^{(1-x)}}{c} \tag{12}$$

$$Velocity\ (\frac{ft2}{hr}) = \left(Q(cfh)^{(1-x)} * 3600^{x}\right)/c \tag{13}$$

Explanation of Decay rate: Natural attenuation plays a key role in decontamination of triclosan. This attenuation is represented by the "decay rate" outflows from the triclosan stocks. The decay rate can be determined based on its half life. According to Bester (2005), the half-life of triclosan in the river is 11 days or 264 hours. A decay rate constant of triclosan in surface water per hour can be calculated by the following equation:

$$T_m = T_0 * (1-k)^m \tag{14}$$

Since triclosan decays 50 percent in 264 hours, $T_{264} = 0.5\ T_0$

Therefore $$0.5T_0 = T_0 * (1-k)^{264}$$

$$k = 1- e^{(\ln 0.5/264)}$$

$$k = 0.0026$$

where T_0 is the initial amount of triclosan (g)

T_m is the amount of triclosan (g) at time m hours

k is a decay rate constant of triclosan(g) in water per hour

While triclosan travels along the river, it could transform to methyl-triclosan via methylation and could convert to dioxin by the photolysis reaction. Both triclosan by-products are more toxic than triclosan itself (Canosa et al., 2005). Although natural conditions cause triclosan transformation into a number of compounds, we made a simplifying assumption that triclosan would not transform to other compounds. Triclosan flows out of a stock via stream flushing and compound degradation. Therefore, the amount of triclosan in the T1stock where the HRSA discharge treated wastewater at any time t is calculated as:

$$\text{T1}(t) = \int_0^t [\text{HRSA Discharge rate} - (\text{Traveling rate1} + \text{Decay rate1})(S)]ds \qquad (15)$$

Moreover, water temperature is excluded from the model boundary even though fluctuating temperatures in the seasons may affect the degradation rate.

As we mentioned previously, triclosan traveling rates correspond to stream velocity. It flows at the same rate as the streamflow rate in a river segment where it presented. Since we divided river segments differently for the streamflow and triclosan sectors, Figure 15 illustrates the stocks in the streamflow sector (N1, N2, M1, M2, and NM) that the triclosan stocks (T1, T2, T3, T4, T5, and T6) correspond to. For instance, triclosan in the stock T2 and T3 move downstream with the streamflow velocity expressed in the stock N2.

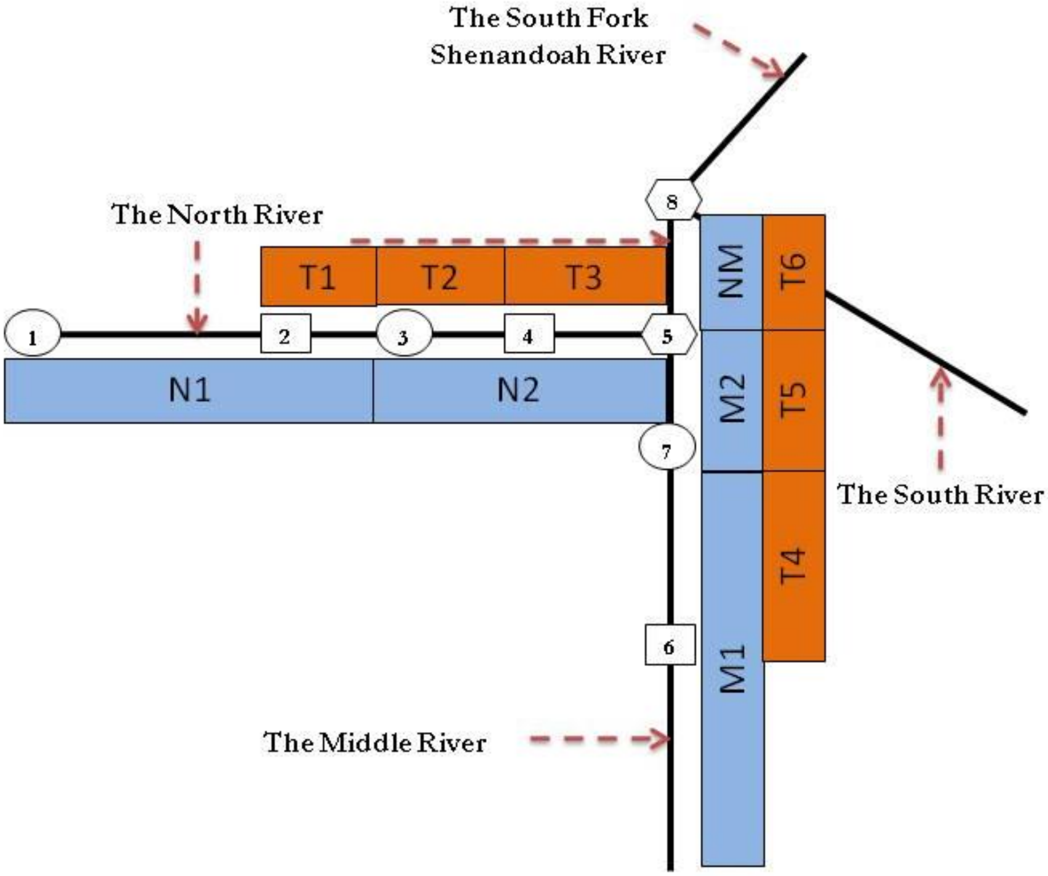


Figure 16. Stocks' boundary in the streamflow and triclosan sectors.

We developed our simple model (Figure 14) by applying the same concept as explained in the first sector. The whole triclosan sector is given in Figure 17.

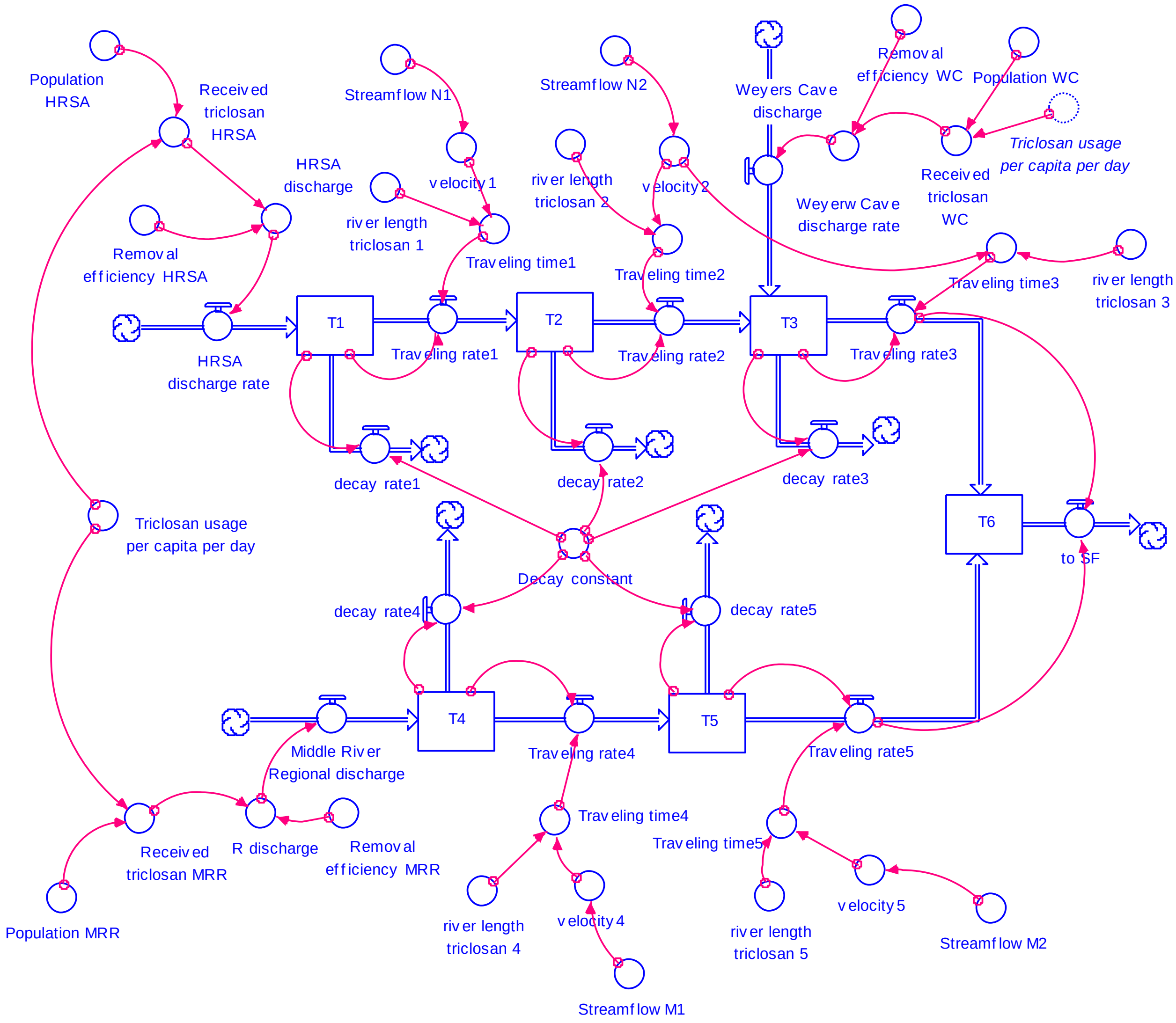


Figure 17. Triclosan sector of TCNMR model.

Description of the Triclosan Concentration Sector

The triclosan concentration sector is the combination of the streamflow and the triclosan sectors. The model of triclosan concentration sector is shown in Figure 18.

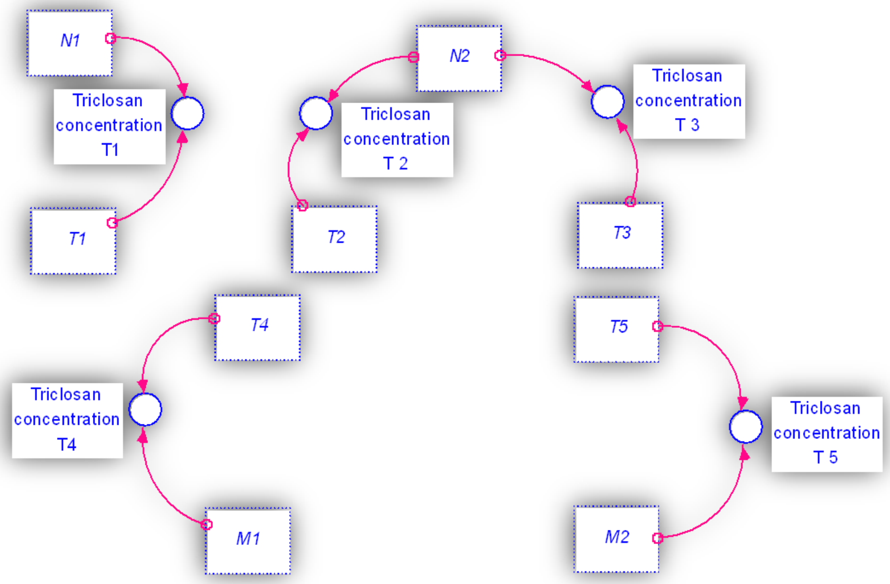


Figure 18. Triclosan Concentration sector of TCNMR model..

Triclosan concentrations in the stocks at any given time vary in response to the volume of water and the amount of triclosan in the stocks. Concentration levels are expressed in nanograms per liter (ng/L) or parts per trillion for convenient data interpretation. .A triclosan concentration is an amount of triclosan in ng over a volume of water in liters.

