Modeling the Transportation of Select Trace Organic Contaminants from Source to Ecosystem in the Grand River

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners. I understand that my thesis may be made electronically available to the public.

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Abstract

Trace organic contaminants (TOrC) have been observed in waters downstream of wastewater treatment plants (WWTP) in the Grand River in southern Ontario, Canada. These contaminants have been correlated with adverse impacts on aquatic ecosystem health. This study aimed to create a unified modeling framework for predicting the generation, transportation, and fate of select TOrCs. The TOrCs selected for this study were carbamazepine, naproxen, triclosan, and venlafaxine. These contaminants were chosen based on their degradation properties and on the availability of measured concentration data in WWTPs and in the Grand River. The model was set to extend from Waterloo to Ohsweken and to include the impacts of the Waterloo WWTP and the Kitchener WWTP.

Modeling of TOrCs took place across three model compartments, which were combined into one source-to-fate model. TOrC generation in the urban sewage system was estimated using a population-based consumption-excretion model. Removal of TOrCs in WWTPs was simulated using conventional steady-state WWTP modeling equations with the sorption and biodegradation TOrC removal mechanisms included. Biodegradation of TOrCs in WWTPs was split into two components: heterotrophic biodegradation by ordinary heterotrophic organisms, and autotrophic biodegradation by ammonia oxidizing bacteria. This approach allowed for the model to account for expected differences in TOrC concentrations in WWTP effluent as a result of nitrification processes. Transportation of TOrCs in the Grand River was modeled hydraulicly using WASP 8.0, with the removal mechanisms of biodegradation and photolysis.

The model was run for two time periods: one preceding the implementation of nitrifying upgrades to the Waterloo and Kitchener WWTPs, and one after. Model results were compared with observed TOrC concentration data at WWTP outfalls and at select points downstream in the Grand River. Predicted concentrations of TOrCs near Ohsweken were found to be the most sensitive to autotrophic biodegradation rates in the WWTPs, suggesting that particular attention be paid to modeling this removal

mechanism. The model was found to predict some contaminants at concentrations close to observed values, but not others, indicating that further refinement is needed. Removal of TOrCs in the river due to natural processes was particularly under-estimated. More frequent measurements of TOrC concentrations in the Grand River and in WWTPs would allow for a better calibration of the model.

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This study was a collaborative effort, and would not have been possible without the help of many people from a variety of backgrounds. I was very fortunate to have the supervision of Professors Wayne Parker and Mark Servos, who offered me their expertise from their backgrounds in wastewater engineering and aquatic biology.

Much of my work was built directly upon that of Maricor Arlos, who was incredibly helpful to me starting out this study and providing me with the resources and connections I needed to carry on this work. I owe most of the source model portion of the study to the work done by Bill McLaren, who in his time as a co-op student was able to compile all the consumption, excretion, and population data I needed and more.

I would like to thank Nasim Hosseini for all her help in creating, calibrating, and validating the WASP 8.0 hydraulic model used in this study. Her experience was invaluable in making this model come to life, and here guidance in automated calibration and analysis methods using OSTRICH was critical to my ability to complete my study.

I would like to express my gratitude for all those who worked to provide data for my models. A model is only as good as its data, and this modeling project was very data-hungry. I want to thank Leslie Bragg, along with all the graduate students and technicians of the Servos Group laboratory for gathering and processing the contaminant concentration data that drove this project. I would also like to thank Dominika Celmer-Repin and Jose Bicudo from the Region of Waterloo for providing me with the data I needed to run my wastewater treatment plant simulations, and the Grand River Conservation Authority for providing the data used to make the river simulations.

Finally, I want to thank my family and friends for supporting me through this process, with special thanks to my father who gave up his comfortable home office so that I could work from home during COVID.

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1. Introduction

One of the many ways human activity impacts the natural environment is through the wastewater we discharge to surface waters. The pollutants in untreated wastewater are mostly human excrement but can contain many other chemical products of human activity. Pharmaceutical substances, recreational drugs, and various artificial chemicals can increasingly be found in human wastewater. These substances are of concern because traditional wastewater treatment processes are not designed to remove them. As pollutants, these contaminants can collectively be known as Trace Organic Contaminants (TOrCs). While some TOrCs have been found to experience rapid removal in wastewater treatment plants (WWTPs), others have been observed in relatively high concentrations downstream of treatment facilities (Miao et al., 2005; Ternes, 1998). In some cases, such as in the Grand River, these measurements have been found to coincide with adverse ecological impacts (M.J. Arlos et al., 2015).

1.1. Background

A variety of TOrCs are increasingly present in human wastewater, including substances such as painkillers, antidepressants, and birth control hormones, among others. These are substances which are organic in nature and which are typically present at very low concentrations. An example of a TOrC would be triclosan, an antimicrobial agent that is commonly used in household personal care products (Dhillon et al., 2015).

When tested for, TOrCs are commonly found in surface waters downstream of WWTPs. A study in Germany examined medicinal drug residues in the effluents of 49 different treatment plants, finding that over 80% of the drugs tested for survived treatment processes (Ternes, 1998). Other studies have consistently found that conventional aerobic bioreactor technology fails to remove all TOrCs present in WWTP influent (Miao et al., 2005; Skees et al., 2018; Zhang et al., 2008). These contaminants may then travel downstream and have an impact on local aquatic ecosystems (M.J. Arlos et al., 2015).

According to a 2019 report by the government of Canada, many TOrCs have been measured throughout the Great Lakes, after originating from municipal WWTPs. The report found that a variety of pain killers, hormones, endocrine disruptors, antibiotics, and psychiatric drugs had become persistent in the ecosystem. While most of these contaminants were not found to be present in high enough concentrations to cause risks to human health or the environment, exceptions commonly exist downstream of WWTPs and in areas of high-density population or agriculture. These high-risk areas coincided with impacts on the mortality and reproductive abilities of aquatic wildlife (Environment and Climate Change Canada, 2019).

While TOrCs in surface waters are not currently thought to pose serious risks to human health (Cunningham et al., 2010; Khan & Nicell, 2015; Lienert et al., 2007), the ecological impacts are more direct. The Grand River ecosystem has a history of being impacted by TOrCs, and impacts seem to have been reduced drastically by improvements to the Kitchener and Waterloo wastewater treatment plants. In 2010, prior to the upgrades to the Kitchener WWTP, the stretch of the Grand River from Waterloo to Brantford was observed to be heavily ecologically impacted and to contain relatively high levels of many emerging contaminants. More recently, since the nitrifying upgrades to both the Waterloo and Kitchener WWTPs, concentrations of TOrCs were found to be much lower. This coincided with a rebound in ecological diversity, indicating a possible link between TOrCs and adverse ecosystem impacts (M.J. Arlos et al., 2015).

Fortunately, TOrC measurement data in the Grand River exists for before, during, and after the WWTP upgrades. Using this data, we can better inform an understanding of how these contaminants are transported and removed through WWTP and natural ecosystem processes. Hosseini (2011) and Arlos (2015; 2018) have used models to study the transportation of TOrCs from source to fate in the Kitchener-Waterloo area, and modeling techniques exist which can predict the behavior of TOrCs in WWTPs and in river ecosystems. This presents an opportunity to assemble a comprehensive, source-to-fate framework for linking emerging contaminant use to adverse ecosystem impacts.

1.2. Goal

The purpose of this study is to establish a unified modeling approach for predicting the transportation of TOrCs through wastewater, from their generation in human waste to their fate in the ecosystem. This includes modeling the mechanisms by which TOrCs may be transformed or removed in both wastewater treatment processes and natural ecosystem processes, as well as predicting the source loadings of TOrCs from human populations into the wastewater system.

1.3. Objectives

- Building upon the work of Arlos et. al. (2015), this study aimed to: Integrate a model for calculating removal of TOrCs in WWTPs into a source, wastewater treatment, river transport simulator s.
- Expand the geographic scope of the river model to account for impacts of TOrC loadings on downstream communities.
- Develop a framework of scripts, files, and databases linking the above models together to facilitate automation.

1.4. Scope

The target area for this model is Grand River in southwest Ontario, Canada. Specifically, this study aims to model the TOrC loading of the Kitchener-Waterloo municipal area and the transportation of these contaminants through the Grand River as far downstream as Ohsweken. For this study, only TOrC loadings from the Kitchener-Waterloo municipal area are considered. Contaminant contributions from upstream or from tributaries to the Grand River are neglected.

Four TOrC species (triclosan (TRC), carbamazepine (CBZ), naproxen (NAP), and venlafaxine (VEN)) were selected for modeling. These species were chosen due to a combination of data availability and anticipated transformation mechanisms, which is elaborated on further in section 2.

2. Literature Review

2.1. Estimation of Pharmaceutical Loadings in Sewage

Human excretions typically represent the major input of pharmaceuticals to sewersheds, and hence prior studies that have estimated loadings based upon population metrics were examined to identify the best approaches for most closely approximate loadings. Population data is typically tracked by local governments, making it easy to use in modeling.

A population-based model of contaminant generation requires knowledge of the average per-capita excretion of compounds of interest. This is typically calculated using consumption data (i.e. how much of the population consumes the product) and metabolism data (i.e. how much they excrete). While metabolism rates are product-specific, consumption rates depend on the population in question. A consumption-metabolism model was employed by Grill et al. (2016) to model TOrC loading across the St. Lawrence basin in both Ontario and Quebec. In this study, consumption data was not available at the community scale, so a Canada-wide per-capita average was used. However, a study of analgesic drug use in eastern European nations found that consumption rates could vary greatly between populations, even among similar nations (Hudec et al., 2012). Arlos (2018) used a statistic-based approach to estimate contaminant loadings from a population in the Grand River watershed. The population was divided into sub-categories of people based upon anticipated discrepancies in consumption rates (i.e., university students vs. average residents for birth control pills). Hence, the literature implies that consumption-metabolism models of TOrC sources can, while simple, be useful if given appropriate data for the population.

2.2. Modeling of Pharmaceuticals in Wastewater Treatment

Wastewater treatment plants provide an opportunity to reduce the loading of pharmaceuticals into a watershed and hence prior models of pharmaceutical removal in wastewater treatment were reviewed. Empirical models have been reported by Arlos (2018) where the fractions of estrogen removed were

estimated from existing data and Grill et al. (2016) where pharmaceutical removals were based on WWTP type and population served. While relatively simple to implement, these models could not reflect the impact of operating conditions on pharmaceutical removal. The following sections review models that incorporate removal mechanisms.

2.2.1. Primary Settling

Primary settlers remove a portion of suspended particulate matter (and hence adsorbed pharmaceuticals) from wastewater. When designed and operated efficiently, primary sedimentation can remove 50 to 70 percent of suspended solids before a wastewater enters into a bioreactor (Metcalf & Eddy, 2014). This removal rate is commonly estimated in conventional WWTP operations using an empirical curve, as shown in Figure 1.

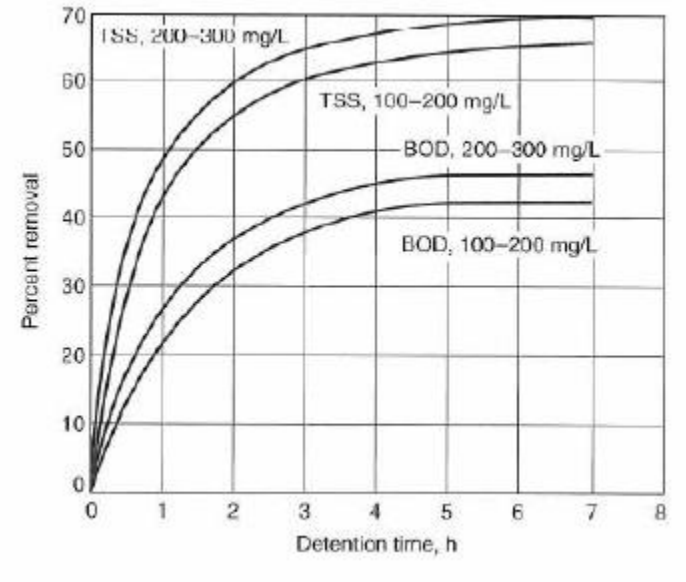

Figure 1: Expected removal of suspended solids through primary settling (Metcalf & Eddy, 2014)

When a fraction of suspended solids is removed from wastewater, it can be assumed that the fraction of contaminants adsorbed onto those solids will be carried with it.

Sorption of TOrCs has been estimated previously by studies attempting to model TOrC behavior in WWTPs (Baalbaki et al., 2017; Inyang et al., 2016; Lakshminarasimman et al., 2018). These studies make use of the sorption distribution coefficient to estimate steady-state sorption according to Equation 1:

$$K_d = \frac{C_s}{C_w} \quad (1)$$

in which K_d is the sorption distribution coefficient and C_s and C_w are the sorped and aqueous concentrations, respectively. The values of sorption distribution coefficients for many TOrCs have been measured or estimated (ChemAxon, 2014; Stevens-Garmon et al., 2011; Salveson, 2013). By combining sorption distribution knowledge of TOrCs with conventional modeling approaches to primary sedimentation, it is possible to predict the removal of TOrCs between raw WWTP influent and treatment bioreactors.

2.2.2. Secondary Treatment

Secondary treatment removes organic and inorganic (ammonia) through microbially mediated processes and through wastage of the sludge generated. Pharmaceuticals may be removed through either of these pathways and hence models that address these mechanisms were separately reviewed.