Since the length of the T1, T2, T3, and T4 stocks are unequal to the lengths of the stocks that they correspond to (N1, N2, and M1 respectively) (see Figure 15), we use fractions of water to determine triclosan concentrations in those stocks. A fraction is a length of determined stock over a total length of stock that the determined stock corresponds to. For example, the concentration T1 can be determined as:

Triclosan concentration T1 = T1 stock value /N1 stock value * (length of T1 stock/length of N1stock) (16)

Note that triclosan concentration T6 would not be determined since the net flow of the NM stock would be stable.

Chapter 3

Model Testing

In Chapter 2, the model assumption, boundaries are describes in details. This chapter will evaluate whether the model is useful and good enough to fulfill its defined purpose. Any simulating model is constructed based on limited simplified assumptions to represent the real world; thus, a simulation model cannot be validated in absolute senses (Sterman, 2000). In order to determine if the model is good enough and is appropriate for its purposes, we employ many established criteria as follows:

- *Face validity*: this assesses the model boundaries whether it includes appropriate variables that are relevant to fulfill its purpose. Are important variables addressing the problem endogenous to the model?
- *Structural validity:* this tests logic of the model structure. Are the stock and flow structured constructed with logical relationship among variables and consistent to real world systems?
- *Dimensional consistency:* this assesses that the numeric values in the model are consistent in the units used.
- *Behavior under extreme condition:* this assesses the models response to changed conditions. Does the model exhibit appropriate or common sense behaviors if key parameters are modified?
- *Behavior reproduction:* this test is to evaluate how well the model mimics relevant aspects of historical behaviors and to assess the correspondence with the past behaviors close enough to fulfill the intended purpose of the model.

> Does the model generate the various behaviors observed in the real world scenarios?

The following section describes model testing on these criteria, actual test run, and the changes made to the model.

Face Validity and Structural Testing

An important aspect of model testing in the structural assessment test asks whether the model is consistent with knowledge of the real system. Model components (stocks, flows, and converters) are sufficiently relevant to its purpose. One approach of evaluating this is through face validity testing which is the qualitative analysis of the model structure against the knowledge of experts.

For the streamflow sector, the expert advice was provided by Professor Thomas Benzing. Regarding the model structure, the system input and the behaviors of the water were reasonable. Precipitation was identified as the input. When rain falls into the watershed, water flows towards the stream via run-off mechanisms. Our model consists of the Precipitation rate as an input of water, as well as the Interflow rate and Streamflow rate. A fraction of water traveling on land surface and through soil depends on watershed area and capacity. We include the Fractional traveling on surface and Surface transit time in our model to determine how much water from precipitation would flow towards a stream via interflow and surface flow.

Moreover, we included the evapotranspiration factor which represents a fraction of water that is evaporated from the soil matrix and is used by plants. An evapotranspiration fraction in the upper South Fork Shenandoah River is 0.7 (Daniel, 2007). However, we assumed the value could rise up to 0.8 to 0.9 in the summer time.

Setting this value in the model generated behaviors fitting the real-world history. Details will be discussed in the behavior reproduction test.

Dimensional consistency

Another criterion of model testing is dimensional consistency. That is units used in the equation for stocks and flows should maintain unit consistency. In this case, the stocks contain water in cubic feet, then all the flows associated the stocks must be expressed in cubic feet per unit of time. Moreover, the model is run on an hourly basis. All flow velocity must be calculated in the unit of hour. This can be checked only by a careful examination of the units used in model equations. Throughout the streamflow sector, triclosan sector, and triclosan concentration sector, all equations were repeatedly examined and changes were made in order to satisfy this test.

Extreme conditions

The extreme condition test is another test used to evaluate the model logic boundary assumptions and equations used in the model. The model should behave in a realistic fashion no matter how extreme the inputs. Several inputs were examined in this way. For the streamflow model, we set the “precipitation” value to zero by turning off the “rain event” switch to simulate streamflow at a steady state. The expected behavior would be that streamflow are stable at any time “t” and should match historical average streamflow. Moreover, the “precipitation measurement” variable was adjusted in various values in order to test model sensitivity to rainfall intensity. Initially, we test the model response to a precipitation input. The shape of streamflow should have a little lapse time, peak off and eventually level off to a normal baseflow. This is because water on watershed land surface and water in soil take a certain time to flow towards a stream.

The more volume of water in the river channel, the higher streamflow rate is. Since it stops raining, no water add to a stream resulting in a gradually decrease of the streamflow. A shape of streamflow generated in the model looks as we expected (see Figure 19). Our further step is to adjust various values of precipitation measurement in order to test model sensitivity to rainfall intensity.

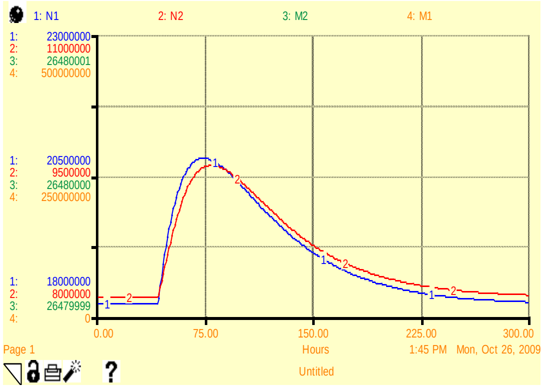


Figure 19. Hydrographic shapes from the streamflow sector.

In addition to the streamflow model, the triclosan model examined the behaviors under extreme conditions. We modified the amount of triclosan input by using the step and pulse functions. The model should behave reasonably under setting conditions. The last sector needed to test is the triclosan concentration. Triclosan concentrations in the stocks at any given time vary in response to the volume of water and the amount of triclosan in the stocks. The model should generate reasonable concentrations if triclosan surged or the precipitation volumes changed. Table 2 lists extreme values for all sector tests, expected behaviors, and testing results.

Table 3. Extreme value tests for the streamflow sector, triclosan sector, and triclosan concentration sector .

Sector	Variable	Test	Expected Behavior	Observed Behavior
Streamflow	Rain Event	No rain event	Streamflow would be the same as baseflow and stable at a steady state	As expected
	Precipitation Measurement	Introduced rainfall at 0.5 inches per day	Streamflow shape is similar to a theoretical hydrograph	As expected
	Precipitation Measurement	Introduced higher intensity rainfall at 1 inches per day	Streamflow graph would have shape similar to a theoretical hydrograph and peak at higher rate	As expected
Triclosan	Triclosan Surge	Spike triclosan into WWTPs	Amount of triclosan peaks off and gradually levels off	As expected
Triclosan concentration	Precipitation Measurement	Introduced rainfall at 0.5 inches per day	Triclosan concentrations decline, and rise slowly to the levels at a steady state after rain stopped.	As expected
	Triclosan Surge	Spike triclosan into WWTPs	Amount of triclosan peaks off and gradually levels off	As expected

Behavior reproduction

Once the model logic is established, the next test process is to evaluate whether the model reproduces historical system behaviors. In this case, the streamflow sector was tested by simulating discharge of the mimicked historical rain events and comparing the results with the USGS discharge values at the particular gage stations. Precipitation values were retrieved from the Automated Flood Warning System available at http:// www.afws.net. The average precipitation data from Stokesville, Dundorn Mountain, and Briery Branch gage stations represent the precipitation in the North River watershed. The precipitations data for the Middle River watershed were the average rainfalls at Middlebrook, Churchville, and Brands Flat gage stations. In order to test the model, precipitation on September 25, 2009, were set and simulated. The discharge and streamflow shapes of **Discharge N1** were compared to historic data from the USGS01622000 North River near Burketown. The simulated discharges behaved closely to the historic data (see Figure 20). For instance, elapsed time, time duration to peak, and streamflow peak values were not different in this comparison. The streamflows took approximately 11 days or 264 hours to level off to baseflow in both historic data and simulated model.

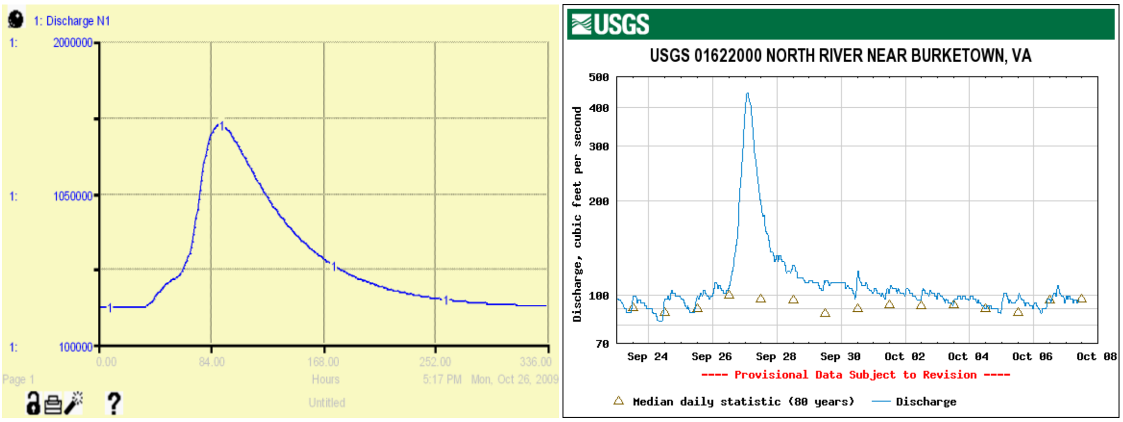


Figure 20. The streamflow (cubic feet per hour) from the simulation model compared to the streamflow (cubic feet per second) from the USGS01622000 North River near Burketown. http://waterdata.usgs.gov/va/nwis/uv/?site_no=01622000&PARAmeter_cd=00065,00060,62620,00062

In addition to test system behavior reproduction in the North River, streamflows from the **Discharge M1** variable were compared to those from the USGS01625000 Middle River near Grottoes. Precipitation values on September 25, 2009, were set and simulated. Although the hydrographic shape was slightly different, elapsed time, the peak value, and leveling off time were similar to historic data from USGS (see Figure 21).

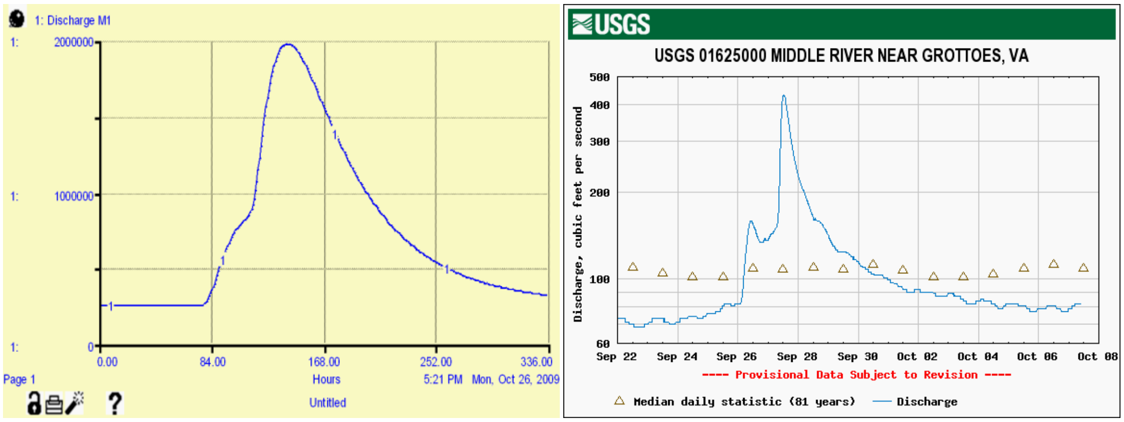


Figure 21. The streamflow (cubic feet per hour) from the simulation model compared to the streamflow (cubic feet per second) from the USGS01625000 Middle River near Grottoes. http://waterdata.usgs.gov/va/nwis/uv/?site_no=01625000&PARAmeter_cd=00065,00060,62620,00062

Limited data is available regarding real-world triclosan concentrations in the North and Middle Rivers. Thus we could not test whether the model reproduces the known historic triclosan concentrations. However, the model predicted triclosan concentrations at a steady state in the North and Middle Rivers were 98.4ng/L and 65.0ng/L respectively. Low concentrations in nano levels are expected because most recent studies reported detected triclosan concentrations in nanograms per liter or micrograms per liter (ppb).

Throughout the validation process, model logic and variables were adjusted or modified to improve the model. Several changes were made in order to fine tune the model for accurate behaviors. Specifically, the evapotranspiration factor had a significant impact on the system behaviors overtime as it accounts for the fraction of water containing in the watersheds. The factor was adjusted so that the model could closely reproduce historic system behaviors (i.e. rain events on September 25, 2009).

Chapter 4

Implications and Conclusions

Implications of the Model

Pharmaceuticals including triclosan have been detected in the South Fork Shenandoah River and its main tributaries, the North and Middle Rivers. Although triclosan contaminates the rivers at low concentrations, concerns about its cumulative effects have been considered as a possible factor leading to fish kills and intersex phenomena since scientists found triclosan in dead and dying fish tissues (Luellen, 2009).

The TCNMR model developed in this thesis aims to help quantify and predict triclosan concentrations over time, based on known factors such as triclosan usage per capita and efficiency of removal triclosan from wastewater in WWTPs. TCNMR consists of three sectors: streamflow, triclosan, and triclosan concentration. By adjusting the values of key variables in the model, we can predict triclosan concentrations and evaluate the dynamic effects of those factors. Ultimately, the understanding of the system's behaviors and the simulated results may deepen our understanding and may identify an important strategy to reduce the amount of triclosan in water.

Model Scenarios

To fulfill the model purpose, we set some experiments to quantify triclosan concentrations in the North and Middle Rivers and evaluated effects of modified variables to triclosan concentrations. We will run the model under normal and drought conditions for each experiment since we considered that drought conditions will possibly exist and will lead to a worse case due to higher triclosan concentrations in the rivers.

Initial conditions: Triclosan concentrations at a steady state in normal and drought conditions.

For this step, we predict triclosan concentrations in drought conditions where baseflows and the amount of water in the river significantly drop. The initial values under normal conditions with no rain are listed in Appendix C. We ran the model under normal condition and then decreased normal baseflow in the North and Middle Rivers for drought conditions. According to historical discharge data from the USGS (see Figure 22), the lowest baseflow during 1990 to 2009 in the North and Middle Rivers are 30 cfs (1999) and 20 cfs (2002) respectively.

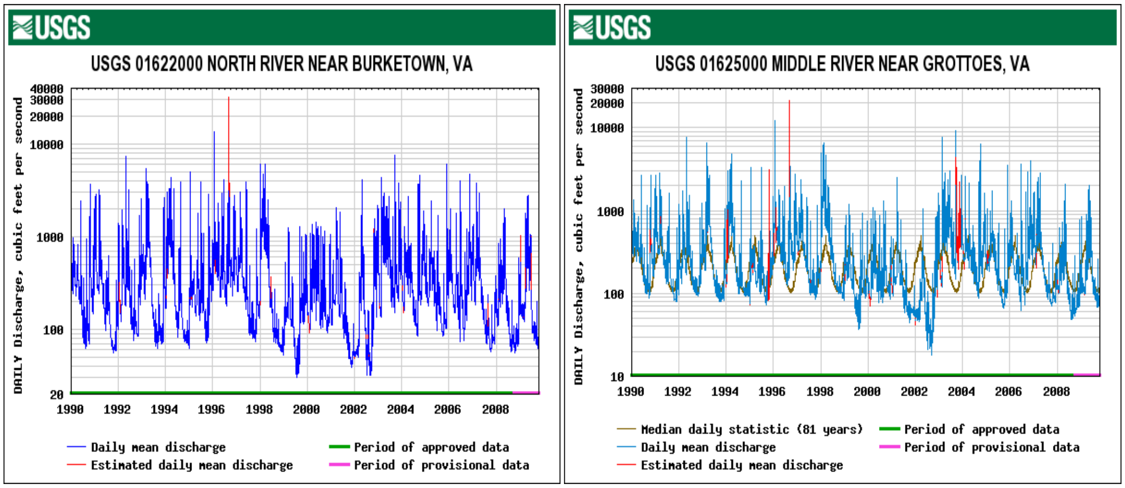


Figure 22. Daily mean discharges during 1990 to 2009 at the USGS 01622000 North River near Burketown and the USGS01625000 Middle River near Grottoes.
Sources:
http://waterdata.usgs.gov/va/nwis/dv/?dd_cd=01_00060_00003&format=img_default&site_no=01622000&set_logscale_y=1&begin_date=19900101&end_date=20091106 and
http://waterdata.usgs.gov/va/nwis/dv/?dd_cd=01_00060_00003&format=img_default&site_no=01625000&set_logscale_y=1&begin_date=19900101&end_date=20091106

The results of this simulation are shown in Table 3. Figure 23 (showing triclosan concentration over time in normal conditions) and Figure 24 (showing triclosan concentration over time in drought conditions). At its steady state under normal conditions, the concentrations are stable. When the baseflows drop during drought time, less water runs into and accumulates in the stocks (N1, N2, M1, and M2) and the amount of triclosan is unchanged. The concentrations increase from 184 to 226 % and become stable when the system reaches a steady state

Table 4. Triclosan concentrations in the North and Middle Rivers under normal and drought conditions.

Conditions	**Triclosan Concentrations (ng/L)**				
	T1	**T2**	**T3**	**T4**	**T5**
Steady state *Normal condition*	101.46	98.08	95.74	65.25	64.76
Steady state *Drought condition*	303.33	285.75	272.16	212.77	209.95
%increase of triclosan concentrations	198.97	191.34	184.27	226.08	224.20

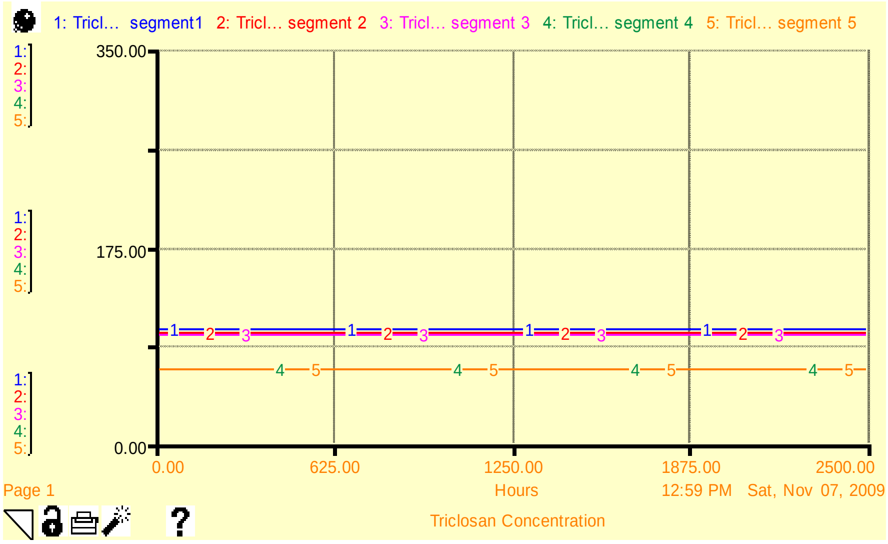


Figure 23. Simulated triclosan concentrations under the normal condition**.**

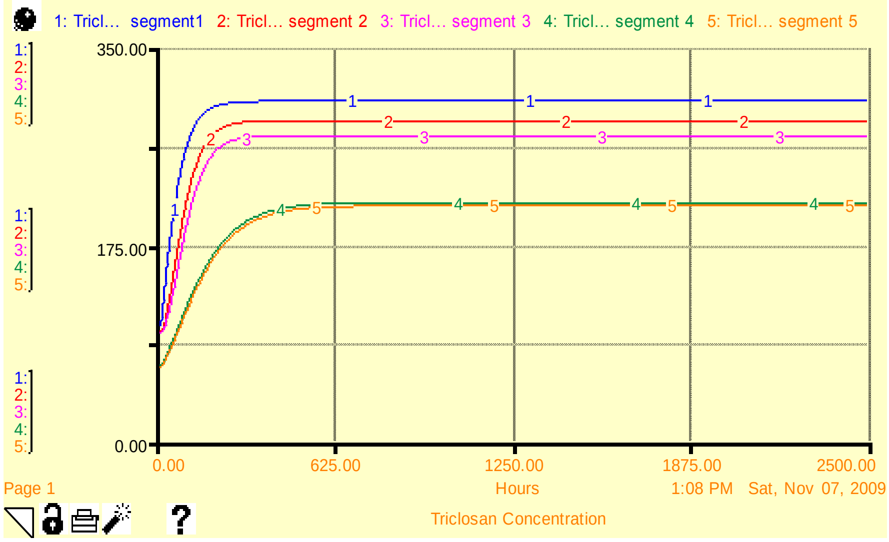


Figure 24. Simulated triclosan concentrations under the drought condition.

Experiment #1: Simulated triclosan concentrations under rain events.

This experiment introduced rainfall events into the system to determine effects of precipitation on triclosan concentrations. We set precipitation for every two days (48 hrs) at 0.1 inches/hr for 3 hours, and repeatedly introduced the rainfall for five cycles. As more water flows into and accumulates in the rivers (N1, N2, M1, and M2 stocks) without any modification of the amount of triclosan, the triclosan concentrations dramatically drop (see Figure 25). However, the concentrations recover to the same level as they are in a steady state (without rain). Furthermore, we consider how frequency of rain events affects the system behaviors. Rain events are introduced every week (168 hrs) at the same intensity and duration. Triclosan concentrations decrease when rain events occur (see Figure 26) but they are higher than those in short rain intervals (every 48 hrs) (see Table 4). This is possibly because streamflows do not yet level off to a steady state and then start to increase again when another rain event happens leading to an elevated stream velocity. Thus triclosan moves out the river more quickly resulting in dropping of triclosan concentrations in river segments.