The biotransformation mechanism describes the removal of TOrCs from solution due to consumption by organic metabolism. This is the removal mechanism for which a bioreactor is designed. Much of WWTPs biological treatment takes place under aerobic conditions, in which the dominant microorganisms are ordinary heterotrophic organisms (OHO). This type of organism is responsible for the consumption of organic carbon in wastewater. Other environmental conditions include anoxic (in which the reactor is unaerated, but may contain nitrate) and anaerobic (in which negligible dissolved oxygen is present). Other types of organism present in bioreactors include ammonia oxidizing bacteria (AOB), which consume ammonia as substrate, and phosphate accumulating organisms (PAO), which accumulate phosphate (Metcalf & Eddy, 2014).

TOrC concentrations in bioreactor effluent show that TOrCs experience biotransformation to various degrees. Servos et al. (2015) found vastly different levels of contamination downstream of a WWTP before and after upgrades to the plant which increased the level of AOBs in the bioreactor. Multiple studies have examined at the rates of removal of TOrCs under aerobic, anaerobic, and/or anoxic conditions (Inyang et al., 2016; Lakshminarasimman et al., 2018; O. O. Ogunlaja & Parker, 2015; Treguer et al., 2011). In these situations, TOrC biotransformation is typically considered specific to the conditions of the reactive zone, rather than by the of microorganism populations present. For example, Baalbaki et al (2017) aggregates OHO, AOB, and PAO into a total active biomass concentration, which is then used to calculate both aerobic and anoxic biotransformation. Ogunlaja (2018) was able to take this a step further by quantifying the removal of a select TOrC (trimethoprim) by different bacterial populations. The study found that TOrC removal could be described by first-order biotransformation, with AOB having the highest rate of biotransformation and PAO having the lowest.

There are multiple ways to mathematically model the biodegradation mechanism. A standard method is using Monod kinetics, in which the rate of substrate consumption is approximately first-order at low substrate concentrations and approaches zero-order behavior at high concentrations (Metcalf & Eddy, 2014). This relationship can be seen in Figure 2 below.

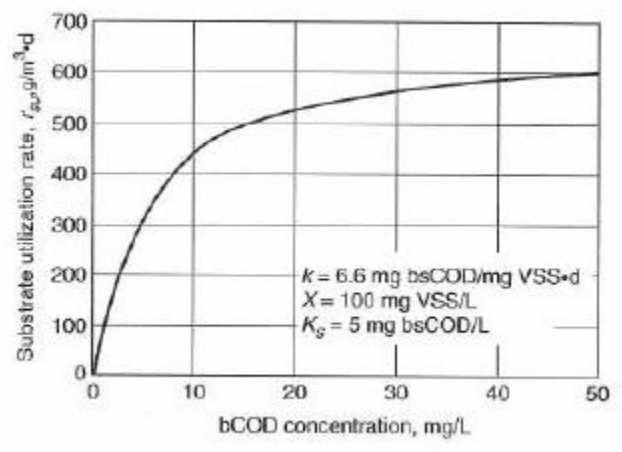

Figure 2: Relationship between substrate biotransformation rate and substrate concentration according to Monod kinetics (Metcalf & Eddy, 2014).

Monod kinetics are typically applied to common measures of substrates such as biochemical oxygen demand (bCOD). While this kinetic relationship may be appropriate for much of the waste in wastewater, TOrC concentrations are often very low in comparison to conventional substrates. Thus, it might be expected that the relationship between TOrC biotransformation rate and TOrC concentration be linear (i.e. a first order mechanism). Indeed, this expectation is supported by observations (Delli Compagni et al., 2020; Olumuyiwa O. Ogunlaja & Parker, 2018). This leads to a biotransformation mechanism described by Equation 2

$$r_{het} = k_{het} X_{het} C \quad \text{2.a}$$

$$r_{aut} = k_{aut} X_{aut} C \quad \text{2.b}$$

in which $r_{het/aut}$ is the rate of TOrC biotransformation, X is the concentration of a type of biomass (heterotrophic or autotrophic), C is the concentration of TOrC, and $k_{het/aut}$ is the specific biotransformation rate constant for that TOrC and biomass type. This equation was used by Baalbaki et al (2016) and it was found that biotransformation of TOrCs by both OHOs and AOBs could be driving factors in TOrC removal.

Besides biotransformation, the other noteworthy mechanism for TOrC removal in secondary treatment is sorption. Secondary clarifiers, located downstream of the bioreactor, separate out sludge with higher levels of suspended solids for diversion to sludge treatment (known as "wasting" flow) or for recycle back into the bioreactor. The wasting flow represents another avenue for the removal of TOrCs. The wasting flow rate and suspended solids concentration may be calculated using models of secondary clarification and recycle rates but, in the case of this study, were provided by the WWTPs being studied. Knowing this, the amount of TOrCs exiting the system due to secondary settling can be estimated in a manner similar to that described for primary settling, using Equation 1.

2.3. Modeling of Pharmaceuticals in Watersheds

The concentrations of pharmaceuticals within rivers are influenced by physical transport and by physical, chemical and biological fate mechanisms. Hence, models that integrated these processes to describe fate

and transport in rivers were reviewed. In this section, the model structures that have been employed to describe each of the processes are reviewed. Subsequently, aspects of applying the models to riversheds are discussed.

2.3.1. Flow and Transport

Flow models describe the movement of water within a system. Surface water systems can be modeled using either hydraulic or hydrologic methods (Fread, 1993). Hydrologic modeling takes a mass-balance approach to flow routing, using rainfall and runoff data to calculate inflows, outflows, and storage of pre-defined segments of rivers in a watershed. This approach has been used for studies of TOrC transport at relatively large scales, such as southern Ontario and Quebc (Grill et al., 2016). Existing models for use at this scale include iSTREEM, PhATE, and GREAT-ER (Ferrer & Deleo, 2017; Grill et al., 2016; Hosseini, 2011). Hydraulic models, in contrast, take a physics-based approach to water flow. This entails using conservation of mass, energy, and momentum equations to determine not just the volume of water stored in a segment, but the dynamic surface profile as well (Fread, 1993). This added complexity allows the model to better account for spatial and temporal variability, and has been found to be more accurate than hydrologic modeling at predicting non-uniform flows in rivers (Fread, 1993). A common example of an hydraulic watershed model is HEC-RAS, which is used by the GRCA to model flows of the Grand River (GRCA, 2020).

Within an hydraulic model, transport mechanisms describe the movement of contaminants. These mechanisms include advection, dispersion, and diffusion. Advection is the longitudinal transport of contaminants within moving water. Dispersion refers to the mixing of contaminants due to varying velocity within a water column. Diffusion is the molecular spreading-out of molecules from areas of high concentration to low concentration due to random movement. In moving water, diffusion is typically considered to be negligible. Advection-dispersion models have been used to effectively predict the transport of contaminants in river systems (Ji, 2008).

2.3.2. Biotransformation

Contaminants may be subject to biological transformation while in surface water systems. Similar to in a WWTP bioreactor, this is a result of microorganisms in the water consuming TOrCs as part of a metabolism. These processes can be highly complicated, varying with factors such as dissolved oxygen, pH, nutrient availability, algal growth, and light exposure, among others (Ji, 2008). Whole-ecosystem models such as AQUATOX have been used to predict the impacts of TOrCs on freshwater ecosystems (Clouzot & Vanrolleghem, 2019). However, when only the concentrations of TOrCs in the system are of immediate interest, it has been found to be more practical to assume first-order biodegradation similar to that employed in bioreactors. This approach was employed by Arlos (2015). When assuming a relatively static concentration of metabolizing biomass, this biodegradation takes the form of Equation 3:

$$r_{bio} = -k_{bio}C \quad (3)$$

where r_{bio} is the rate of biotransformation, C is the concentration of TOrC in the river, and k_{bio} is a biodegradation coefficient which can be obtained through calibration to measured data.

2.3.3. Phototransformation

Exposure to sunlight may induce chemical transformation of contaminants, known as phototransformation. This process can be either direct or indirect. Indirect phototransformation occurs when sunlight induces other agents in the water to react with the contaminant, rather than inducing the contaminant to degrade directly. This process can be modeled using a series of first order reactions in the form of Equation 3, in which the k is the first-order rate constant for a given contaminant and solar wavelength (Chapra, 1997). This degradation rate is then aggregated across the solar spectrum leading to the form of Equation 4:

$$r_{photo} = \sum -k_{wv}P_{wv}C \quad (4)$$

in which r_{photo} is the rate of phototransformation, C is the TOrC concentration, P_{wv} is the intensity of light in each waveband, and k_{wv} is a first-order rate constant for that waveband. This is the phototransformation mechanism equation used by WASP for ecotoxicology river modeling (US EPA, 2019).

2.3.4. Other Mechanisms

Other mechanisms may contribute to loss of TOrCs in river environments, but were not implemented in this study. Volatilization is the transformation of a substance from liquid to gaseous phase. The relationship between a dissolved contaminant and its gaseous pressure can be characterized using the Henry's law constant. Dynamic modeling of TOrC volatilization can be performed using Equation 5, provided all parameters are known for the TOrC (Chapra, 1997):

$$J = v\left(\frac{P}{H} - C\right) \quad 5$$

where J is mass flux volatilized, C is the concentration of TOrC in aqueous phase, P is the partial pressure in gaseous phase, H is the Henry's constant of the contaminant, and v is the net transfer velocity in air-water interface. The process of volatilization was neglected for the purposes of this study as most pharmaceuticals have relatively low Henry's Law coefficients.

Aqueous contaminants may be subject to hydrolysis or oxidation/reduction in water. These processes involve the degradation of the contaminant by hydrogen or oxygen in the water, and can be modeled using first order kinetics (Chapra, 1997). While not specifically addressed, these mechanisms can be accounted for indirectly within the biotransformation calculation, which similarly uses first-order kinetics.

As with in wastewater treatment, TOrCs in surface waters may be susceptible to removal by sorption. This occurs when an aqueous contaminant partitions onto suspended solids in the river, which then settle out of the water column. These contaminated sediments may then undergo re-suspension at a later time, leading to long-term impacts of contamination in rivers. While the partitioning of TOrCs between aqueous and sorped phases can be done using a simple partitioning coefficient, as expressed in Equation 1, modeling the removal of sorbed contaminants from surface water requires modeling the sediment behavior in the river (Chapra, 1997). This includes modeling suspended solids in the water column as well as settling and re-suspension with the sediment layer. These mechanisms were left out of this study due to constraints of time and data available.

2.3.5. Modeling Trace Organic Contaminants in the Grand River

The Grand River is the largest river in southern Ontario, with a watershed area of 7,000 square kilometres. It has received substantial attention from scientists looking to model water quality. In 2011, the spatial and temporal distribution of TOrCs in the Grand River were modeled using the PhATE program (Hosseini, 2011). This study took a hydrologic approach to modeling the Grand River watershed, and included a simplified estimation of population sources and WWTP removal of contaminants. The study looked to identify key areas where high concentrations of TOrCs were to be expected, and determined that the portion of the river at highest risk was that between the Kitchener and Waterloo treatment plants and the municipality of Brantford. Concentrations of TOrCs were predicted to occur at concentrations high enough to be harmful to aquatic species in the watershed (Hoseini, 2011). Following this, a 2014 study used WASP 7 to generate a hydraulic model of TOrCs in the Grand River (Maricor Jane Arlos, 2013). Focusing in on the portion of the river between the Waterloo WWTP and the confluence of the Speed River (approximately 14 km in length), this study found that even with a smaller scope, TOrC concentrations in the ecosystem were sensitive to variations in rates of biodegradability and photodegradability . The model included simplified inputs from WWTPs based on population data. These studies provide valuable starting points, showing that TOrCs are present and environmentally relevant in the Grand River and that surface water modeling can be valuable in predicting environmental risks of these TOrCs. In particular, the impacts of the Kitchener and Waterloo WWTPs on downstream waters emerge as important areas of consideration. There is however an opportunity for improvement beyond these studies in two key areas. First, the scope of hydraulic modeling could be expanded downstream to or past the city of Brantford. Second, the method by which TOrC removal in WWTPs is modeled can be expanded upon to include known WWTP removal mechanisms, thereby allowing for predicting of how changes to WWTP operation impact the distribution of TOrCs in the environment.

3. Methodology for Modeling of Transport and Fate in the Central and Lower Grand River

A source-to-fate model of TOrCs was built to describe how trace contaminants are introduced into the wastewater system, transported through the wastewater treatment system and the Grand River. This was done by integrating two numerical models and one spreadsheet model.

This section details the approaches taken to:

- construct and configure a model for simulating the transport and removal of contaminants from residential sources into the Grand River.
- Select target contaminants for study
- Calibrate the models
- Validate the models (where possible)
- Assess the sensitivity of selected model outputs to parameter values

3.1. Selection of Targeted Contaminants

The TOrCs chosen for modeling in this study were Triclosan, Carbamazepine, Naproxen, and Venlafaxine. These chemicals were chosen from among those which the University of Waterloo Servos Lab has been collecting environmental measurements for since 2010.

- Carbamazepine is an anticonvulsant commonly used as medication to prevent seizures (UK NHS, 2019). It has been found to resist degradation in environmental systems, making it a convenient conservative tracer among TOrCs (M.J. Arlos et al., 2015).
- Venlafaxine is a common antidepressant which has been known to experience biodegradation in WWTP and river systems (M.J. Arlos et al., 2015).
- Naproxen is an anti-inflammatory medication commonly used for pain relief (UK NHS, 2019). In addition to biodegrading in biologically active environments, it has been observed to undergo photodegradation in natural systems (M.J. Arlos et al., 2015).

- Triclosan is an antibacterial agent commonly found in many consumable products, including soaps and toothpastes(US FDA, 2019). It is known to be susceptible to biodegradation, photodegradation, and sorption onto suspended solids (M.J. Arlos et al., 2015).