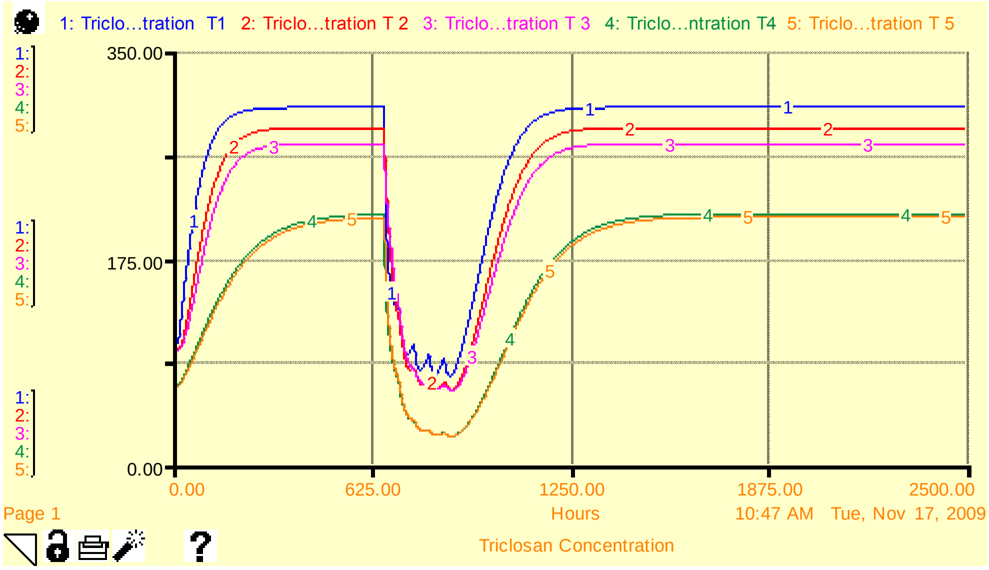


Figure 25. Triclosan concentrations under drought conditions after precipitation 0.1 inches/hr for 3 hours in every 48 hours

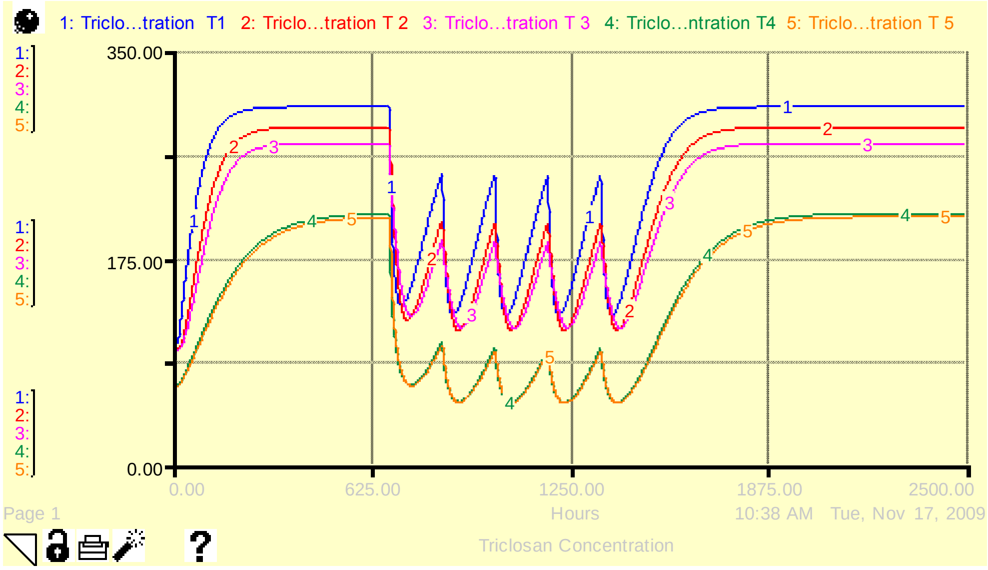


Figure 26. Triclosan concentrations under drought conditions after precipitation 0.1 inches/hr for 3 hours in every 168 hours.

Table 5. Simulated triclosan concentrations under rain events.

Conditions	Normal					Drought				
	Triclosan concentrations (ng/L)					Triclosan concentrations (ng/L)				
	T1	T2	T3	T4	T5	T1	T2	T3	T4	T5
Steady state (No rain)	101.46	98.08	95.74	65.25	64.76	303.33	285.75	272.16	212.77	209.95
Rain (5 cycles) every 48 hrs	49.48	47.07	44.21	18.59	18.47	74.52	63.41	63.20	37.28	37.06
Rain (5 cycles) every 168 hrs	65.99	61.36	63.56	32.35	32.04	126.89	116.28	123.56	51.69	51.27

Experiment # 2: Simulated triclosan concentrations with changes of triclosan usage per capita.

This experiment is set based on the steady state baseline values, except triclosan usage per capita is increased by 50 %. As the triclosan usage rises leading to the increase of the amount of triclosan loaded into wastewater, more triclosan enters into the rivers. Thus, triclosan concentrations increase as shown in Figure 27. In contrast, if triclosan usage per capita drops, triclosan concentrations reduce (see Figure 28). These simulated consequences take place in the same fashion under normal and drought conditions.

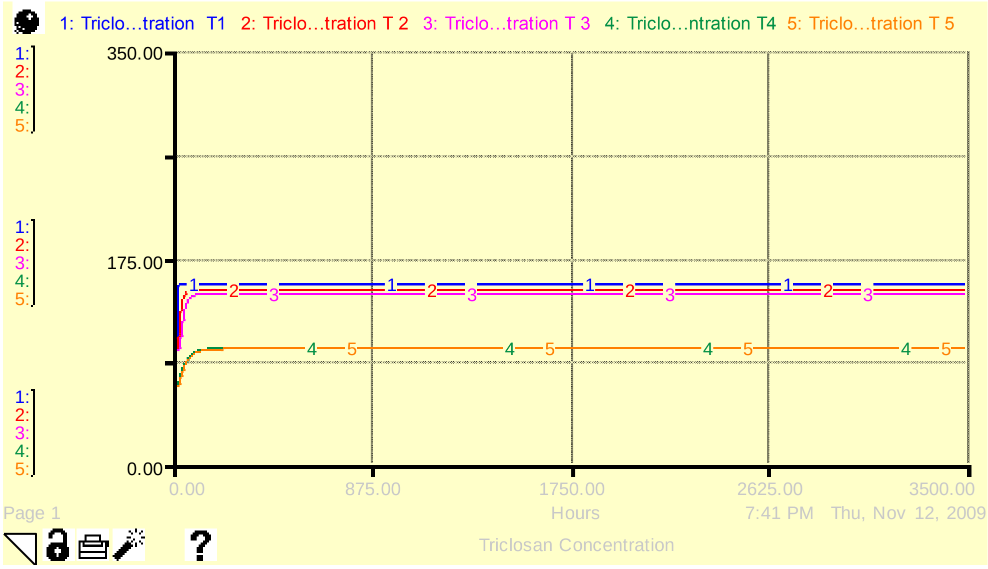


Figure 27. Triclosan concentrations after increased triclosan usage per capita.

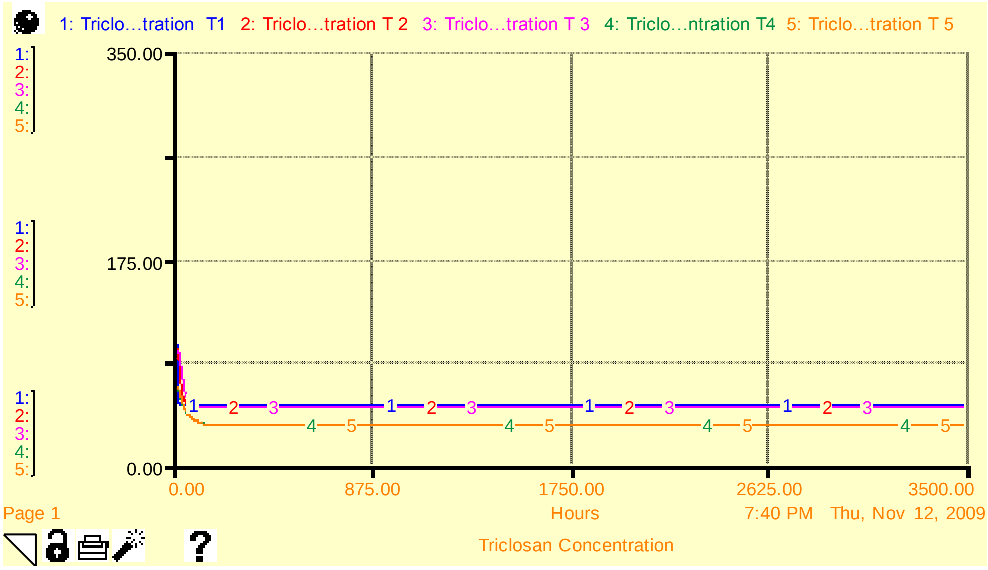


Figure 28. Triclosan concentrations after reduced triclosan usage per capita.

Table 6. Simulated triclosan concentrations with changes of triclosan usage per capita.

Conditions	**Normal**					**Drought**				
	Triclosan concentrations (ng/L)					**Triclosan concentrations (ng/L)**				
	T1	**T2**	**T3**	**T4**	**T5**	**T1**	**T2**	**T3**	**T4**	**T5**
Steady state (No rain)	101.46	98.08	95.74	65.25	64.76	303.33	285.75	272.16	212.77	209.95
Triclosan usage increased by 50%	152.32	147.23	143.73	97.96	97.22	455.36	428.97	408.57	319.42	315.18
Triclosan usage decreased by 50%	50.85	49.16	47.99	32.71	32.46	152.03	143.22	136.41	106.65	105.23

Experiment # 3: Simulated triclosan concentrations with improvement of removal efficiency of triclosan in WWTPs.

This experiment is to simulate triclosan concentrations if the WWTPs improve their efficiency to remove triclosan from treated wastewater. When the efficiency is set to remove to 95% of the triclosan (2% improvement), concentrations drop about 30% on average. We further test sensitivity of percentage of removal to the triclosan concentrations by increasing the efficiency up to 98% (see Figure 29 and 30). Triclosan concentrations dramatically decrease (about 70% reduction) in both normal and drought conditions. This is because a small efficiency improvement leads to a significantly larger amount of triclosan removed compared to the amount removed by the baseline treatment.

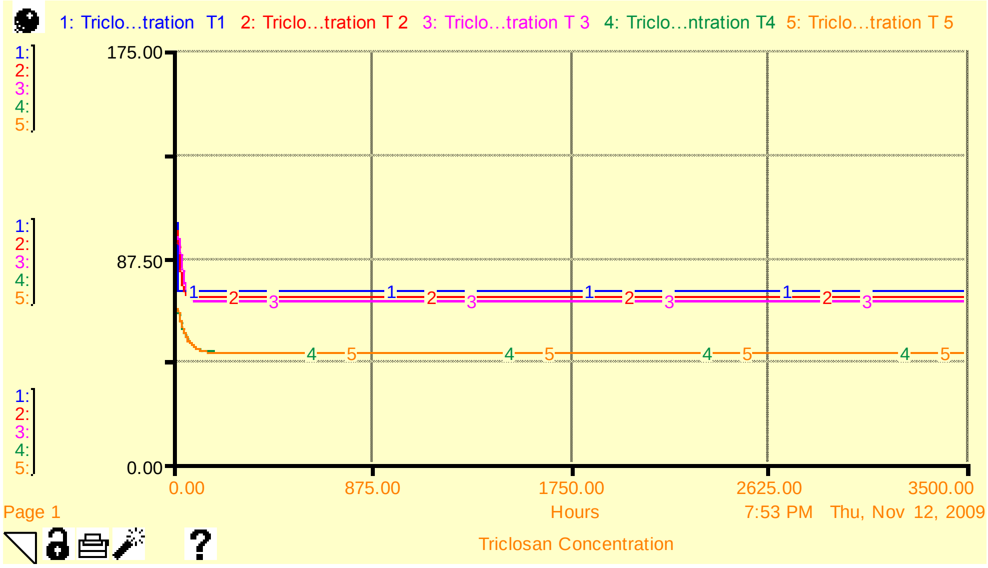


Figure 29. Triclosan concentrations after WWTPs improve efficiency of removal 2 %.

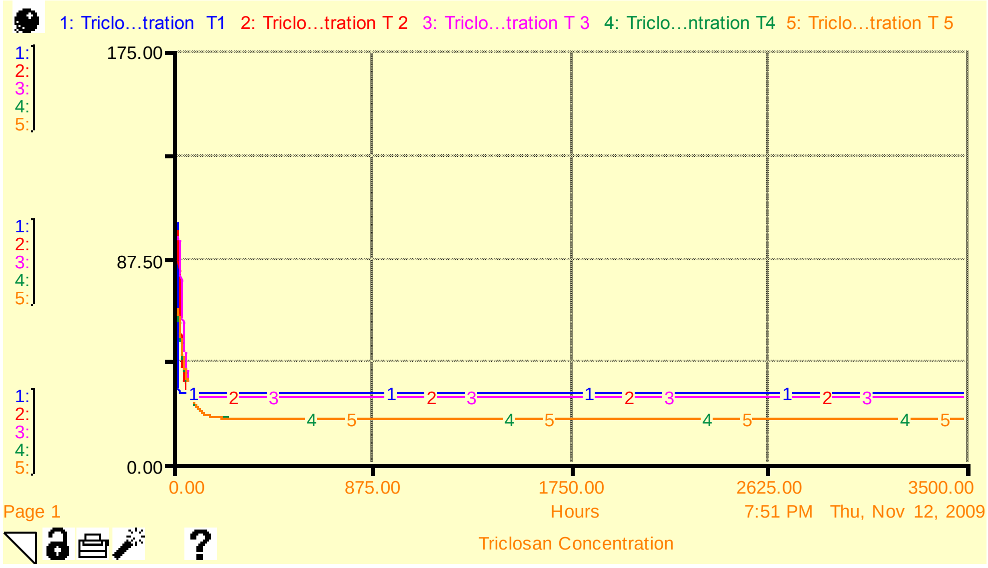


Figure 30. Triclosan concentrations after WWTPs improve efficiency of removal 5 %.

Table 7. Simulated triclosan concentrations with improvement of removal efficiency of triclosan in WWTPs.

Conditions	**Normal**					**Drought**				
	Triclosan concentrations (ng/L)					**Triclosan concentrations (ng/L)**				
	T1	**T2**	**T3**	**T4**	**T5**	**T1**	**T2**	**T3**	**T4**	**T5**
WWTPs 93% removal efficiency (default value)	101.46	98.08	95.74	65.25	64.76	303.33	285.75	272.16	212.77	209.95
WWTPs 95% removal efficiency	72.47	70.05	68.36	46.61	46.26	216.66	204.11	194.46	151.98	149.96
WWTPs 98% removal efficiency	28.99	28.02	27.35	18.64	18.50	86.66	81.64	77.76	60.79	59.99

Regarding our previous simulated results, the removal efficiency factor is sensitive to the triclosan concentrations in North and Middle River segments. We further set an experiment to determine sensitivity of the triclosan concentrations to deterioration of WWTPs' efficiency of treatment. The efficiency of removal of the HRSA is set to be deteriorated gradually at about 2% per year. The triclosan concentrations increase 21% approximately over a year (see Table 6).

Table 8. . Simulated triclosan concentrations under deterioration of WWTPs

Conditions	**Normal**			**Drought**		
	Triclosan concentrations (ng/L)					
	T1	**T2**	**T3**	**T1**	**T2**	**T3**
Steady state (No rain)	101.46	98.08	95.74	303.33	285.75	272.16
Efficiency of removal decreased by 2% per year	123.94	119.77	116.72	370.52	348.87	331.63
% increase of triclosan concentrations	22.48	22.11	21.91	22.15	22.09	21.85

Options to Reduce Triclosan Concentrations in Surface Water

Triclosan concentration levels in surface waters depend on various factors, such as the volume of water and the amount of triclosan in water. Although precipitation can reduce triclosan concentrations, concentrations recover to the same levels as they were before a rain event. Based on simulated results, triclosan usage reduction and WWTPs' technology improvement are likely to reduce triclosan concentration levels in the long run because the concentrations decrease to the lowest point and stay at that level at a steady state.

Improving efficiency of removal of triclosan in WWTPs significantly reduces triclosan concentrations in the North and Middle Rivers regarding simulated results. A small percentage of improvement in removal systems or deterioration of treatment efficiency contributes to large potential changes of the system's behaviors. With a bit higher treatment efficiency, the amount of triclosan remaining in the discharge is significantly lower than the amount that remains when using the baseline treatment efficiency. This leads to a significant reduction of triclosan concentrations. In contrast, decreasing per capita triclosan usage by half, however, does not reduce triclosan concentration as much as improving treatment technology by 5%.

Policy makers should consider controlling treatment efficiency of WWTPs rather than limiting triclosan consumption since this approach will provide a huge impact on triclosan concentration levels whether treatment systems are improved or deteriorated. Moreover, governmental agencies have authority to regulate pollutants and their limitations in WWTP discharges, but they do not have authority to control consumer decisions.

The Environmental Protection Agency (EPA) plays a key role in treatment technology improvement in WWTPs by regulating effluent limitations, specifying pollutants, and restricting how much a given discharger is allowed to emit into the water. The Clean Water Act (CWA) authorizes the EPA to control water pollution by establishing water quality standards and new provisions for toxic water pollutants. The agency controls dischargers by issuing a permit operating under the Natural Pollutant Discharge Elimination System (NPDES). Discharges into water bodies must meet water quality standards and effluent limitations (Kraft, 1995). Thus, technologies for wastewater treatment have developed in order to make effluents levels comply with the EPA requirements.

Unfortunately, proposing to designate pharmaceuticals including triclosan as water pollutants would take the EPA a long period of time due to the regulatory process. Pharmaceuticals have not yet been proven to have environmental risks. These significant data gaps limit the ability of the EPA to regulate pharmaceuticals. Much more research will be required before the EPA makes any decision (Kallaos, Wheeler, Wong, & Zahller, 2007). For example, the agency needs to evaluate drug pathways and levels of exposure along with potential effects on public health and aquatic life (Grumbles, 2008).

Simultaneously, the EPA needs to consider treatment technologies that support its regulation if any pharmaceuticals are controlled. The membrane bioreactor (MBR) may be a prospective technology to treat pharmaceuticals in wastewater. According to the study of Kantiani et al., membrane bioreactor technology shows the highest percentage of triclosan removed from wastewater among other technologies (activated sludge and oxidation ditches) (Kantiani et al., 2008). This promising technology can be integrated with existing wastewater treatment systems (Noble, 2006) Installation cost of MBR varies depending on numerous factors including treatment capacity and membrane types. Although operating costs for MBR are higher than conventional activated sludge treatment due to high aeration energy, MBR provides better effluent quality and less sludge footprint (Li, 2008).

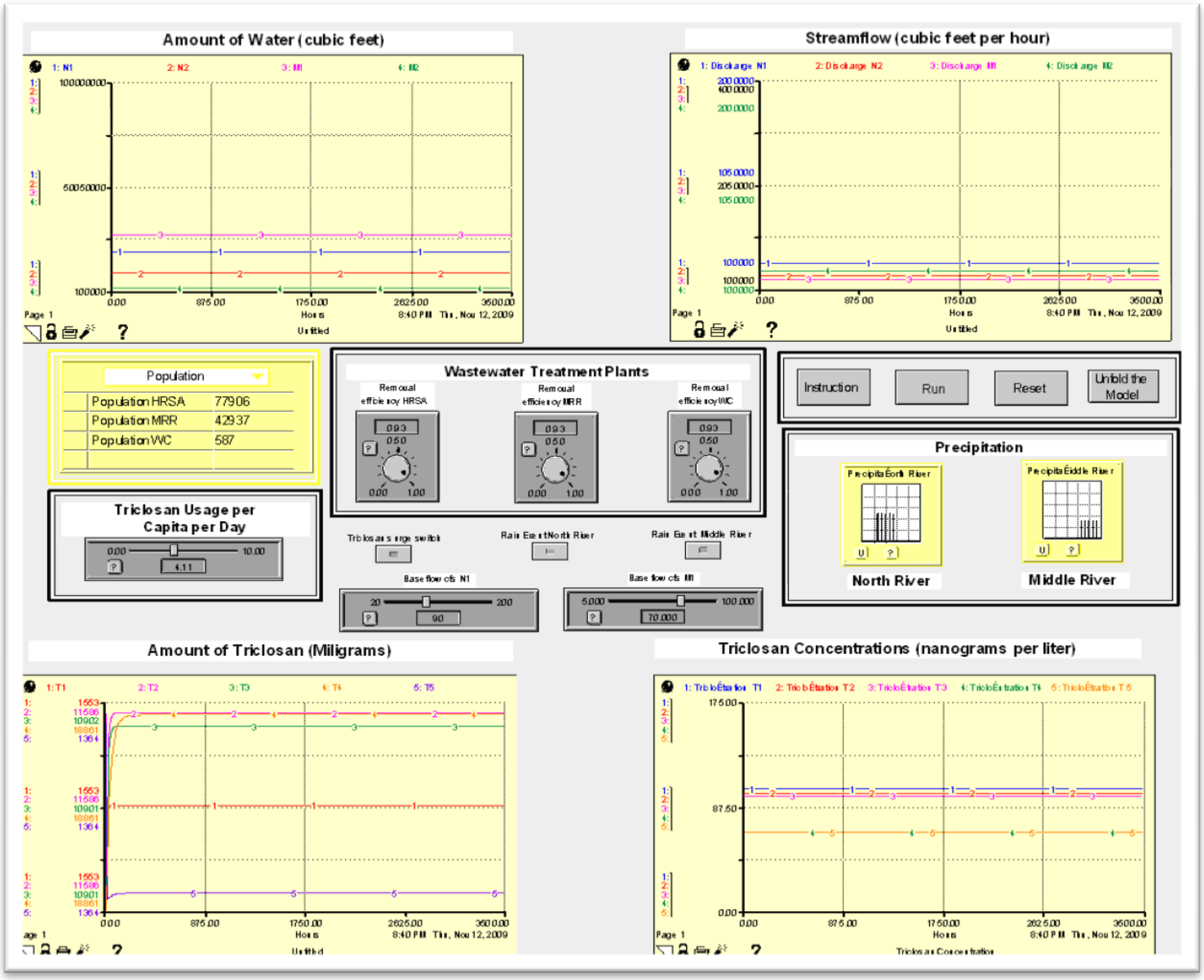
Decreasing per capita triclosan usage can be another approach to reduce triclosan concentrations even it does not reduce triclosan concentration as much as improved treatment technology in the simulated results. The market of antibacterial soaps is growing. As antimicrobial soap usage has proliferated, its benefits in terms of reducing infections in households have not been demonstrated (Larson, Lin, Gomez-Pichardo, & Della-Latta, 2004). Numerous research studies suggested that using antibacterial soap is not more effective than washing with regular soap to fight infections (Liu, 2005; Jagger, 2008). Healthcare professionals should advise consumers against the routine use of antimicrobial household and personal care products that are unnecessary and harmful to the environment (Glaser, 2004). Increased public knowledge about the environmental hazards of antimicrobial products, including those that contain triclosan, might result in a reduction of their use.

Moreover, consumers may not recognize which products contain antimicrobials because companies are not required to label product ingredients if products are claimed as cosmetics. The FDA can regulate only post-market cosmetics. Neither cosmetics nor cosmetic ingredients are approved by the FDA before they are in the marketplace (Glaser, 2004). Some manufacturers such as Tom’s of Maine and Marks & Spencer are concerned about triclosan and its environmental effects, so they voluntarily ban triclosan in their products (Glaser, 2004; Jagger, 2008). Triclosan-free companies should advertise to consumers by putting a “triclosan-free” indicator on their products. This will help consumers differentiate triclosan-free products without looking product labels closely.