Together, these four contaminants allow for analysis and comparison of sorption, photodegradation, and biodegradation mechanisms within a single model run.

3.2. Source Model Construction

The introduction of TOrCs into wastewater was modeled as the product of the population within the sewersheds, pharmaceutical usage rates, and excretion rates. Equation 6 calculates the per capita mass flow of a pharmaceutical into the sewershed while Equation 7 calculates the concentration of the pollutant at the wastewater treatment influent.

$$M = S \times E \quad (6)$$

$$C = \frac{M \times P}{Q} \quad (7)$$

where *S* is the average daily per-capita consumption of the chemical (in units of mass/time/person), *E* is the fraction of chemical excreted (unitless), *M* is the per-capita mass loading of TOrC (mass/time/person), *C* is the concentration of the chemical in WWTP influent (mass/volume), *P* is population in sewershed, and *Q* is sewage flow rate entering WWTP (volume/time).

The populations for the Kitchener and Waterloo sewersheds were estimated from the annual Region of Waterloo Water and Wastewater Monitoring Reports. Daily population values were interpolated. Equation 8 was used to generate interpolated populations, with a constant growth rate *k* being fit for each year.

$$P_{t+1} = P_t \times (1 + k) \quad (8)$$

where *P* is the population, *t* is the time step (in days), and *k* is the growth rate (in units of 1/d). Measured population data and interpolated data can be found in Appendix A.

3.2.1. Parameters

The source model predictions required consumption and excretion parameters which were taken from literature. The values employed in the study are shown in Table 1.

Table 1: Consumption and Excretion parameters used in source model. Consumption figures are in mg per capita per day, and Excretion figures are fractions.

Parameter	**CBZ**	**VEN**	**NAP**	**TRC**
Consumption	1.765[a]	1.994[a]	6.671[a]	0.0148[a]
Excretion	0.1492[b]	0.066[c]	0.2[d]	1.0[e]

[a] Health Canada. IMS data, received via e-mail July 2018.
[b] Average value adapted from (Cunningham et al., 2010; Khan & Nicell, 2015; Kim et al., 2005; Lienert et al., 2007; Ternes, 1998; Zhang et al., 2008)
[c] (Khan & Nicell, 2015)
[d] Adapted from (Khan & Nicell, 2015; Lienert et al., 2007)
[e] Triclosan is an antibacterial chemical rather than a pharmaceutical, value of 1.0 used to indicate no loss through human metabolism

Multiple literature values for consumption were compared before selecting the Health Canada values. The Health Canada values were deemed to best portray the consumption of drugs for the Region Waterloo. For the excretion fraction, values were obtained from a range of previous studies and hence there was variability in these values. Naproxen excretion fractions may be as high as 95%, according to (Kim et al., 2005; Lienert et al., 2007; Zhang et al., 2008), with Table 12 being an average of the literature values compiled. This compilation of consumption and excretion values was not exhaustive, and these values were evaluated using limited measured data. This remains an opportunity for improvement in future studies.

3.3. Wastewater Treatment Model

A model was developed to describe the removal of TOrCs in wastewater treatment processes based upon a treatment configuration consisting of a single CSTR using sludge recycle. The model initially estimates

the removal of organic matter and TKN and the corresponding production of biomass to describe performance of the WWTP with respect to conventional wastewater quality parameters. The removal of trace organic compounds was then estimated using measures of biomass concentrations and sludge production that were generated by the conventional sub-models.

Steady state operation of the WWTP was assumed in the development of methods and equations. In reality, it is typical for a WWTP to experience daily variations in biomass concentrations, flow rates, and other relevant variables. To account for this, WWTP influent data was converted to a rolling average to create a moving steady state model. This process is described in more detail in Section 3.3.

3.3.1. Model Description

The WWTP model assumes primary settling followed by activated sludge, as shown in Figure 3. This is the type of configuration used at both the Kitchener and Waterloo WWTPs.

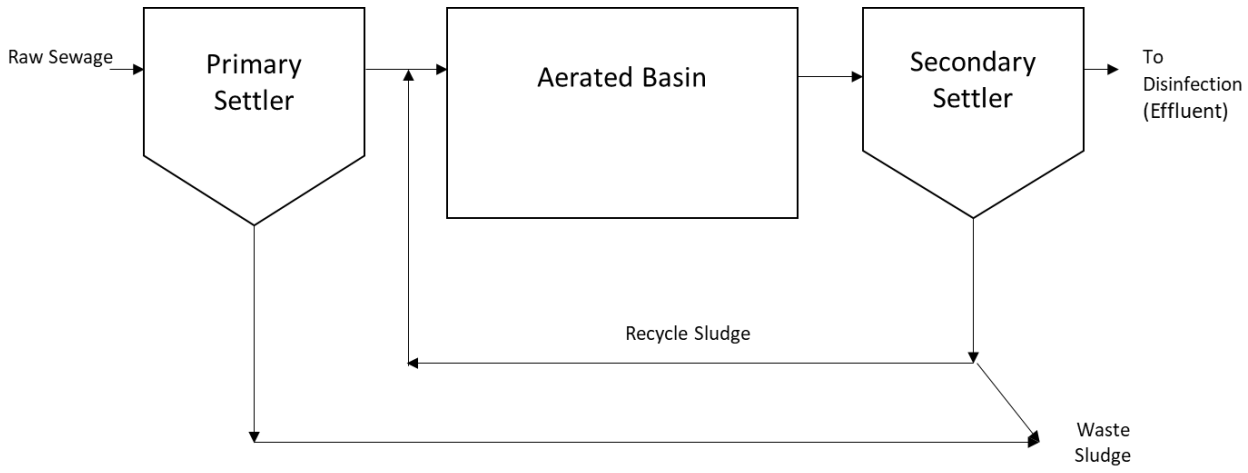

Figure 3: Diagram of Wastewater Treatment Plant Bioreactor System

The WWTP model structure consists of three sections: reading input data, solving conventional WWTP equations, and modeling contaminant removal mechanisms. The model begins by reading in measured data and constants from exterior files, and then simulates primary settling. The conventional and contaminant removal calculations are then performed within a primary loop, which executes for each day

simulated. Calculated contaminant effluent concentrations are then written to a csv file, along with calculated MLSS values for calibration. This structure is shown in the flowchart depicted in Figure 4.

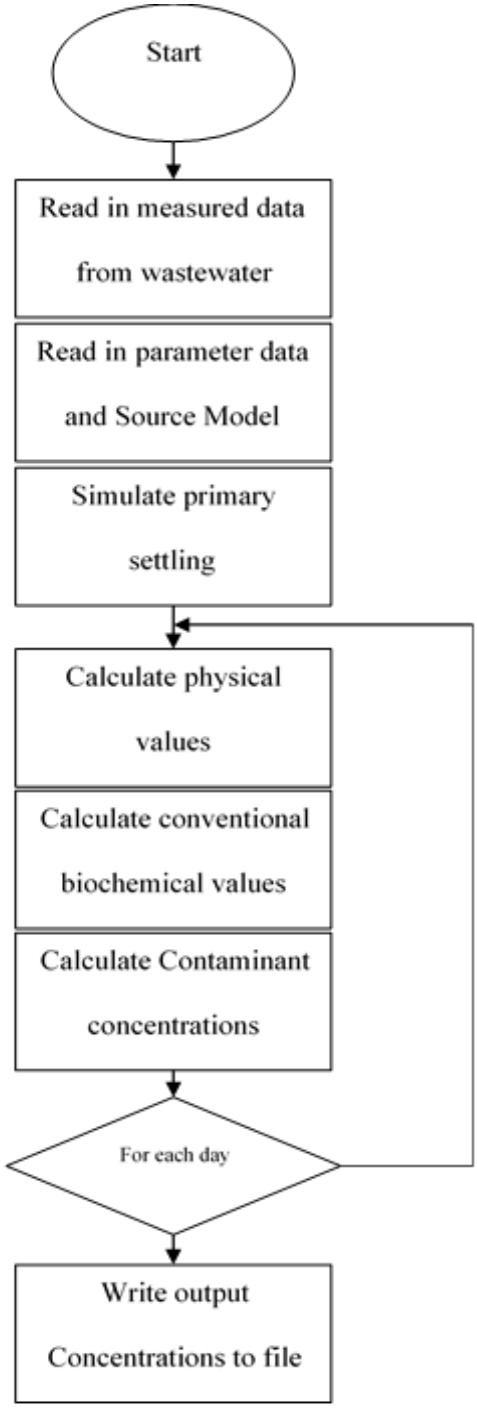

Figure 4: Flowchart of the WWTP model

The data read into the model includes source model output data, chemical and biochemical parameter data, and measured data from the WWTP. The contaminant parameters required are listed in Table 2. These parameters were among the values used in the sensitivity analysis of the combined model as there was uncertainty regarding some of the values taken from literature.

Table 2: Summary of contaminant parameter requirements for wastewater treatment plant model

Contaminant parameters	Units
Sorption Coefficient	l/mg
Specific heterotrophic contaminant degradation	l/mg
Specific autotrophic contaminant degradation	l/mg

The parameters required for modeling the conventional operations of a WWTP are summarized in Table 3. These values were considered to be reliable based on their widespread adoption in practice.

Table 3: Summary of conventional parameter requirements for wastewater treatment plant model (values taken from (Metcalf & Eddy, 2014)

Conventional parameters	Units
Heterotrophic biomass yield coefficient	-
Autotrophic biomass yield coefficient	-
Substrate metabolism coefficient	mg/l
Nitrogen metabolism coefficient	mg/l
Cell decay rate (Heterotrophic)	/d
Cell decay rate (Autotrophic)	/d
Heterotrophic yield coefficient	/d
Autotrophic yield coefficient	/d
Fraction of cells as detritus	-
Volatile fraction of Suspended Solids	-

Operational data from the Kitchener and Waterloo treatment plants was provided by the Region of Waterloo, and includes all measurements listed in Table 4. This data encompassed the periods from

March 2008 to March 2009, and the year of 2015. Frequency of data ranged from daily to weekly, with the exception of flow rate which was often observed hourly at least. All of these datasets were normalized to daily values, using linear interpolation for less-frequent data and averaging for more-frequent data.

Table 4: Summary of operational data requirements for wastewater treatment plant model

WWTP operational data	Units
Biochemical Oxygen Demand (BOD5)	mg/l
Total Kjeldahl Nitrogen (TKN)	mg/l
Flow rate	m3/d
Volume of bioreactor in use	m3
Wasting flow rate	m3/d
Recycle solids concentration	mg/l (VSS)
Mixed liquor suspended sludge (MLSS)	mg/l

After reading in all constants and data sets, the effects of primary settling on Biochemical Oxygen Demand and Total Suspended Solids are simulated. This is done using Equation 9 from (Metcalf & Eddy, 2014) P. 391.

$$R = \frac{t}{a + bt} \qquad 9$$

where R is removal efficiency, t is detention time in hours, and a and b are empirical constants with values shown in Table 5.

Table 5: Empirical constants for Equation 9 at 20 °C, taken from (Metcalf & Eddy, 2014) P. 391

Item	a	b
BOD	0.020	0.018
TSS	0.014	0.0075

The primary settling model estimated the fractional removal of BOD and TSS. Some initial removal of contaminants due to sorption on removed solids is modeled according to Equation 10.

$$C_{ps} = C_{raw}(1 - K_P \times R_{Tss}) \quad (10)$$

where C_{ps} is the total concentration of contaminant after primary settling, C_{raw} is the total concentration of contaminant in raw wastewater, K_P is the liquid-solid partitioning coefficient, and R_{TSS} is the removal efficiency of TSS as calculated in Equation 9.

The secondary treatment model calculations are conducted in a primary loop, which simulates steady-state outcomes daily. Within this loop, measured values of influent BOD and TKN are averaged over a preceding time frame to smooth over daily variations in data. This step is taken so that steady-state equations can be applied to the dynamic system. Time-averaging of measured values is performed by the model using Equation 11:

$$X_{avg_t} = \frac{\sum_{i=t-t_{avg}}^{t} X_t}{t_{avg}} \quad (11)$$

where X_{avg_t} is the time-averaged value at time *t*, X_t is the measured value at time *t*, *t* is the current time-step of the simulation in days, and t_{avg} is the averaging period in days. The value of t_{avg} was one of the calibrated parameters.

The model uses analytical solutions to substrate and biomass mass balances (Metcalf & Eddy, 2014) to estimate the concentrations of heterotrophic and autotrophic biomass present in the bioreactor. These calculations assume a single aeration tank with sludge recycle, as depicted in Figure 6. This configuration was employed to represent both the Kitchener and Waterloo WWTPs, both before and after upgrades. The model equations are shown in Table 6.

Table 6: Equations used for modeling of conventional parameters in wastewater treatment operation.