Applications of TCNMR model

The TCNMR model is the first attempt to predict triclosan concentrations in parts of the North and Middle Rivers. It was done to explore the use of the system dynamics methodology and to provide a simulation platform that could be enhanced in future studies. Figure 31 is a screenshot of the user interface for the TCNMR model. The model offers user-adjustable sliders and knobs for several key variables. All devices for variable modification are located on the middle of the dashboard. Users are allowed to change efficiency of removal for three selected WWTPs, number of people that WWTPs serve, or triclosan usage per capita per year. Moreover, users can modify river baseflow for drought and flood conditions by sliding the Baseflow sliders.

To the right hand side of the interface, users are able to change rainfall patterns (intensity and intervals) by changing values in the precipitation graphs. Users turn on rain events by clicking rain event switches located on the middle of the interface. After adjusted all variables, users hit the RUN button to start simulating the model. There are four graphs showing amounts of water in the stocks, the discharge rates, amounts of triclosan, and triclosan concentrations over time. Therefore, users can observe the system’s behaviors over time. They can explore the model logic by hitting the “Unfold the Model” button to enhance their understanding of the system’s behaviors.



Population	
Population HRSA	77906
Population MRR	42937
Population WC	587

Removal efficiency HRSA: 0.93
Removal efficiency MRR: 0.93
Removal efficiency WC: 0.93
Triclosan Usage per Capita per Day: 4.11
Base flow cfs N1: 90
Base flow cfs M1: 70.000

Figure 31. Dashboard for TCNMR model.

For future research

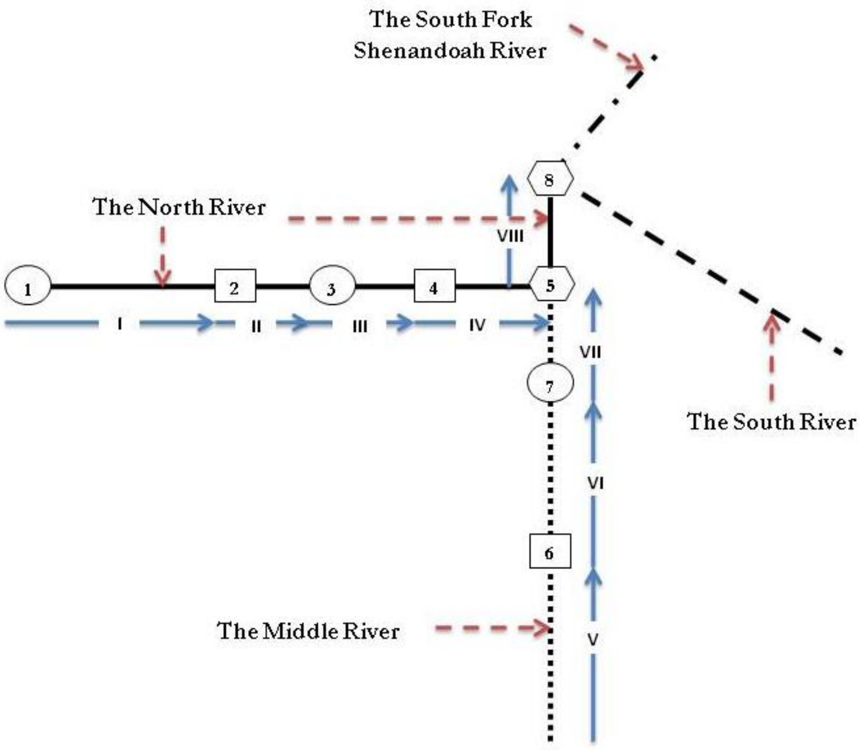
There are several options available for further research. The model could be expanded to examine triclosan concentrations in other segments of rivers in the South Fork Shenandoah River basin (the South River and the South Fork Shenandoah River) with small modification thanks to similar watershed characteristics. Furthermore, the model platform could be applied to predict concentrations of triclosan or other pollutants in other rivers. However, a number of variables including length of river segments, relationship between river length and discharge rate, decay rates of pollutants, fraction of surface run-off and infiltration rate are needed to be modified to fulfill this purpose.

Moreover, there are several simplifying assumptions made in the model that could be refined to provide more accurate outputs. For example, water temperatures fluctuating during seasons may affect triclosan degradation rate or high sunlight in the summer may accelerate photolysis of triclosan in water. More accurate decay rate in different seasons may better predict the system’s behaviors. Half-life of triclosan in the North and Middle Rivers is necessary for the accurate decay rate since the decay constant used in this model calculated based on triclosan half-life in the Ruhr River, Germany.

Appendix A

Stock Descriptions

The schematic diagram of the South Fork Shenandoah, North, Middle, and South River system



Sign	Descriptions
1	USGS 01620500 North River near Stokesville gage station
2	The Harrisonburg-Rockingham Regional SA Sewer treatment plant (STP) (HRSA)
3	USGS 01622000 North River near Burketown gage station
4	The ACSA Weyers Cave STP (WC)
5	The confluence of the North and Middle Rivers
6	The Middle River Regional STP (MRR)
7	USGS 01625000 Middle River near Grottoes gage station
8	The confluence of the North, South, and South Fork Shenandoah Rivers

Sector	**Stocks**	**River Segments (see the schematic diagram)**	**Length of River Segment (miles)**	**Watershed Area (square miles)**
Streanflow	N1	I and II	31.28	177.24
	N2	III and IV	14.08	46.86
	M1	V and VI	69.60	373
	M2	VII	1.83	1.56
	NM	VIII	4.39	6.72
Triclosan	T1	II	0.93	Not Determine
	T2	III	7.17	Not Determine
	T3	IV	6.91	Not Determine
	T4	VI	25.12	Not Determine
	T5	VII	1.83	Not Determine
	T6	VIII	4.39	Not Determine
Triclosan Concentration	Triclosan concentration T1	II	0.93	Not Determine
	Triclosan concentration T2	III	7.17	Not Determine
	Triclosan concentration T3	IV	6.91	Not Determine
	Triclosan concentration T4	VI	25.12	Not Determine
	Triclosan concentration T5	VII	1.83	Not Determine

Length Measurement Method

The lengths of all river segments are determined based on the geographic information system of the Virginia Department of Environmental Quality (VA DEQ). We use the ruler measurement function to measure the lengths on the VA map available on http://gisweb.deq.virginia.gov/deqims/viewer.htm?SERVICE=VA_DEQ.

Watershed Area Calculation

Drainage area is related to river length. Huck (1957) mentioned the relation of length to drainage area in the Shenandoah Valley expressed by the equation

$$L = 1.4\ A^{0.6}$$

where L is length in miles and A is the area in square miles.

All watershed areas for the stocks are calculated by the equation excluding the watershed area of the M1 stock. Because the Middle River is so curvy that calculated watershed might be incorrect, we employ the drainage area data from the USGS website, http://waterdata.usgs.gov/va/nwis/nwismap/?site_no=01625000&agency_cd=USGS.

Appendix B:

USGS field Streamflow Measurement

USGS 01622000 North River near Burketown, VA

Gage Height (ft)	Q (ft3/s)	Area (ft2)	Gage Height (ft)	Q (ft3/s)	Area (ft2)
6.62	3020	678	2.7	317	188
6.33	2490	598	1.97	70.1	110
6.53	2520	646	2.28	168	164
1.96	63.9	123	2.98	414	211
2.05	79.3	113	2.56	270	164
1.92	78.4	91	2	103	125
2.09	94.6	121	1.75	44.3	79.7
2.77	322	187	1.82	57	109
3.46	663	258	1.93	69.9	119
1.92	65.3	109	2.15	128	158
1.86	48.6	91.6	4.12	1000	364
2.08	100	127	3.68	779	333
3.56	721	271	2.32	187	137
2.65	272	170	1.9	71.1	102
3.53	682	248	2.43	211	155
4.16	1080	364	3.97	892	362
2.4	182	140	3.43	601	238
2.24	128	135	2.72	302	182
2.25	128	136	2.6	267	170
2.32	169	139	2.35	197	154
3.18	492	254	2.22	147	135
3.95	904	340	1.9	68.1	104
3.45	616	250	1.97	80.7	109
2.24	134	131	2.29	166	145
1.92	57.5	109	2.88	388	195
1.95	64.3	101	4.38	1180	392
2.68	271	176	2.55	261	168
2.71	306	184	2.35	188	143
3.67	721	309	2	94.7	110
2.14	121	144	1.91	74.1	95.6
2.35	172	139	1.91	66.9	101
2.09	118	133	2.35	189	146
2.14	101	133	2.21	147	136
2.64	266	157	2.38	194	148
2.5	214	165	2.61	259	168
3.28	546	225	2.19	142	135
2.45	202	156.8	1.92	73.5	104
2.87	376	190	2.4	198	148
2.15	116	117	2.53	242	163
3.9	857	290	2.23	153	132
2.37	196	148	2.04	100	115
2.04	101.6	121.9	2.67	283	169
2.02	74.5	111	2.44	204	154
2.02	84	111	1.99	85.6	115
3.03	423	213	2.03	81.2	112

Gage Height (ft)	Q (ft3/s)	Area (ft2)	Gage Height (ft)	Q (ft3/s)	Area (ft2)
3.01	438	213	3.52	678	263
3.39	620	245	2.59	271	170
3.74	788	285	2.52	291	185
2.25	159	133	4.17	1080	385
2.57	254	171	2.12	137	138
1.99	76.3	109	2.36	195	168
2.82	335	190	2.42	155	174
3.15	469	214	1.77	51.9	106
3.02	435	212	1.68	45.3	54
2.56	242	164	1.62	53.8	91.8
6.28	2590	629	2.8	363	214
2.72	318	189	2.57	312	206
2.51	280	179	1.71	79.3	109.8
3.56	733	300	1.54	38.7	117
2.93	453	232	1.76	37.5	65.8
2.64	338	200	1.96	77.5	91.4
2.14	174	143	3.46	658	280
1.96	131	133	2.1	165	137.7
2.04	146	137	3.42	683	281
1.74	90	109	3.15	543	253
1.71	80	103	2.56	302	186
2.11	166	141	2.48	293	180
4.12	1040	397	2.77	389	209
4.42	1260	418	2.9	451	225
3.67	869	314	3.5	730	293
2.05	153	140	3.08	527	246
1.75	79.7	108	2.73	391	200
1.82	93	116	2	150	125
1.7	69	66.6	1.8	84.1	101
1.69	67.5	127	2.72	371	204
2.15	170	149	2.77	399	203
3.22	584	265	2.23	213	157
1.9	105	120	2.94	476	229
1.83	62	84.5	2.14	193	148
1.8	33.6	62.2	2.01	142	131
1.99	58.5	75	2.02	138	129
2.07	164	141	9.17	5280	1050
2.73	387	224	2.57	331	177
2.85	414	221	2.12	171	141
2.66	366	206	2.76	409	207
2.59	312	196	2.35	251	157
1.92	117	127	1.72	82.1	97.9
1.94	114	125	3.38	629	270
2.5	271	183	3.05	528	237
1.89	104	119	2.3	240	155
1.93	121	122.4	2.06	87.2	126
4.22	1210	404	1.82	57.9	103
2.37	255	157	1.8	79	138
1.96	115	114	3.28	567	248
3.24	589	255	1.71	54.8	94.2
2.34	243	157	1.9	62.2	111
1.96	128	118	2.08	153	126

USGS 01625000 Middle River near Grottoes, VA

Gage Height (ft)	Q (ft3/s)	Area (ft2)	Gage Height (ft)	Q (ft3/s)	Area (ft2)
6.62	3020	678	1.97	70.1	110
6.33	2490	598	2.28	168	164
6.53	2520	646	2.98	414	211
1.96	63.9	123	2.56	270	164
2.05	79.3	113	2	103	125
1.92	78.4	91	1.75	44.3	79.7
2.09	94.6	121	1.82	57	109
2.77	322	187	1.93	69.9	119
3.46	663	258	2.15	128	158
1.92	65.3	109	4.12	1000	364
1.86	48.6	91.6	3.68	779	333
2.08	100	127	2.32	187	137
3.56	721	271	1.9	71.1	102
2.65	272	170	2.43	211	155
3.53	682	248	3.97	892	362
4.16	1080	364	3.43	601	238
2.4	182	140	2.72	302	182
2.24	128	135	2.6	267	170
2.25	128	136	2.35	197	154
2.32	169	139	2.22	147	135
3.18	492	254	1.9	68.1	104
3.95	904	340	1.97	80.7	109
3.45	616	250	2.29	166	145
2.24	134	131	2.88	388	195
1.92	57.5	109	4.38	1180	392
1.95	64.3	101	2.55	261	168
2.68	271	176	2.35	188	143
2.71	306	184	2	94.7	110
3.67	721	309	1.91	74.1	95.6
2.14	121	144	1.91	66.9	101
2.35	172	139	2.35	189	146
2.09	118	133	2.21	147	136
2.14	101	133	2.38	194	148
2.64	266	157	2.61	259	168
2.5	214	165	2.19	142	135
3.28	546	225	1.92	73.5	104
2.45	202	156.8	2.4	198	148
2.87	376	190	2.53	242	163
2.15	116	117	3.9	857	290
2.7	317	188	2.37	196	148
3.03	423	213	2.04	101.6	121.9
3.01	438	213	2.02	74.5	111
3.39	620	245	2.02	84	111
2.23	153	132	1.99	85.6	115
2.04	100	115	2.03	81.2	112
2.67	283	169	3.52	678	263
2.44	204	154	2.59	271	170
2.57	254	171	3.74	788	285
1.99	76.3	109	2.25	159	133

Gage Height (ft)	Q (ft3/s)	Area (ft2)	Gage Height (ft)	Q (ft3/s)	Area (ft2)
2.82	335	190	4.17	1080	385
3.15	469	214	2.12	137	138
3.02	435	212	2.36	195	168
2.56	242	164	2.42	155	174
6.28	2590	629	1.77	51.9	106
2.72	318	189	1.68	45.3	54
2.51	280	179	1.62	53.8	91.8
3.56	733	300	2.8	363	214
2.93	453	232	2.57	312	206
2.64	338	200	1.71	79.3	109.8
2.14	174	143	1.54	38.7	117
1.96	131	133	1.76	37.5	65.8
2.04	146	137	1.96	77.5	91.4
1.74	90	109	3.46	658	280
1.71	80	103	2.1	165	137.7
2.11	166	141	3.42	683	281
4.12	1040	397	3.15	543	253
4.42	1260	418	2.56	302	186
3.67	869	314	2.48	293	180
2.05	153	140	2.77	389	209
1.75	79.7	108	2.9	451	225
1.82	93	116	3.5	730	293
1.7	69	66.6	3.08	527	246
1.69	67.5	127	2.73	391	200
2.15	170	149	2	150	125
3.22	584	265	1.8	84.1	101
1.9	105	120	2.72	371	204
1.83	62	84.5	2.77	399	203
1.8	33.6	62.2	2.23	213	157
1.99	58.5	75	2.94	476	229
2.07	164	141	2.14	193	148
2.73	387	224	2.01	142	131
2.85	414	221	2.02	138	129
2.66	366	206	9.17	5280	1050
2.59	312	196	2.57	331	177
1.92	117	127	2.06	87.2	126
1.94	114	125	1.82	57.9	103
2.5	271	183	1.8	79	138
1.89	104	119	3.28	567	248
1.93	121	122.4	3.24	589	255
2.52	291	185	2.34	243	157
2.12	171	141	1.96	128	118
2.76	409	207	1.71	54.8	94.2
2.35	251	157	1.9	62.2	111
1.72	82.1	97.9	2.08	153	126
3.38	629	270	4.22	1210	404
3.05	528	237	2.37	255	157
2.3	240	155	1.96	115	114

Appendix C

Model Equations and Initial Values

The Streamflow Sector

The North River Streamflow sector

N1 (t) = N1 (t-dt) + (Interflow_N1 + Surfaceflow_N1 + Baseflow N1 – Discharge_N1) dt
Initial N1 = 18201651
Interflow_N1 = (N1_watershed/Through_soil_traveling_time_N1)*(1- Fractional_traveling_on_surface_N1)
Surfaceflow_N1 = Graph ((N1_watershed/Surface_avg_transit_time_N1)*Fractional_traveling_on_surface_N1)
Baseflow_N1 = Baseflow_cfh_N1
Discharge_N1 = Streamflow_N1
N1_watershed (t) = N1_watershed (t- dt) + (Precipitation_rate_N1 – Interflow_N1 – Surfaceflow_N1)* dt
Initial N1_watershed = 0
Precipitation_rate_N1 = Precipitation_volume * (1- Evapotranspiration) * Watershed_area_N1

N2 (t) = N1 (t-dt) + (Interflow_N2 + Surfaceflow_N2 + Discharge_N1 – Discharge_N2) dt
Initial N2 = 8193071
Interflow_N2 = (N2_watershed/Through_soil_traveling_time_N2)*(1- Fractional_traveling_on_surface_N2)
Surfaceflow_N2 = (N2_watershed/Surface_avg_transit_time_N2)*Fractional_traveling_on_surface_N2)
Discharge_N2 = Streamflow_N2
N2_watershed (t) = N2_watershed (t- dt) + (Precipitation_rate_N2 – Interflow_N2 – Surfaceflow_N2)* dt
Initial N2_watershed = 0
Precipitation_rate_N2 = Precipitation_volume * (1- Evapotranspiration) * Watershed_area_N2
Baseflow_cfh_N1 = Baseflow_cfs_N1*3600
Baseflow_cfs_N1 = 90
Evapotranspiration = 0.88
Precititation_volume = Precipitation_measurement_North_River * 0.083* Rain_Even_North_River
Rain_Even_North_River = 0
River_length_ft_N1 = River_milage_N1* 5280
River_length_ft_N2 = River_milage_N2* 5280
River_milage_N1 = 31.28
River_milage_N1 = 14.08
Square_mile_N1 = 177.24

Square_mile_N2 = 46.86
Streamflow_N1 = (N1/13.777*River_length_ft_N1))^(1/0.4621)*3600
Streamflow_N2 = (N2/13.777*River_length_ft_N2))^(1/0.4621)*3600
Through_soil_teaveling_time = 45
Watershed_area_N1 = sq_mile_N1* 27878400
Watershed_area_N2 = sq_mile_N2* 27878400
Fractional_traveling_on_surface_N1 = GRAPH (N1_watershed)
(0.00, 0.008), (30000, 0.008), (60000, 0.008), (90000, 0.008), (120000, 0.008), (150000, 0.011), (180000, 0.016), (210000, 0.022), (240000, 0.04), (270000, 0.066), (300000, 0.097)
Fractional_traveling_on_surface_N2 = GRAPH (N2_watershed)
(0.00, 0.008), (30000, 0.008), (60000, 0.008), (90000, 0.008), (120000, 0.008), (150000, 0.011), (180000, 0.016), (210000, 0.022), (240000, 0.04), (270000, 0.066), (300000, 0.097)
Surface_avg_transit_time_N1 = GRAPH (N1_watershed)
(0.00, 12.7), (2e+009, 12.7), (4e+009, 12.7), (6e+009, 12.5), (8e+009, 12.0), (1e+010, 11.3), (1.2e+010, 10.5), (1.4e+010, 9.30), (1.6e+010, 7.63), (1.8e+010, 5.27), (2e+010, 0.763)
Surface_avg_transit_time_N2 = GRAPH (N2_watershed)
(0.00, 12.7), (2e+009, 12.7), (4e+009, 12.7), (6e+009, 12.5), (8e+009, 12.0), (1e+010, 11.3), (1.2e+010, 10.5), (1.4e+010, 9.30), (1.6e+010, 7.63), (1.8e+010, 5.27), (2e+010, 0.763)

The Middle River Streamflow sector

M1 (t) = M1 (t-dt) + (Interflow_M1 + Surfaceflow_N1 + Baseflow M1 – Discharge_M1) dt
Initial M1 = 26480335
Interflow_M1 = (M1_watershed/Through_soil_traveling_time_M1)*(1- Fractional_traveling_on_surface_M1)
Surfaceflow_M1 = (M1_watershed/Surface_avg_transit_time_M1)*Fractional_traveling_on_surface_M1
Baseflow_M1 = Baseflow_cfh_M1
Discharge_M1 = Streamflow_M1
M1_watershed (t) = M1_watershed (t- dt) + (Precipitation_rate_M1 – Interflow_M1 – Surfaceflow_N1)* dt
Initial M1_watershed = 0
Precipitation_rate_M1 = Precipitation_volume * (1- Evapotranspiration) * Watershed_area_M1

M2 (t) = M1 (t-dt) + (Interflow_M2 + Surfaceflow_M2 + Discharge_M1 – Discharge_M2) dt
Initial M2 = 743579
Interflow_M2 = (M2_watershed/Through_soil_traveling_time_M2)*(1- Fractional_traveling_on_surface_M2)

Surfaceflow_M2 = (M2_watershed/Surface_avg_transit_time_M2)*Fractional_traveling_on_surface_M2)
Discharge_M2 = Streamflow_M2
M2_watershed (t) = M2_watershed (t- dt) + (Precipitation_rate_M2 – Interflow_M2 – Surfaceflow_M2)* dt
Initial M2_watershed = 0
Precipitation_rate_M2 = Precipitation_volume * (1- Evapotranspiration) * Watershed_area_M2
Baseflow_cfh_M1 = Baseflow_cfs_M1*3600
Baseflow_cfs_M1 = 70
Evapotranspiration = 0.88
Precititation_volume = Precipitation_measurement_North_River * 0.083* Rain_Even_Middle_River
Rain_Even_Middle_River = 0
River_length_ft_M1 = River_milage_N1* 5280
River_length_ft_M2 = River_milage_N2* 5280
River_milage_M1 = 65.17
River_milage_N1 = 1.83
Square_mile_N1 = 373
Square_mile_N2 = 1.56
Streamflow_M1 = (M1/7.62*River_length_ft_M1))^(1/0.5443)*3600
Streamflow_M2 = (M2/7.62*River_length_ft_M2))^(1/0.5443)*3600
Through_soil_teaveling_time = 45
Watershed_area_M1 = sq_mile_N1* 27878400
Watershed_area_M2 = sq_mile_N2* 27878400
Fractional_traveling_on_surface_M1 = GRAPH (M1_watershed)
(0.00, 0.008), (30000, 0.008), (60000, 0.008), (90000, 0.008), (120000, 0.008), (150000, 0.011), (180000, 0.016), (210000, 0.022), (240000, 0.04), (270000, 0.066), (300000, 0.097)
Fractional_traveling_on_surface_M2 = GRAPH (M2_watershed)
(0.00, 0.008), (30000, 0.008), (60000, 0.008), (90000, 0.008), (120000, 0.008), (150000, 0.011), (180000, 0.016), (210000, 0.022), (240000, 0.04), (270000, 0.066), (300000, 0.097)
Surface_avg_transit_time_M1 = GRAPH (M1_watershed)
(0.00, 12.7), (2e+009, 12.7), (4e+009, 12.7), (6e+009, 12.5), (8e+009, 12.0), (1e+010, 11.3), (1.2e+010, 10.5), (1.4e+010, 9.30), (1.6e+010, 7.63), (1.8e+010, 5.27), (2e+010, 0.763)
Surface_avg_transit_time_M2 = GRAPH (M2_watershed)
(0.00, 12.7), (2e+009, 12.7), (4e+009, 12.7), (6e+009, 12.5), (8e+009, 12.0), (1e+010, 11.3), (1.2e+010, 10.5), (1.4e+010, 9.30), (1.6e+010, 7.63), (1.8e+010, 5.27), (2e+010, 0.763)