Equation	Parameters	Units	Description	Purpose
$\boldsymbol{HRT = \frac{V}{Q}}$	HRT	d	Hydraulic residence time	Using measured data, calculate the hydraulic and solids residence times. These values are employed to calculate other properties of the aerated basin.
	SRT	d	Solids residence time	
	V	m^3	Volume of bioreactor	
	Q	m^3/d	Flow through bioreactor	
$\boldsymbol{SRT_i = \frac{V \times bVSS}{Qw \times Xw}}$	bVSS	mg/l	Organic solids in bioreactor	
	Q_W	m^3/d	Sludge wasting flow	
	X_W	mg/l	Sludge wasting concentration	
$\boldsymbol{bCOD = \frac{K_S(1 + k_d \times SRT)}{SRT(Y_k - k_d) - 1}}$	bCOD	mg/l	Biodegradable COD	Using constant parameters and calculated residence times, calculate the levels of substrate present in the aerated basin.
	K_S	mg/l	Substrate metabolism coefficient	
	k_d	d^{-1}	Cell decay rate	
	Y_k	d^{-1}	Heterotrophic yield coefficient	
$\boldsymbol{TKN = \frac{K_N(1 + k_d \times SRT)}{SRT(\mu - k_d) - 1}}$	TKN	mg/l	Total Kjeldahl Nitrogen	
	K_N	mg/l	Nitrogen metabolism coefficient	
	$\boldsymbol{\mu}$	d^{-1}	Autotrophic yield coefficient	
$\boldsymbol{X_H = \frac{SRT}{HRT} \times \frac{Y_H(bCOD_0 - bCOD)}{1 - k_d \times SRT}}$	X_H	mg/l	Heterotrophic Biomass	Estimate the concentrations of biomass present using measured, calculated, and constant values. These biomass concentrations are used to model contaminant removal.
	Y_H	-	Het. biomass yield coefficient	
$\boldsymbol{X_A = \frac{SRT}{HRT} \times \frac{Y_A(TKN_0 - TKN)}{1 + k_{d_A} \times SRT}}$	X_A	mg/l	Autotrophic Biomass	
	Y_A	-	Aut. biomass yield coefficient	
$\boldsymbol{MLSS = \begin{bmatrix} X_A(1 + k_d \times fd \times SRT) + \\ X_H(1 + k_d \times fd \times SRT) \end{bmatrix} \times (1 + fVSS)}$	MLSS	mg/l	Mixed Liquor Suspended Solids	Calculate total suspended solids in mixed liquor. This value is used for calibration
	f_d	-	Fraction of cells as detritus	
	fVSS	-	Volatile fraction of Suspended Solids	

The model equations are solved in the order presented in Table 4. The heterotrophic biomass (X_H) and autotrophic biomass (X_A) are employed to estimate trace organic contaminant removal through biodegradation. The mixed-liquor suspended solids ($MLSS$) concentration was used for calibration. The removal of contaminants is calculated using the equations in Table 7, with more information included in the following section.

Table 7: Equations used for modeling biological removal of trace organic contaminants.

Equation	Parameters	Units	Description
$\boldsymbol{r_b = (X_H \times k_{b_H} + X_A \times k_{b_A}) \times \frac{V}{Q}}$	r_b	d^{-1}	Contaminant biodegradation factor
	$\boldsymbol{k_{b_H}}$	l/mg-d	Heterotrophic contaminant consumption rate
	$\boldsymbol{k_{b_A}}$	l/mg-d	Autotrophic contaminant consumption rate
	Q	l/d	Flow through bioreactor
	V	l	Volume of bioreactor
$\boldsymbol{r_s = X_W \times K_P \times \frac{Q_W}{Q}}$	r_s	-	Contaminant sorption factor
	K_P	l/mg	Sorption coefficient
	X_W	mg/l	Sludge solids concentration
	Q_W	l/d	Sludge wasting flow
$\boldsymbol{C_e = \frac{C_0}{1 + r_b + r_s}}$	C_e	mg/l	Effluent contaminant concentration
	C_0	mg/l	Influent contaminant concentration

3.3.2. TOrC Fate Mechanisms

In the TrOC model it was assumed that removal of TOrCs occurred through three distinct mechanisms: Sorption, heterotrophic biodegradation, and autotrophic biodegradation (Olumuyiwa Omotola Ogunlaja, 2015). Contaminants are removed from wastewater through being sorbed onto particles which are later removed through settling. Sorption is described as linear partitioning as per Equation 12:

$$R_s = C \times K_P \times X_W \times Q_W \qquad 12$$

where R_s is the loss of contaminant mass to sorption in units of mass/time, C is the concentration of TOrC in the water in units of mass/volume, X_W is the concentration of suspended solids flowing out of the system, Q_W is the wasting flow rate in units of volume/time, and K_P is the partitioning coefficient in units of volume/mass. The default partitioning coefficients used for each contaminant are listed in

Table **8**.

Table 8: Default Values for Sorption Coefficients used in Wastewater Treatment model (in units of l/g).

Contaminant	Sorption Coefficient (K_P)	Source
Carbamazepine	0.036	(Inyang et al., 2016)
Venlafaxine	0	Assumed from (National Center for Biotechnology Information, 2021b)
Naproxen	0.024	(Inyang et al., 2016)
Triclosan	3.61	(Inyang et al., 2016)

For the purposes of this project, biodegradation was split into two mechanisms: heterotrophic and autotrophic biodegradation. In wastewater treatment, heterotrophs make up the majority of biomass, while autotrophs are present at low concentrations in treatment systems with longer residence times (M.J. Arlos et al., 2015). The rate of contaminant removal through biodegradation was modeled according to Equation 13, which assumes first-order consumption by biomass using the TOrC as substrate.

$$R_b = C \times (K_{b_H} \times X_H + K_{b_A} \times X_A) \times V \qquad 13$$

where X_H and X_A are the heterotrophic and autotrophic biomass concentrations respectively (units of mass/volume), and K_{b_H} and K_{b_A} are specific biodegradation coefficients (units of volume/mass-time). R_b is the rate of contaminant mass loss to biodegradation, in units of mass/time, assuming constant volume of the reactor.

The default values used for the biodegradation rate coefficients are shown in Table 9. Heterotrophic degradation rates were taken from literature, while autotrophic rates were calibrated based on data available for the Kitchener and Waterloo WWTPs. This process is shown in more detail in Appendix C. These default values were used as the starting point for calibration of the full model.

Table 9: Default biodegradation rate constants used in WWTP model (in units of l/mg/d).

Contaminant	K_{b_H}	K_{b_A}	Source of K_{b_H}
Carbamazepine	0.001	12	(Suarez et al., 2010)
Venlafaxine	0.01	0.7	Assumed based on (Rúa-Gómez & Püttmann, 2012)
Naproxen	0.001	400	(Suarez et al., 2010)
Triclosan	0.34	4.0	(Salveson, 2013)

3.3.3. Calibration

The model was initially calibrated with respect to conventional wastewater quality parameters using measured wastewater treatment effluent data. For this purpose, data was made available by the Region of Waterloo and OCWA for the Kitchener and Waterloo WWTPs. This data covered the period from May 5th, 2008 to May 1st, 2009 for both the Kitchener and Waterloo plants, and the period of September 2nd 2015 to October 31st, 2016 for the Kitchener WWTP. The parameters for which data was obtained are noted in Table 10.

Table 10: Types of data received from the Region of Waterloo for the Kitchener and Waterloo WWTPs.

Type of Measurement	Name	Description
Influent Concentrations	BOD5	Five Day Biochemical Oxygen Demand
	TKN	Total Kjeldahl Nitrogen
Physical Operational Values	Q	Flow into Aerated Basin
	Q_W	Wasting Flow from Secondary Settling
	V	Volume of Aerated Basins in use
Internal Concentrations	X_W	Total Suspended Solids in Wasting Flow
	MLSS	Mixed Liquor Suspended Solids (Total Suspended Solids)

Design values of the actual aeration tank volumes employed during the study periods was not available in all cases. Hence volumes were estimated for each case based on expected average hydraulic and solids residence times. These expected values were approximately six hours for hydraulic residence time in each case, and approximately four or ten days for solids residence time before and after nitrifying upgrades. The values employed for the volumes are shown in Table 11. Moving forewords, these values should be replaced with known actual values .

Table 11: Values assumed for volume or aerated basin in WWTP models.

WWTP Model	Assumed Volume of Aerated Basin (m^3)
Kitchener B Pre-upgrades	16,600
Waterloo Pre-upgrades	10,000
Kitchener A Post-upgrades	25,000
Kitchener B Post-upgrades	21,100
Waterloo Post-upgrades	10,000

Calibration of conventional parameters was performed using the 2008-2009 dataset for the Kitchener plant. The conventional parameters that were calibrated are shown in Table 12 below.

Table 12: Calibration parameters for conventional WWTP operation

Parameter	Description
Y_H	Heterotrophic biomass yield coefficient
Y_A	Autotrophic biomass yield coefficient
K_S	bCOD half rate coefficient
K_N	Ammonia half rate coefficient
k_d	Cell decay rate
Y_k	Heterotrophic yield coefficient
μ	Autotrophic yield coefficient
f_d	Fraction of cells as detritus
f_{VSS}	Volatile fraction of suspended solids

The response used for calibration was the daily time series of MLSS values. An automated calibration method was set up to minimize the root-mean-sum of squared errors (RMSE) of the MLSS output, calculated according to Equation 14.

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n_{days}} (MLSS_{obs} - MLSS_{calc})^2}{n_{days}}} \quad 14$$

where n_{days} is the number of days modeled, $MLSS_{obs}$ is the measured MLSS value for each day, and $MLSS_{calc}$ is the modeled MLSS value for each day. The calibration was performed using the OSTRICH tool v.17.12.19, (Matott, 2017).

3.4. River Transportation Model

The transport and fate of TOrC in the Grand River was modeled using WASP 8 (Water Quality Analysis Simulation Program), that was developed by the US EPA (acquired from https://www.epa.gov/ceam/water-quality-analysis-simulation-program-wasp).

This model includes parts of the Grand River affected by the urban areas of Guelph, Cambridge, and Brantford; however, TOrC loadings from these municipalities were not included in the model as part of this study. Consequently, the results of this model could be improved by adding the additional wastewater treatment plant discharges.

3.4.1. River Transport and Fate Mechanisms

Only the biodegradation and photodegradation removal mechanisms were modeled for river transportation. WASP 8 is capable of modeling sedimentation and re-suspension, but this functionality was not employed in this study as sorption of the target compounds to river sediments was considered to be minimal.

The WASP software models surface waters using a box-model approach, solving for hydraulic conditions and applying a variety of transformation mechanism calculations to each contaminant. Mechanisms can

be toggled on and off as desired, and include but are not limited to biodegradation, photolysis, settling and resuspension, volatilization, and oxidation. For this assessment, only the biodegradation and photolysis mechanisms were used.

WASP 8 was set up to model biodegradation of each TOrC according to independent first-order decay, according to Equation 15:

$$\frac{dC}{dt} = R_{bio} = -k_B \times C \qquad 15$$

where R_{bio} represents the rate of TOrC loss to biodegradation (in mg/l/day), k_B is the biotransformation rate constant (1/day), and *C* is the concentration of TOrC (mg/l). The default biotransformation rate constants are shown in Table 13.

Table 13: Default values of biotransformation rate of TOrCs in the river, taken from literature.

Contaminant	Biotransformation Rate Constant (1/d)	Source
Carbamazepine	0.0001	(Tixier et al., 2002)
Venlafaxine	0.0054	(Rúa-Gómez & Püttmann, 2012)
Triclosan	0.5000	(M.J. Arlos et al., 2015)
Naproxen	0.0256	(Grenni et al., 2013)

Photodegradation in WASP 8 is modeled according to Equation 16:

$$\frac{dC}{dt} = R_{photo} = \sum -k_P \times C \times I \qquad 16$$

where R_{photo} represents the rate of TOrC loss to photodegradation (in mg/l/day), k_P is the phtotransformation rate constant for the TOrC at each waveband (1/day / W/m2), *C* is the concentration of TOrC (mg/l), and *I* is the intensity of light reaching the TOrC (W/m2). WASP 8 estimates the intensity of solar radiation based on latitude and water depth using a built-in algorithm. More detailed estimates

can be achieved using more detailed data input by the user (Lavecchia & Zuorro, 2009; National Center for Biotechnology Information, 2021a), but the basic method was used for this study.

Table 14: Phototransformation rates from literature.

Contaminant	Waveband (nm range)	Phtotransformation Rate Constant (1/d)/(W/m2)	Source
Carbamazepine	235-304	0.0001	(Doll & Frimmel, 2003)
Venlafaxine	235-304	0	(National Center for Biotechnology Information, 2021b; Rathore et al., 2009)
Triclosan	235-304	0.08	(Lavecchia & Zuorro, 2009; National Center for Biotechnology Information, 2021a)
	305-314	0.04	
Naproxen	235-304	0.0036	(Marotta et al., 2013; Srivastava et al., 2018)
	305-314	0.0072	
	315-334	0.0090	
	335-354	0.0036	

Surface water systems can be modeled in WASP using one, two, or three dimensions. A one-dimensional approach was used for this study for simplicity. In sections of the river where contaminant concentration was judged likely to vary across the river cross-section, the model was branched into parallel one-dimensional segments which re-joined at a downstream point. The model uses conservation of volume and momentum equations to solve for hydrodynamic profile, as described below.

$$\frac{\partial A}{\partial t} + \frac{\partial Q}{\partial x} = 0 \quad (17)$$

$$-gS_0 + gS_f = 0 \quad (18)$$

where A is area, t is time, Q is flow, x is distance, g is the gravitational constant, S_0 is the physical slope, and S_f is the friction slope. WASP employs numerical methods to solve these equations for each river segment for each time step.

WASP 8 is the first version of WASP to swap out a customizable input file providing the ability to extract values from a database. This functionality was useful in automating the combined model program but caused complications in the sensitivity analysis process which will be subsequently elaborated on.

3.4.2. Geographic Extents

The GRCA provided HEC-RAS models of the Grand River, including segmentation, cross-sections, and boundary conditions that were employed to configure the hydraulic model of the river. The geographical extent of these models can be seen in Figure 5. The WASP model used in the previous study by Arlos comprised the Grand River from the Waterloo WWTP to the Speed River confluence. Using the GRCA HEC-RAS models, the physical scope was extended downstream of the Speed River confluence, as shown in Figure 5.