NM (t) = NM (t-dt) + (Discharge_M2 + Discharge_N2 – To_SFS) dt

The Triclosan Sector

Triclosan_1 (t) = Triclosan_1 (t-dt) + (HRSA_discharge_rate – Traveling_rate1 – decay_rate1) * dt
Initial Triclosan_1 = 1553
HRSA_discharge_rate = HRSA_discharge + Triclosan_surge
Traveling_rate1 = Triclosan_1*(1/Traveling_time1)
Decay_rate1 = Triclosan_1*Decay constant

Triclosan_2 (t) = Triclosan_2 (t-dt) + (Traveling_rate1 – Traveling_rate2 - decay_rate2) * dt
Initial Triclosan_2 = 11586
Traveling_rate2 = Triclosan_2*(1/Traveling_time2)
Decay_rate2 = Triclosan_2*Decay constant

Triclosan_3 (t) = Triclosan_3 (t-dt) + (Traveling-rate 2 + Weyers_Cave_discharge_rate – Traveling_rate3 – decay_rate3) *dt
Initial Triclosan_1 = 10901
Weyers_discharge_rate = Weyers_discharge
Traveling_rate3 = Triclosan_3*(1/Traveling_time3)
Decay_rate3 = Triclosan_3*Decay constant

Triclosan_4 (t) = Triclosan_4 (t-dt) + (Middle River Regional_discharge_rate – Traveling_rate4 – decay_rate4)* dt
Initial Triclosan_4 = 18861
MRR_discharge_rate = MRR_discharge + Triclosan_spike
Traveling_rate4 = Triclosan_4*(1/Traveling_time4)
Decay_rate4 = Triclosan_4*Decay constant

Triclosan_5 (t) = Triclosan_5 (t-dt) + (Traveling_rate4 – Traveling_rate5 - decay_rate5) * dt
Initial Triclosan_5 = 1364
Traveling_rate5 = Triclosan_5*(1/Traveling_time2)
Decay_rate5 = Triclosan_5*Decay constant

Triclosan_6 (t) = Triclosan_6 (t-dt) + (Traveling_rate3 – Traveling_rate5 – to_SF) * dt
To_SF = Traveling_rate_3 + Traveling_rate5
Decay constant = 0.0026
HRSA_discharge = Received_triclosan_HRSA* (1-Removal_efficiency_HRSA)
MRR_discharge = Received_triclosan_MRR* (1-Removal_efficiency_MRR)
Weyers_Cave_discharge = Received_triclosan_WC * (1-Removal_efficiency_WC)
Population_HRSA = 77906
Population_MRR = 42937
Population_WC = 587
Produced_triclosan_HRSA = Population_HRSA* Triclosan_usage_per_capita_per_day/24
Produced_triclosan_MRR = Population_MRR* Triclosan_usage_per_capita_per_day/24

Produced_triclosan_WC = Population_WC* Triclosan_usage_per_capita_per_day/24
Removal efficiency_HRSA = 0.93
Removal efficiency_MRR = 0.93
Removal efficiency_WC = 0.93
River_length_triclosan_1 = 0.93*5280
River_length_triclosan_2 = 7.17*5280
River_length_triclosan_3 = 6.91*5280
River_length_triclosan_4 = 25.12*5280
River_length_triclosan_5 = 1.83*5280
Traveling_time = River_length_triclosan/ velocity
Troclosan_spike = PULSE (1000, 500, 300)*Triclosan_surge_switch
Triclosan_surge = (Step(600,100)-step(600,150)) *Triclosan_surge_switch
Triclosan_surge_switch = 0
Triclosan_usage_per_capita_per_day = 4.11
Velocity1 = ((Streamflow_N1^(1-0.4621))* (3600^0.4621))/13.777
Velocity2 = ((Streamflow_N2^(1-0.4621))* (3600^0.4621))/13.777
Velocity4 = ((Streamflow_M1^(1-0.5443))* (3600^0.5443))/7.62
Velocity5 = ((Streamflow_M2^(1-0.5443))* (3600^0.5443))/7.62

The Triclosan Concentration Sector

Triclosan_concentration_segment_1 = (Triclosan_1*1000000)/ (N1*28.316*0.0297)
Triclosan_concentration_segment_2 = (Triclosan_2*1000000)/ (N2*28.316*0.5092)
Triclosan_concentration_segment_3 = (Triclosan_3*1000000)/ (N2*28.316*0.4908)
Triclosan_concentration_segment_4 = (Triclosan_4*1000000)/ (N1*28.316*0.3855)
Triclosan_concentration_segment_5 = (Triclosan_5*1000000)/ (N1*28.316)

References

Bennett, K. (2008).

Testimony for may 13, 2008 oversight hearing on

reports of pharmaceutical contamination in public water supplies. Retrieved April 30, 2009, from http://www.peer.org/docs/ma/08_12_5_ppcp_testimony.pdf

Bester, K. (2003). Triclosan in a sewage treatment process - balances and monitoring data. *Water Research*, *37*(16), 3891-3896.

Bester, K. (2005). Fate of triclosan and triclosan-methyl in sewage treatment plants and surface waters. *Archives of Environmental Contamination and Toxicology*, *49*(1), 9-17.

Canosa, P., Morales, S., Rodriguez, I., Rubi, E., Cela, R., & Gomez, M. (2005). Aquatic degradation of triclosan and formation of toxic chlorophenols in presence of low concentrations of free chlorine. *Analytical and Bioanalytical Chemistry*, *383*(7-8), 1119-1126. doi:10.1007/s00216-005-0116-4

Capdevielle, M., Van Egmond, R., Whelan, M., Versteeg, D., Hofmann-Kamensky, M., Inauen, J., Cunningham, V., & Woltering, D. (2008). Consideration of exposure and species sensitivity of triclosan in the freshwater environment. *Integrated Environmental Assessment and Management*, *4*(1), 15-23.

Daniel, W. (2007). ***Regional landscapes and the hydrologic cycle***. Retrieved October 01, 2009, from www.mawaterquality.org/publications/pubs/manmh/chapter2.ppt

Davie, T. (2008). *Fundamentals of hydrology* (2nd ed.) London ; New York : Routledge.

Dunne, T., & Leopold, L. (1995). *Water in environmental planning*. USA: W.H. Freeman.

Environmental Protection Agency. (2009). *Clean watersheds needs survey (CWNS) 2004.* Retrieved October 15, 2009, from http://cfpub.epa.gov/cwns04/rpt_ffs2_04.cfm?RequestTimeOut=180

Friends of the North Fork of the Shenandoah River. (2008). *Organic chemicals/ river health report*

Garman, G., & Orth, D. (2007). *Fish kills in the shenandoah river basin: Preliminary report of the shenandoah basin science team.* Retrieved August, 18, 2009, from http://www.deq.state.va.us/export/sites/default/info/documents/2007.02.23ScienceTeamReport.pdf

Glaser, A. (2004). The ubiquitous triclosan: A common antibacterial agent exposed. *Pesticides and You, 24*(3), 12-17.

Gordon, N. (2004). ***Stream hydrology : An introduction for ecologists*** (2nd ed.) Chichester, West Sussex, England ; Hoboken, N.J.

Grumbles, B. (2008). *Testimony of benjamin H. grumbles.* Retrieved March 20, 2009, from http://transportation.house.gov/Media/File/water/20080918/EPA%20Testimony.pdf

Hack, J. (1957). *Studies of longitudinal stream profiles in virginia and maryland* No. 294B)U.S. Geology of Survey.

Jagger, A. (2008). Antibacterial debate. *ICIS Chemical Business, 273*, 24-27.

Kallaos, J., Wheeler, K., Wong, C. & Zahller, M. (2007). *Pharmaceuticals in wastewater streams: Disposal practices and policy options in santa barbara.* Retrieved November 20, 2008, from http://www.bren.ucsb.edu/research/documents/PharmaceuticalsFinalReport.pdf

Kantiani, L., Farré, M., Asperger, D., Rubio, F., González, S., López de Alda, M. J., Petrović, M., Shelver, W. L., & Barceló, D. (2008). Triclosan and methyl-triclosan monitoring study in the northeast of spain using a magnetic particle enzyme immunoassay and confirmatory analysis by gas chromatography-mass spectrometry. *Journal of Hydrology, 361*(1-2), 1-9.

Kraft, M. E. (1995). In Wiefman L. (Ed.), *Environmental policy and politics*. New York: HarperCollins.

Larson, E., Lin, S., Gomez-Pichardo, C., & Della-Latta, P. (2004). Effect of antibacterial home cleaning and handwashing products on infectious disease symptoms. *Annals of Internal Medicine, 140*(5), 321-330.

Li, N. (2008). *Advanced membrance technology and applications* Retrieved from http://books.google.com/books?id=HZpgKZtxrqwC&dq=membrane+bioreactor+installation+cost&source=gbs_navlinks_s

Liu, D. (2005). *Expert panel refutes anibacterial soap claims.* Retrieved April 13, 2009, from http://www.ewg.org/node/17961

Luellen, D. (2009). *Shenandoah river basin fish kills: Refinement of a chemical contaminant profile*

McAvoy, D. C., Schatowitz, B., Jacob, M., Hauk, A., & Eckhoff, W. S. (2002). Measurement of triclosan in wastewater treatment systems. *Environmental Toxicology and Chemistry, 21*(7), 1323-1329.

Mizel, N., Papadakis, M., Degner, K., Shepard, K., & Havinga, M. (2008). *South fork shenandoah rapid watershed assessment*

Morrall, D., McAvoy, D., Schatowitz, B., Inauen, J., Jacob, M., Hauk, A., & Eckhoff, W. (2004). A field study of triclosan loss rates in river water (cibolo creek, TX). *Chemosphere, 54*(5), 653-660.

Noble, J. (2006). GE ZeeWeed MBR technology for pharmaceutical wastewater treatment. *Membrane Technology,* (9), 7-9.

Ramirez, A. J., Mottaleb, M. A., Brooks, B. W., & Chambliss, C. K. (2007). Analysis of pharmaceuticals in fish using liquid chromatography-tandem mass spectrometry. *Analytical Chemistry, 79*(8), 3155-3163.

Sterman, J. (2000). *Business dynamics: Systems thinking and modeling for a complex world* . Lexington MA.: McGraw-Hill.

Virginia Department of Environmental Quality. (2007). *Chesapeake bay program.* Retrieved August, 2009, from www.deq.state.va.us/bay/wqif/Staunton.html

Virginia Department of Environmental Quality. (2009). *DEQ geographical environmental information system.* Retrieved August 01, 2009, from http://gisweb.deq.virginia.gov/deqims/viewer.htm?SERVICE=VA_DEQ

Winkler, G., Fischer, R., Krebs, P., Thompson, A., Cartmell, E., & Griffin, P. (2007). Mass flow balances of triclosan in rural wastewater treatment plants and the impact of biomass parameters on the removal. *Engineering in Life Sciences, 7*(1), 42-51.

Ying, G. -., & Kookana, R. S. (2007). Triclosan in wastewaters and biosolids from australian wastewater treatment plants. *Environment International, 33*(2), 199-205.