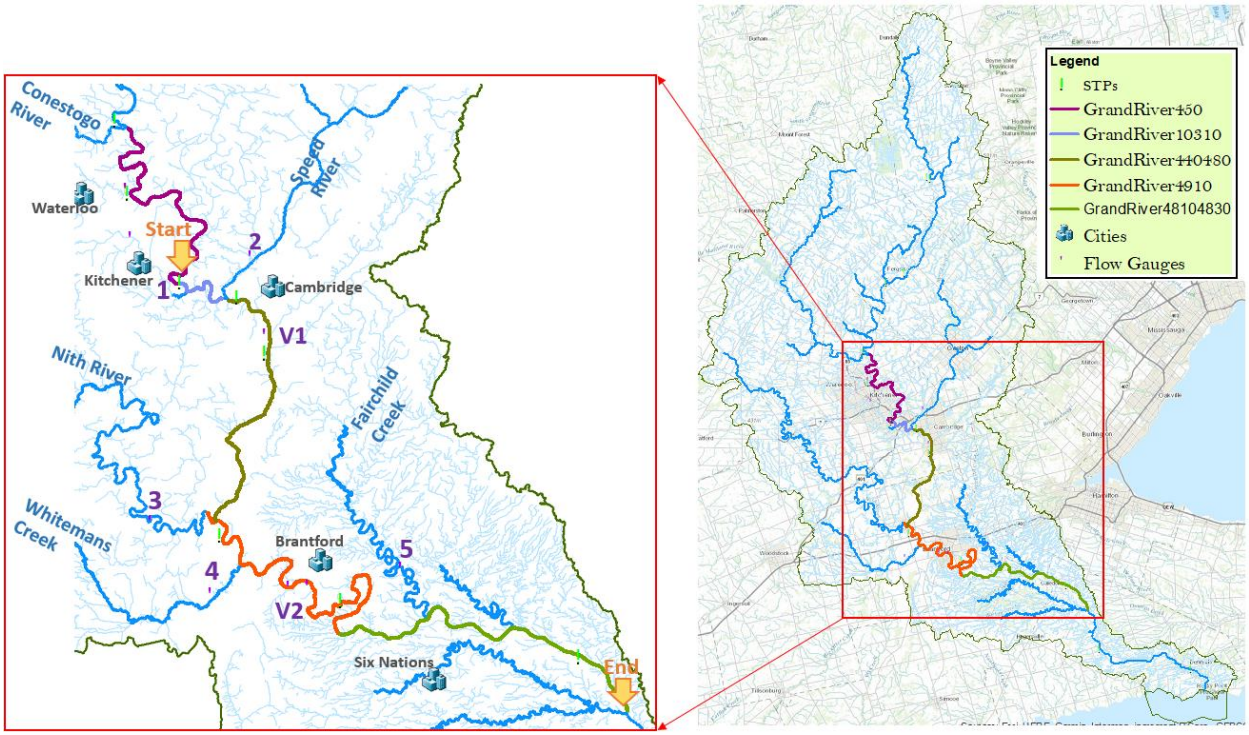

Figure 5: Map of the modeled portion of the Grand River (Nasim Hosseini)

The resulting river model includes the four GRCA models GrandRiver10310, GrandRiver440480, GrandRiver4910, and GrandRiver48104830 as listed in Figure 5. It has boundaries at the confluences of the Speed River, the Nith River, Whitemans Creek and Fairchild Creek, but does not model activities within these rivers.

3.4.3. WASP Hydraulic Model Generation

The WASP hydraulic model was configured using HEC-RAS models that were obtained from the GRCA. Four HEC-RAS models (Figure 5) were combined into a single hydraulic model in HEC-RAS. Upstream boundaries were identified at the Grand River near Doon, the Speed River, the Nith River, Whitemans Creek, and Fairchild Creek, shown on Figure 5 as locations 1 through 5, respectively. Daily flow gauge data at these sites was provided by the GRCA. Flow gauge data was also provided for the Grand River at Galt and Brantford, shown in Figure 5 as locations V1 and V2, respectively. This flow data was used for calibration and validation of the hydraulic functionality of the model. Table 15 summarizes these data sources and their locations, which are also indicated on Figure 5.

Table 15: Daily flow gauges used at WASP model boundaries

Site Number	Gauge Location Description
1	Grand River near Doon
2	Speed River at Cambridge
3	Nith River near Canning
4	Whitemans Creek near Mount Vernon
5	Fairchild Creek near Brantford
V1	Grand River at Galt
V2	Grand River at Brantford

After configuration, the hydraulic model in WASP consisted of 178 segments forming a chain 166 segments in length, with 12 parallel segments. Parallel routes were used in parts of the river in which some degree of lateral heterogeneity in contaminant concentration was expected, as segments in WASP are assumed to be perfectly mixed. This primarily consisted of WWTP outlets and tributary confluences, where water with different contaminant concentrations enters the river from one side. Parallel segmentation was implemented immediately downstream of the Kitchener WWTP; at the Preston, Galt, Paris, and Brantford WWTPs; and at the Speed River confluence. Except for parallel segmentation, segments were not added, removed, or modified. Segments also varied in length, with the shortest segment being 200 metres long (a particularly wide segment of the Grand River between Whitemans Creek and Brantford) and the longest segment being 1494 metres long (spanning the area immediately upstream of the Kitchener WWTP plant before the majority of contaminant is loaded into the river).

The combined hydraulic model was calibrated for Manning's constant in HEC-RAS before importing to WASP, to ensure that combining the GRCA models and adding parallel segmentation did not result in modeling conflicts with respect to hydraulic flow. This took the form of applying multipliers to the existing coefficients in the model. The calibration response used was water level, with daily observations available from GRCA monitoring stations. The model was calibrated for water elevation at the GRCA

Galt monitoring station for the year of 2014. This was then validated by comparing modeled results to measured observations for Galt in 2008, and Brantford for 2014.

The combined hydraulic model was imported from HEC-RAS into WASP, maintaining segmentation and channel geometry. This model was then validated with respect to contaminant flow (i.e., advection and dispersion of contaminants), using chloride concentration as the variable of comparison. Observed chloride concentrations were once again made available through the GRCA from monitoring stations. Modeled and observed concentrations were compared at the Galt, Blair, Glen Morris, and Brantford monitoring sites, as well as at the Kitchener, Preston, and Galt WWTPs. These comparisons were performed for the period from 2007 to 2015.

3.5. Integrated Model

The source, treatment, and river models were integrated using a series of scripts and data files such that the entire system could be modeled using a single executable.

3.5.1. Model Integration Framework

The source model runs in Microsoft Excel, and therefore does not need to be executed. Constants, inputs, and date ranges can be entered directly into the spreadsheet, immediately updating the results of the model.

The WWTP model was developed in both MATLAB and R platforms. Upon execution, it reads input data directly from the source model spreadsheet. Additionally, it reads parameter data and input data from a series of CSV set up for this purpose. After modeling WWTP mechanisms, the output is written to another CSV file as a table of concentrations organized by date and TOrC.

The input of contaminants from WWTPs was programmed in WASP as a fixed-concentration boundary condition. WASP 8 is the first version of WASP to introduce a database link method for importing large amounts of data, rather than using an input file. A custom script in R was used to read the outputs from the WWTP model and format them as an SQL database for WASP import. This script generates WWTP

effluent concentration tables for each contaminant at each treatment plant train, to which WASP 8 is linked. River boundaries were assumed to have negligible levels of contaminant loading for the purpose of this study.

While contaminant loadings can be imported into the WASP model using an automated process, constants such as decay rates must be changed in WASP 8 using the GUI. Previous versions of WASP allowed for these constants to be written to a text-based input file, and future releases are anticipated to have a built-in function for automatically updated these values similar to how boundary conditions are handled. However, as the model currently stands, it is still necessary to manually edit values in WASP any time different biodegradation or phototransformation rates are tested.

3.5.2. Sensitivity Analysis

The combined model was analyzed for sensitivity to key removal mechanism rates. These constants are shown in Table 16.

Table 16: Parameters used for sensitivity analysis of integrated model.

Model	Parameter
WWTP (Matlab/R)	Sorption Coefficient (l/mg)
	Heterotrophic Decay Rate (l/mg)
	Autotrophic Decay Rate (l/mg)
River (WASP 8)	Biotransformation Rate (1/d)
	Phtotransformation Rates (1/d)/(W/m2)

Sensitivity analysis was performed manually (i.e., one run at a time) due to the necessity of editing parameters in WASP 8 through use of the GUI. As a result, comprehensive methods of analysis such as Monte Carlo were not feasible. Instead, each parameter was assigned five values, ranging between the expected minimum and maximum values. Default values of each parameter were taken from literature, and typically were used as the center of the five values. The model was run five times for each parameter, using each value while holding the other parameters to their default values. This analysis was performed

for the period of March 2008 to 2009, as this was the time frame for which the best WWTP data existed. Results were examined and contrasted between three locations along the Grand River, to gauge the relative impacts of WWTP and river removal mechanisms.

4. Results

The source, WWTP, and river model compartments were run sequentially for two 1-year periods, one before and one after upgrades to each plant. The results of these runs are presented in this section.

4.1. Source Model

A consumption-metabolism model using population data for the Kitchener-Waterloo area was used to generate TOrC concentration profiles for the WWTP influents. The concentration profiles generated are shown for the 2008 and 2015 model runs in Figure 6 and Figure 7 for Kitchener and in Figure 8 and Figure 9 for Waterloo, respectively.

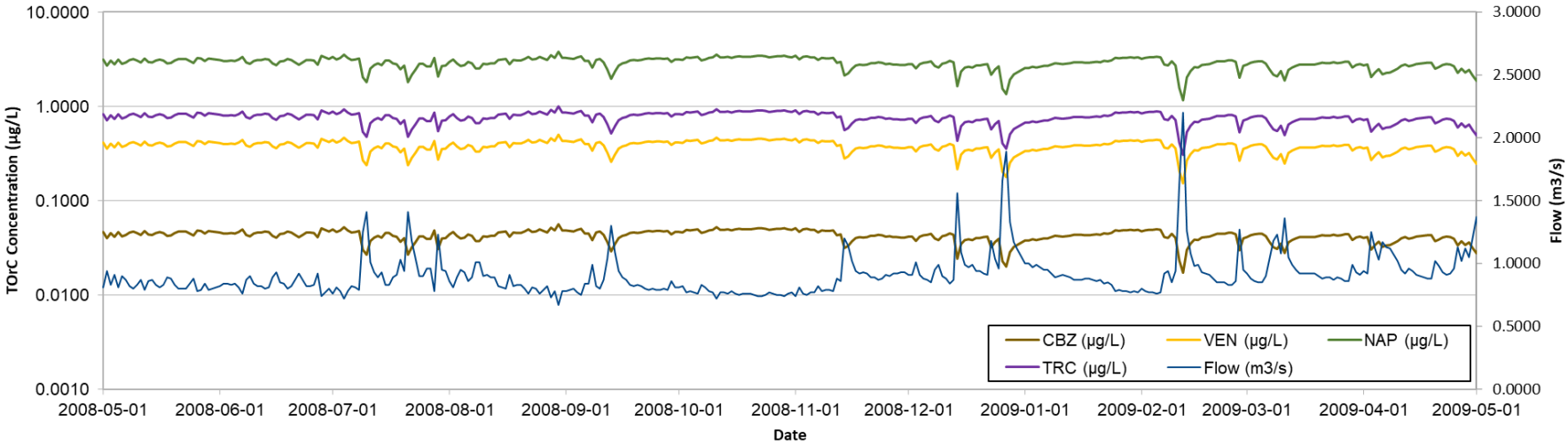

Figure 6: Simulated WWTP influent profiles, generated for Kitchener 2008 using consumption-metabolism model

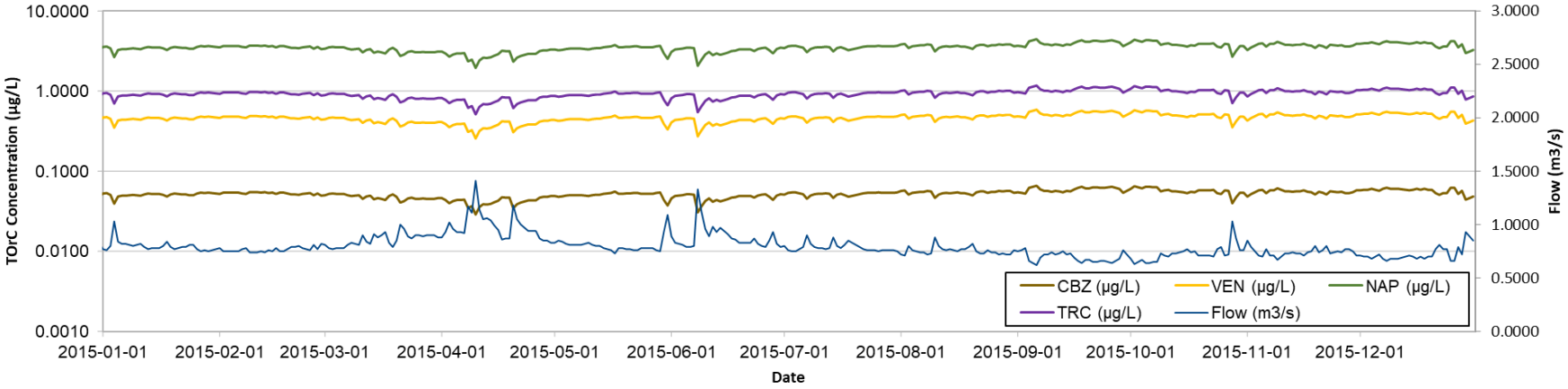

Figure 7: Simulated WWTP influent profiles, generated for Kitchener 2015 using consumption-metabolism model

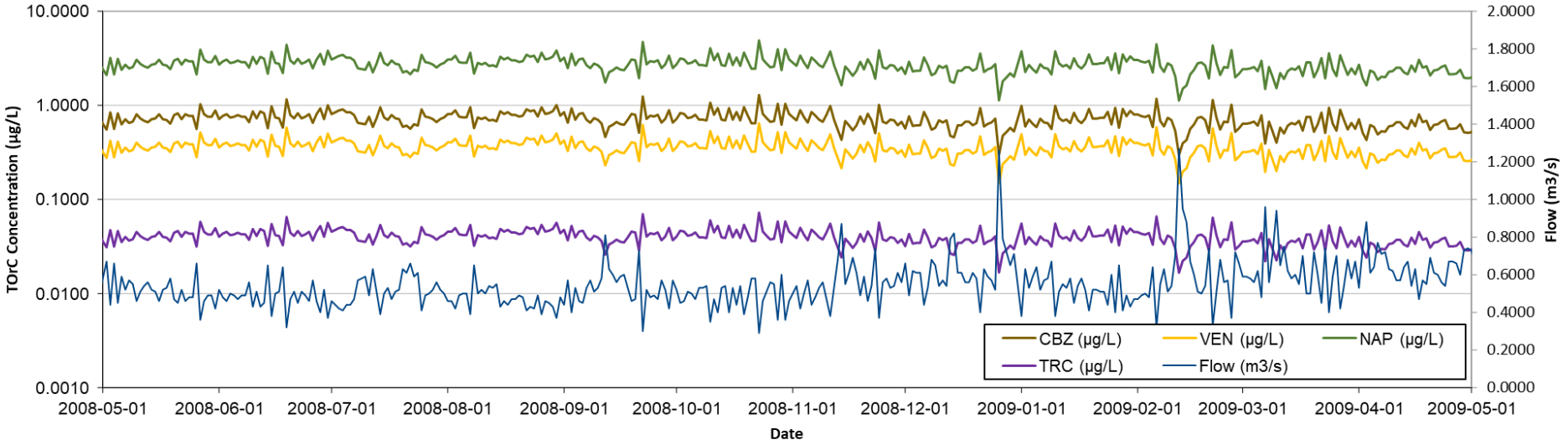

Figure 8: Simulated WWTP influent profiles, generated for Waterloo 2008 using consumption-metabolism model

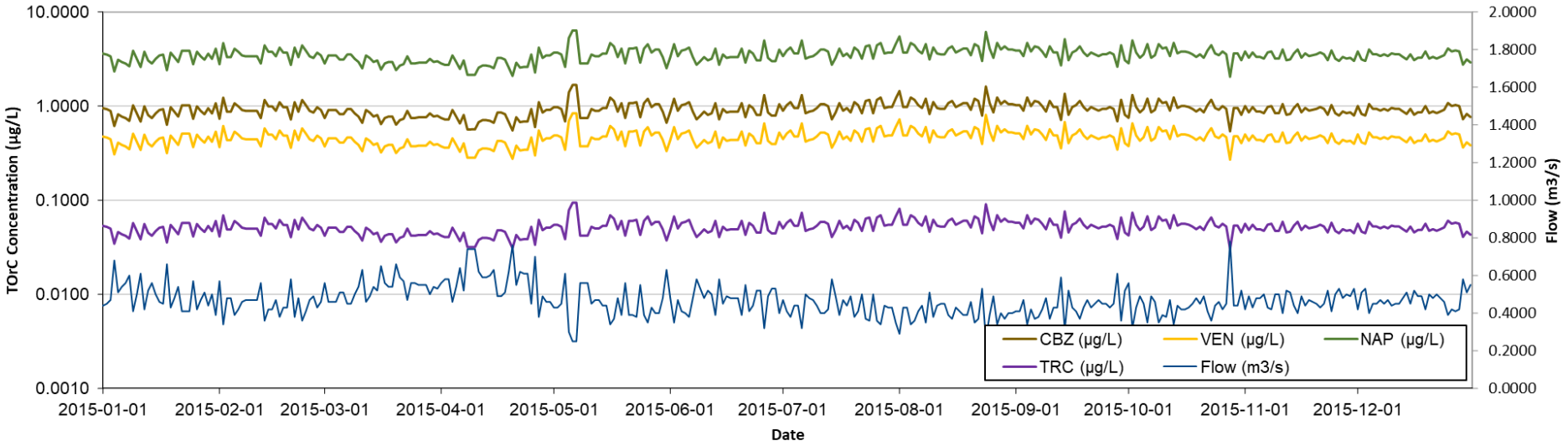

Figure 9: Simulated WWTP influent profiles, generated for Waterloo 2015 using consumption-metabolism model

The source model predictions formed a necessary first step in the integrated modeling process. Data on TOrC concentration in WWTP influent was not available and hence the values could not be validated independently. However, the consumption-metabolism approach to surface modeling has been shown to effectively describe the loading of pharmaceuticals into the Grand River from the Kitchener WWTP (Maricor Jane Arlos, 2013).

The model results show a negative correlation between TOrC concentration and flow rate, resulting from the source-limited nature of the system. Contaminant mass flow is driven by consumption-excretion parameters (which remain constant) and population (which is relatively stable).

4.2. Wastewater Treatment Model

The WWTP portion of the model used first-order biodegradation kinetics and sorption partitioning to simulate TOrC removal in treatment and to generate effluent concentration profiles. For the pre-upgrade simulations, the model was run for the period of May 2008 to June 2009. This was done to best make use of WWTP data available for both the Kitchener and Waterloo plants. However, effluent TOrC measurements were only present for years from 2010 onwards. As both datasets predated the upgrades to the Kitchener and Waterloo plants, it was deemed reasonable to use the 2010 Kitchener effluent data to calibrate the WWTP model. The predicted effluent profiles for the pre-upgrade model runs are presented in Figure 10-7 for the two Kitchener treatment trains and the Waterloo WWTP.

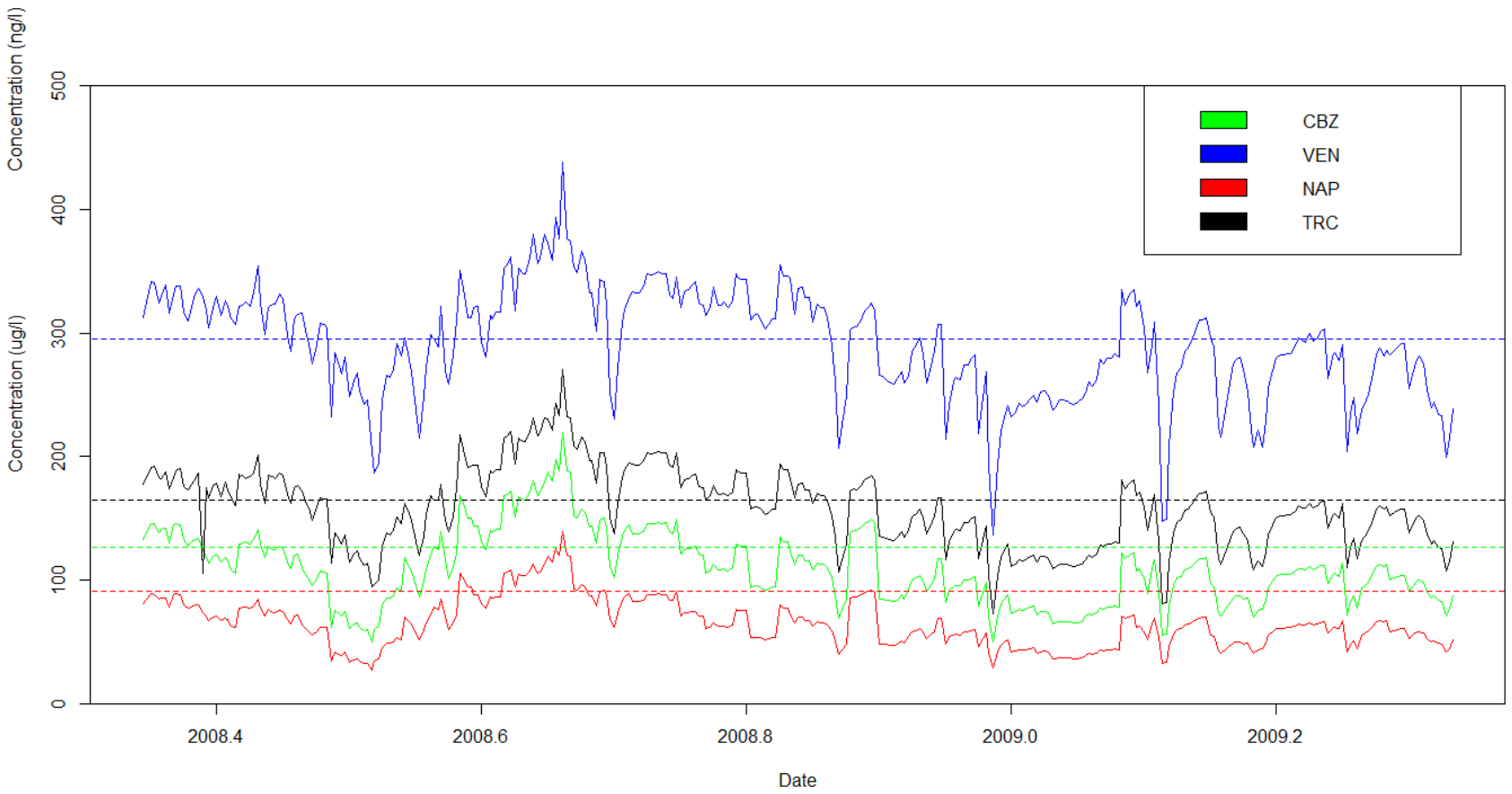

Figure 10: Kitchener WWTP train A modeled effluent TOrC concentration, pre-upgrade. Dashed lines represent observed average Kitchener WWTP effluent concentrations from 18 Nov, 2010.

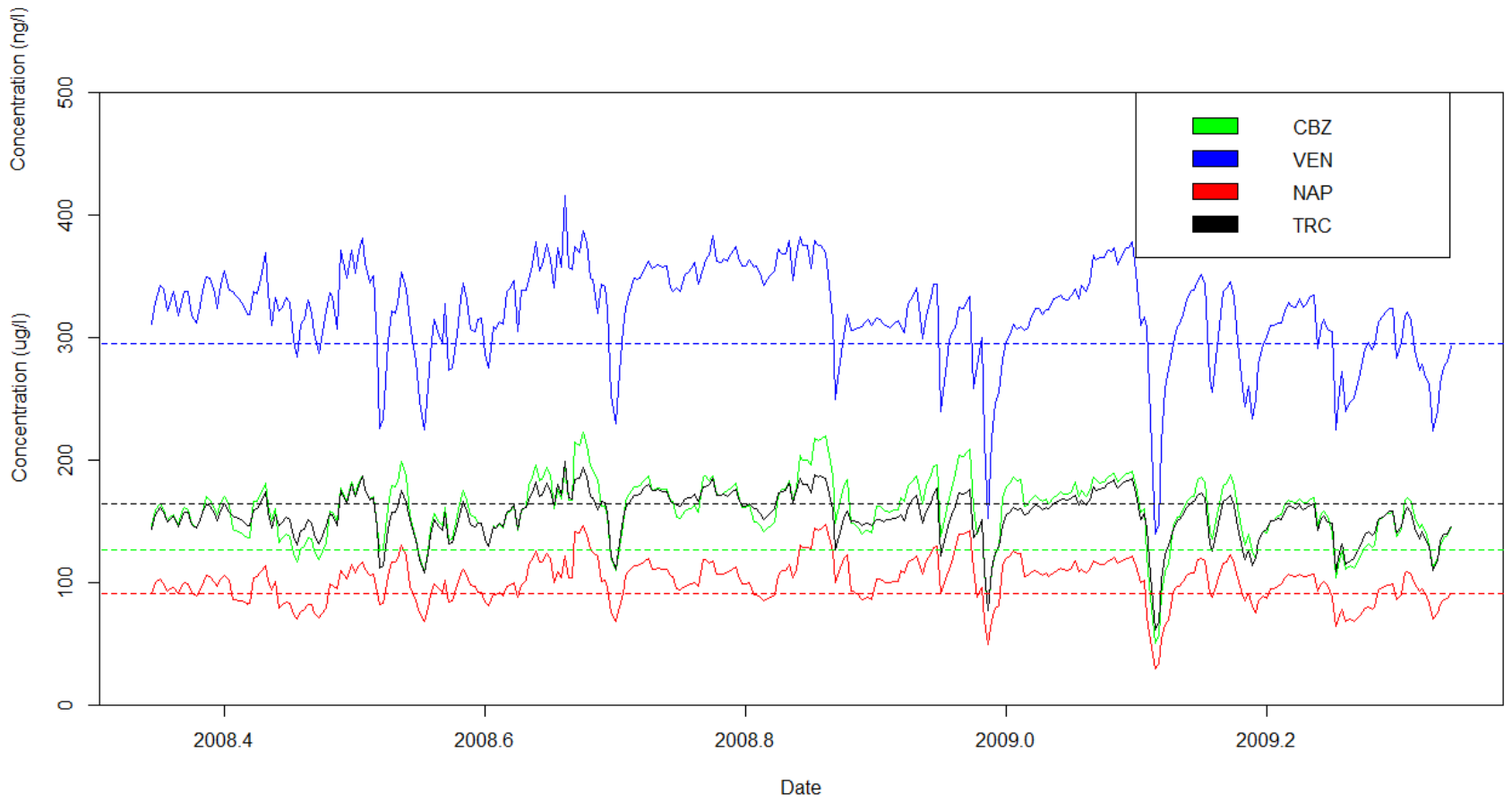

Figure 11: Kitchener WWTP train B modeled effluent TOrC concentration, pre-upgrade. Dashed lines represent average observed Kitchener WWTP effluent concentrations from 18 Nov, 2010

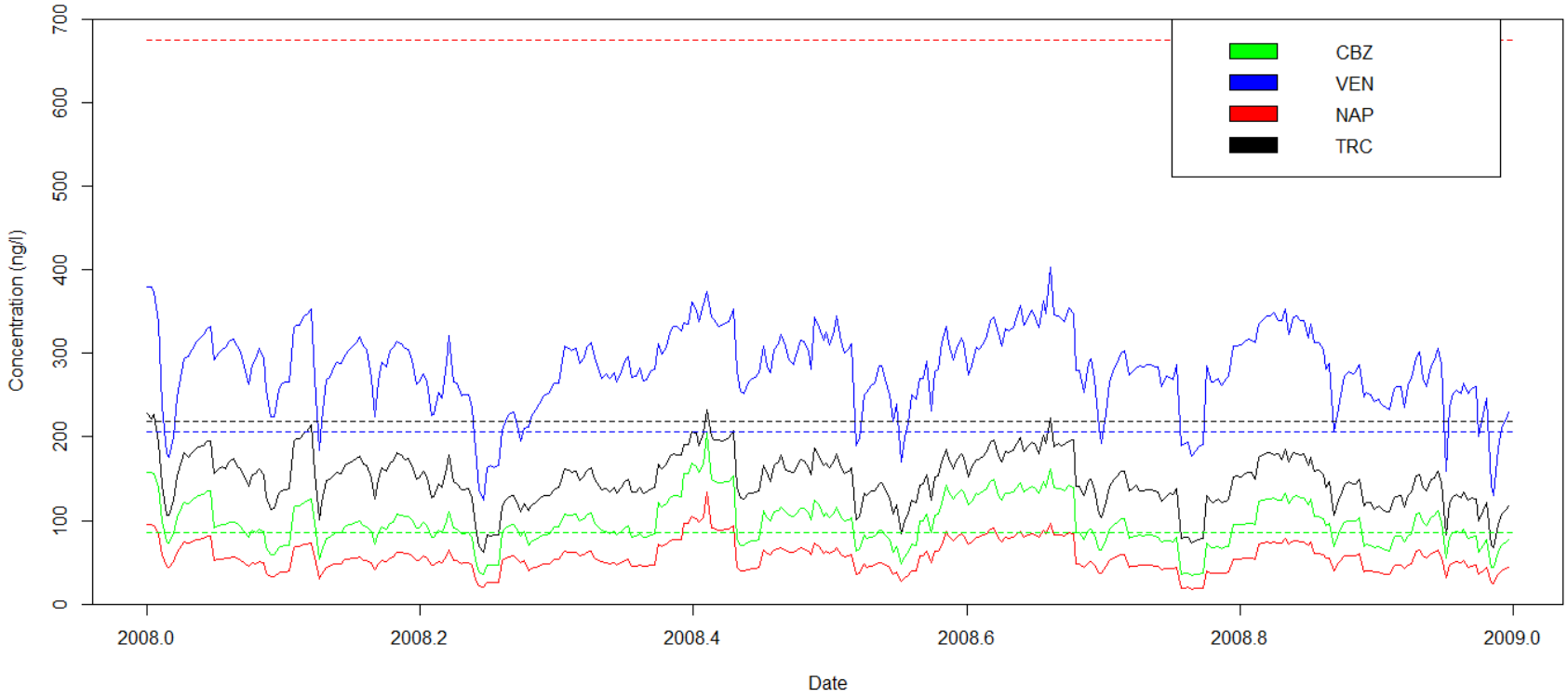

Figure 12: Waterloo WWTP modeled effluent TOrC concentration, pre-upgrade. Dashed lines represent average observed Waterloo WWTP effluent concentrations from Fall 2011.

It is worth noting that the Kitchener A train data was used to calibrate the autotrophic degradation rates used in the models (shown in Appendix C). Hence, the model output for Kitchener A matched the observed data, while the other two were less closely matched.

There is relatively little noticeable difference between the modeled effluent profiles. The predicted concentrations for the Waterloo and Kitchener B WWTP models were generally consistent with the measured concentrations. The exception to this is the naproxen predictions, which fall below the measured value for Fall 2011. More frequent and relevant measurements would be required to quantify the differences between modeled and observed concentrations for validation purposes.

The factors driving TOrC removal in this model are heterotrophic biodegradation, autotrophic biodegradation, and removal of contaminants sorbed onto suspended solids. The primary drivers of these mechanisms within the WWTP model are heterotrophic biomass, autotrophic biomass, and wasting suspended solids, respectively. The mean values of these factors for the pre-upgrade model runs are shown in Table 17 below, along with mean modeled TOrC concentrations.

Table 17: Mean modeled WWTP values (2008)

		Kitchener A	**Kitchener B**	**Waterloo**
Times	HRT (hours)	4.4	6.1	5.3
	SRT (days)	4.9	3.4	4.3
Biomass (mg/l)	Heterotrophic Biomass	857.1	929.4	647.3
	Autotrophic Biomass	129.6	53.8	123.3
	Wasting TS	3667	3646	3071
TOrC (ng/l)	CBZ	110.1	159.7	97.40
	VEN	292.5	321.1	281.7
	NAP	65.31	101.0	56.75
	TRC	159.2	155.2	149.7

Examining the mean modeled internal WWTP values produces some key observations. The biomass concentrations appear largely similar between WWTP models, with the exception that the Kitchener B

plant has a predicted autotrophic biomass less than half that of the other two. As these simulations are before nitrifying modifications to the WWTPs, low levels of autotrophic biomass are to be expected. Heterotrophic and wasting biomass are modeled at lower values in the Waterloo plant relative to the Kitchener plants.

Comparing the mean modeled TOrC concentration in the effluent between WWTPs reveals higher levels of most TOrCs in the Kitchener B simulation relative to the other two. The Kitchener A and Waterloo values are similar for all TOrCs, with the Waterloo concentrations slightly lower. The Kitchener B concentrations in contrast are approximately 15% higher for VEN, and 50 to 80% higher for CBZ and NAP. This corresponds to the lower autotrophic biomass concentration in the Kitchener B simulation. The only TOrC relatively unaffected by this is TRC, which has a higher heterotrophic degradation rate relative to the others. This demonstrates that removal VEN, CBZ, and NAP is dominated by autotrophic degradation in the model, even under pre-upgrade conditions, while removal of TRC is dominated by either heterotrophic degradation or sorptive removal.

It is worth noting that the data available for calibrating or validating the WWTP model was limited. For best results, the model would be calibrated using multiple observed effluent concentrations during the time period of the model. Future attempts to model TOrC removal in wastewater may prefer to use years for which more data is available to perform model calibrations.

Using the calibrated autotrophic biodegradation rates along with WWTP and source model data, the WWTP model was run for the year of 2015. The modeled effluent concentrations were compared with measured WWTP effluent concentrations from the fall of the same year. These results are shown in FiguresFigure **13** toFigure **15** below.

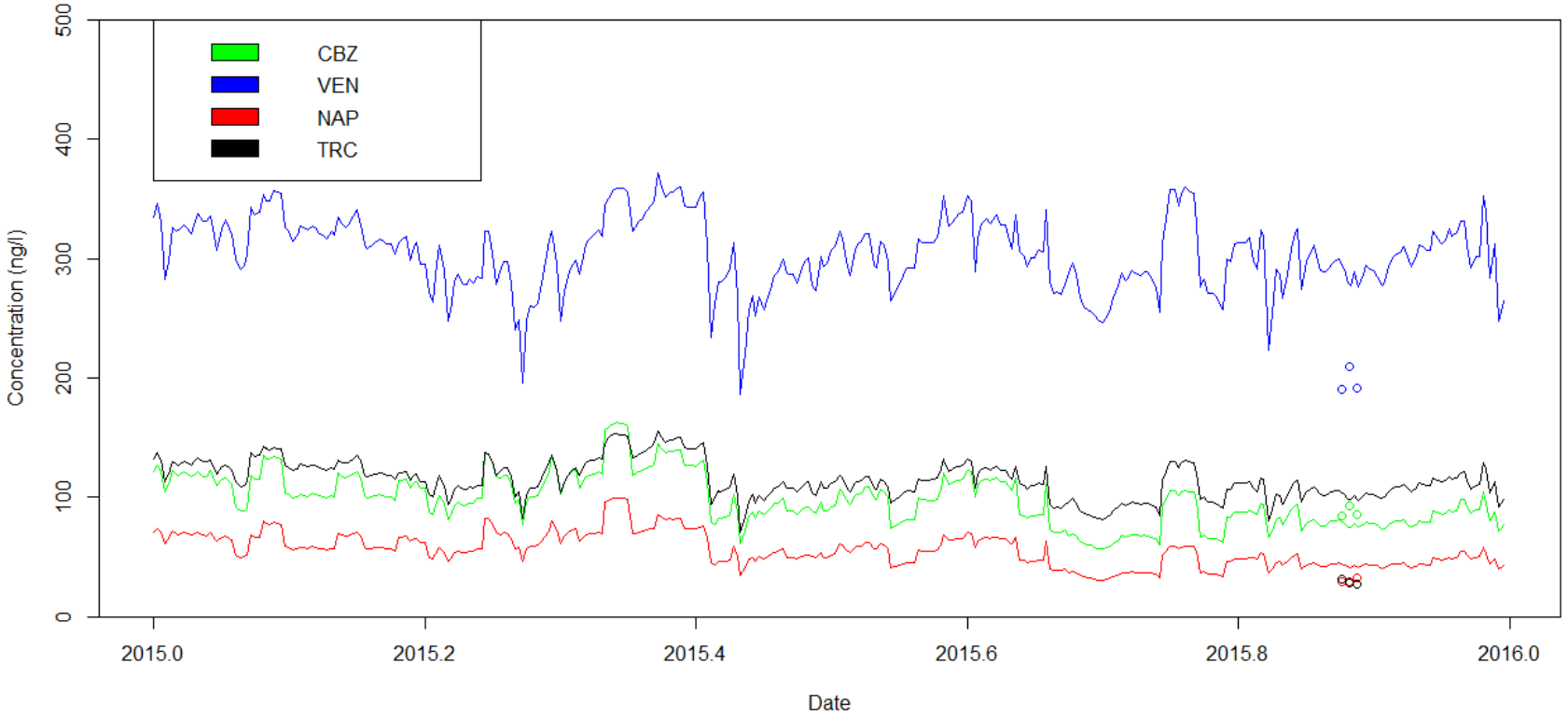

Figure 13: Kitchener WWTP train A modeled effluent TOrC concentration, post-upgrade. Circles represent observed Kitchener WWTP effluent concentrations.

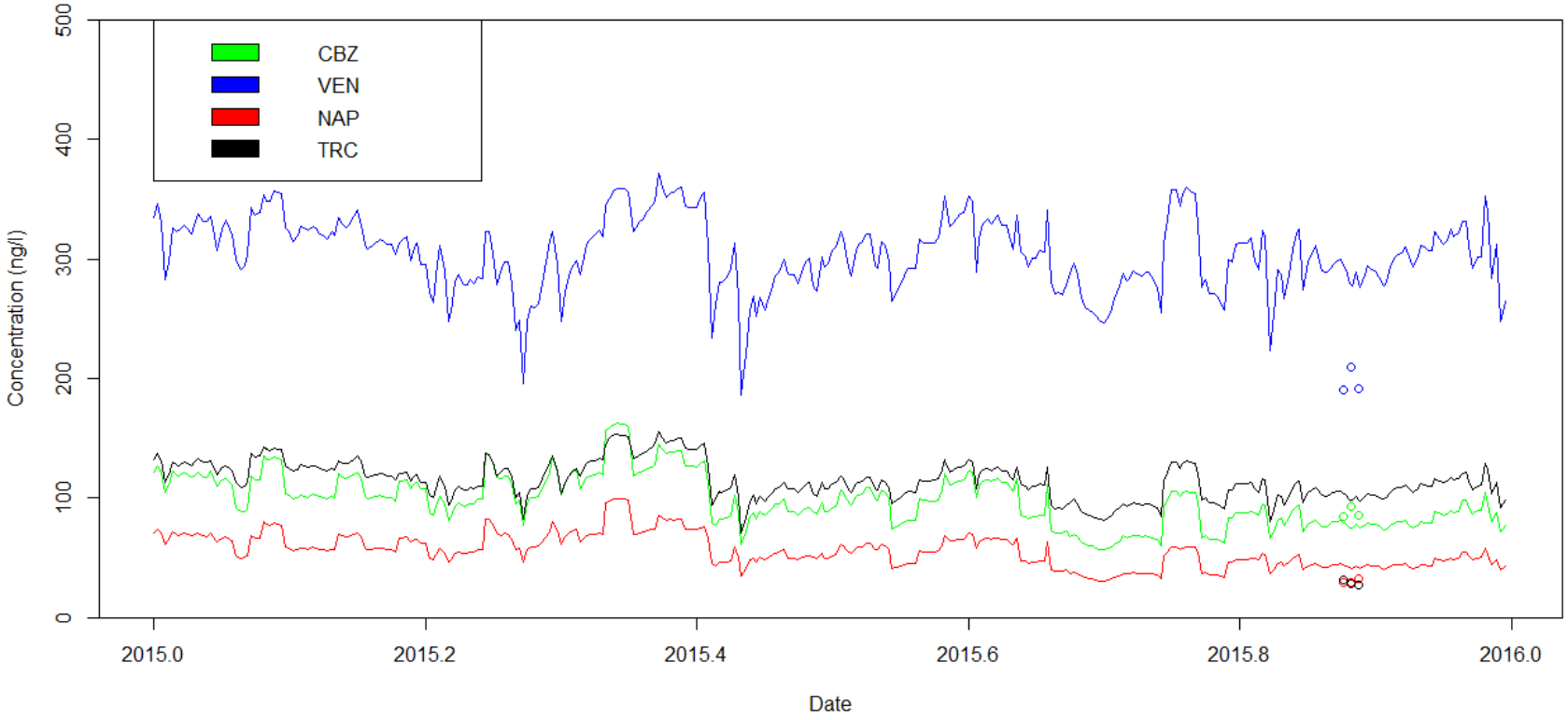

Figure 14: Kitchener WWTP train B modeled effluent TOrC concentration, post-upgrade. Circles represent observed Kitchener WWTP effluent concentrations.

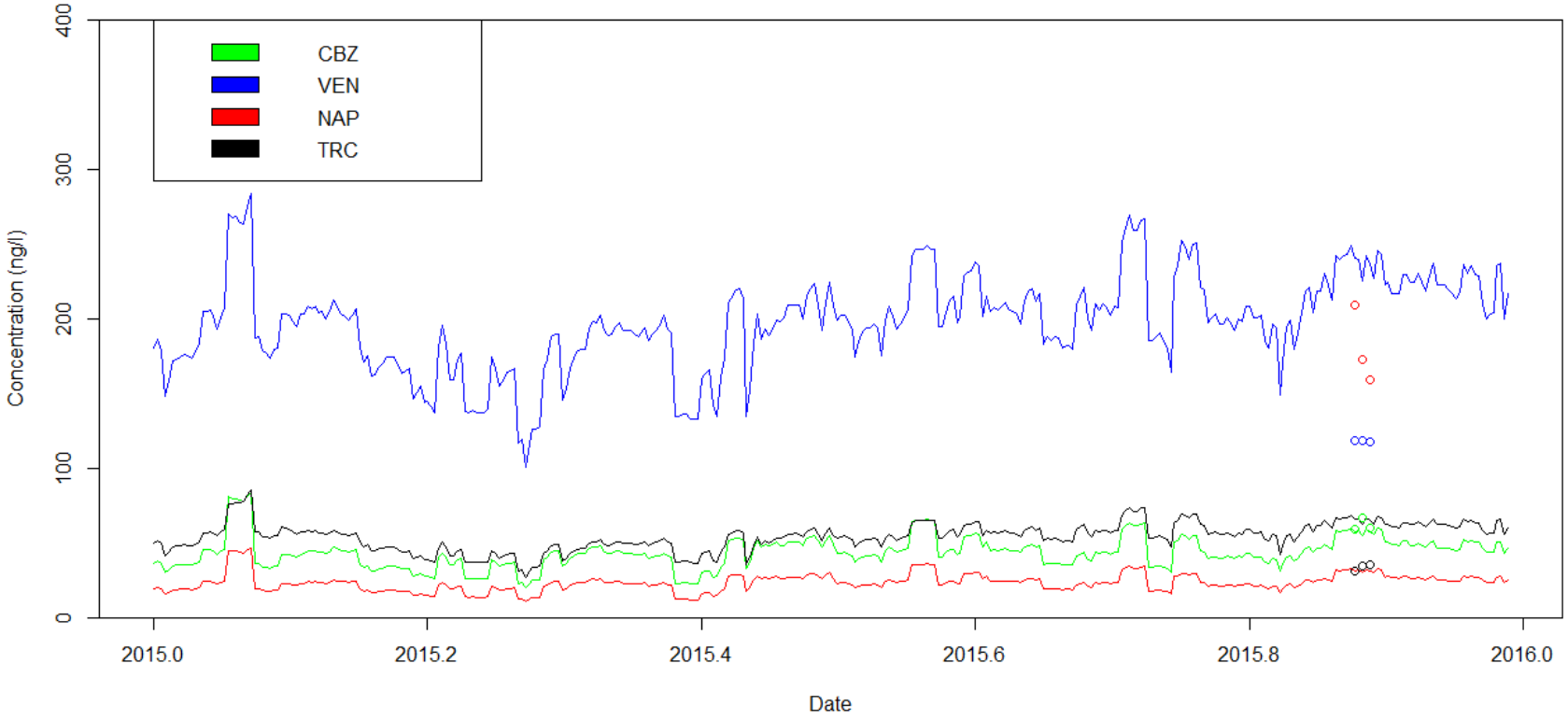

Figure 15: Waterloo WWTP modeled effluent TOrC concentration, post-upgrade. Circles represent observed Waterloo WWTP effluent concentrations.

The 2015 model WWTP outputs show TOrC concentration profiles that somewhat overlapped with observed data. The most obvious outlier to this was NAP in the Waterloo simulation, which was measured at concentrations of over 200 ng/l during the three-day sampling period. Without more WWTP effluent TOrC data, it is uncertain whether these observations were regular or anomalous. The Kitchener model predictions were more similar with regards to the NAP observations. For the other contaminants, all simulations appeared to over-estimate VEN and TRC somewhat, while the CBZ predictions generally matched up with observed values. The mean modeled values of TOrC concentration are presented in Table 18 below, along with mean internal WWTP conditions.

Table 18: Mean modeled WWTP values (2015)

		Kitchener A	**Kitchener B**	**Waterloo**
Times	HRT (hours)	9.2	6.1	6.1
	SRT (days)	8.0	9.2	13.1
Biomass (mg/l)	Heterotrophic Biomass	1083	842.2	3832
	Autotrophic Biomass	83.48	166.4	301.5
	Wasting TS	3665	3070	1070
TOrC (ng/l)	CBZ	98.02	91.07	43.31
	VEN	304.8	287.2	197.5
	NAP	55.95	59.76	23.25
	TRC	114.8	132.5	54.08

It is worth noting that NAP concentrations predicted by the Waterloo WWTP model fell below observed concentrations both pre- and post-upgrade simulations. The other most noticeable difference between the Waterloo plant and the others in both simulations was the wasting suspended solids, which was lower in the Waterloo model. This implies that NAP removal may be more driven by sorption than was previously thought, and that the autotrophic degradation rate for NAP may have been over-calibrated to compensate for an under-estimated sorption coefficient. Modeling NAP removal with a higher sorption coefficient and a lower autotrophic biodegradation coefficient could generate results that are similar to the current results

for the Kitchener models but much greater in concentration for the Waterloo models, to be more in line with observations.

To compare the 2015 and 2008 model results, the percent change in mean values are presented in Table 19. These values were obtained by dividing the difference in mean values by the 2008 values.

Table 19: Change in mean modeled WWTP values (2008 to 2015)

		Kitchener A	Kitchener B	Waterloo
Times	HRT	109%	0%	15%
	SRT	63%	171%	205%
Biomass	Heterotrophic Biomass	26%	-9%	492%
	Autotrophic Biomass	-36%	209%	145%
	Wasting TS	0%	-16%	-65%
TOrC	CBZ	-11%	-43%	-56%
	VEN	4%	-11%	-30%
	NAP	-14%	-41%	-59%
	TRC	-28%	-15%	-64%

These changes in the model were largely what would be expected after upgrades, with some exceptions. Most notably, the autotrophic biomass computed in the Kitchener A model fell relative to its pre-upgrade simulation. This is very unlikely to reflect reality, as the primary purpose of the upgrades was to facilitate nitrification by autotrophic ammonia-oxidizing bacteria. This is most likely a consequence of assuming values for volumes of aerated basins for the post-upgrade Kitchener A simulation, and implies that either the assumed volume for 2015 or the design volume used for 2008 are incorrect. In the TOrC effluent concentrations, this led to an increase in modeled VEN concentrations, and a reduced decrease in CBZ and NAP concentrations relative to the other WWTPs. TRC concentrations appear to fall more in line with the other WWTP simulations, supporting the observation that TRC is more driven by sorption and heterotrophic degradation relative to the autotrophic degradation, as modeled.

In the Waterloo and Kitchener B models, SRT increased relative to HRT after upgrades. This is what would be expected from WWTP upgrades, as both autotrophic and heterotrophic biomass are highly influenced by the solids residence time. However, the Kitchener B and Waterloo models differ in how biomass concentrations increased. In the Waterloo WWTP simulation, heterotrophic biomass concentration increased by nearly 500%, while autotrophic biomass increased 145%. This led to reductions in modeled effluent concentration that were greater than the other WWTPs for all four TOrCs. In contrast, the Kitchener B simulation had an increase in autotrophic biomass of over 200%, but had a slight reduction in modeled heterotrophic biomass. It is worth noting that while both biomass concentrations are largely driven by SRT, the heterotrophic and autotrophic biomass levels are also driven by influent BOD5 and TKN respectively, both of which are measured values. This led to reductions in modeled CBZ and NAP concentrations of approximately 40%, and VEN and TRC concentrations of 10-15%. This shows that autotrophic biodegradation was a driver of TOrC removal in the model.

Wasting sludge suspended solids concentration was seen to hold constant or decrease in each model after upgrades. Unlike the other values in Tables Table **17** to Table **19**, the wasting solids was one of the measured datasets provided by the Region of Waterloo, and is thus assumed not to be in error.

As the second in a series of three serialized models, these results inherit any errors present in the source model. In future uses of this model, data on WWTP influent TOrC concentrations can allow for better verification of the source model output, and therefore more confident analysis of the WWTP model results.

4.3. River Transportation Model

A WASP model of the Grand River was run using the Waterloo and Kitchener WWTP effluent predictions as loadings. The hydraulic conditions in the model were calibrated on the basis of river geometry and flow data provided by the GRCA. Results of the hydraulic calibration process can be seen in Appendix D and E. The downstream river concentration profiles of each contaminant can be seen in Figure 16 and 10 for 2008 and 2015, respectively. Multiple lines in the upstream sections represent

concentrations present in the parallel flow compartments which subsequently merged downstream (for example, due to the addition of WWTP effluent into the river).

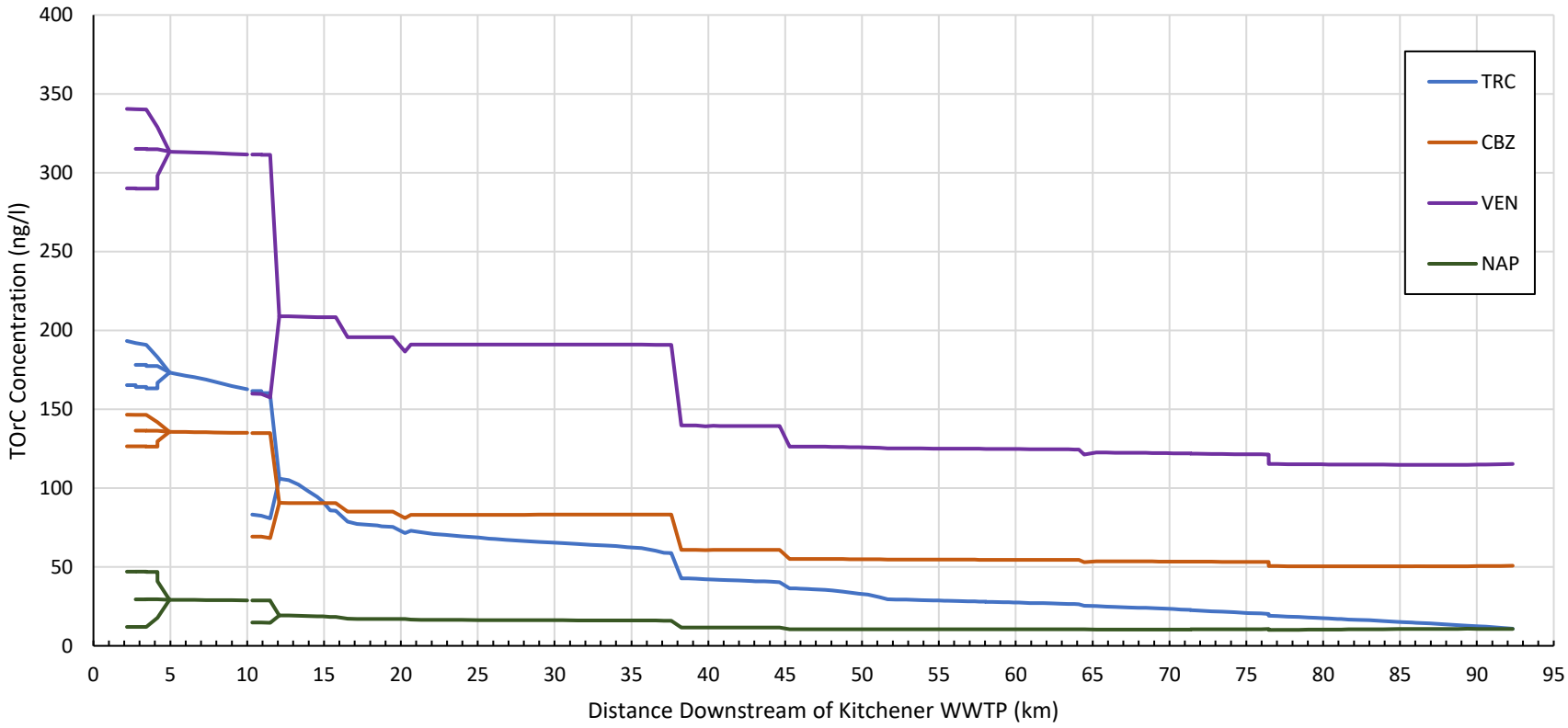

Figure 16: Modeled concentration profile in Grand River downstream of Kitchener-Waterloo for 2008 June 5th.

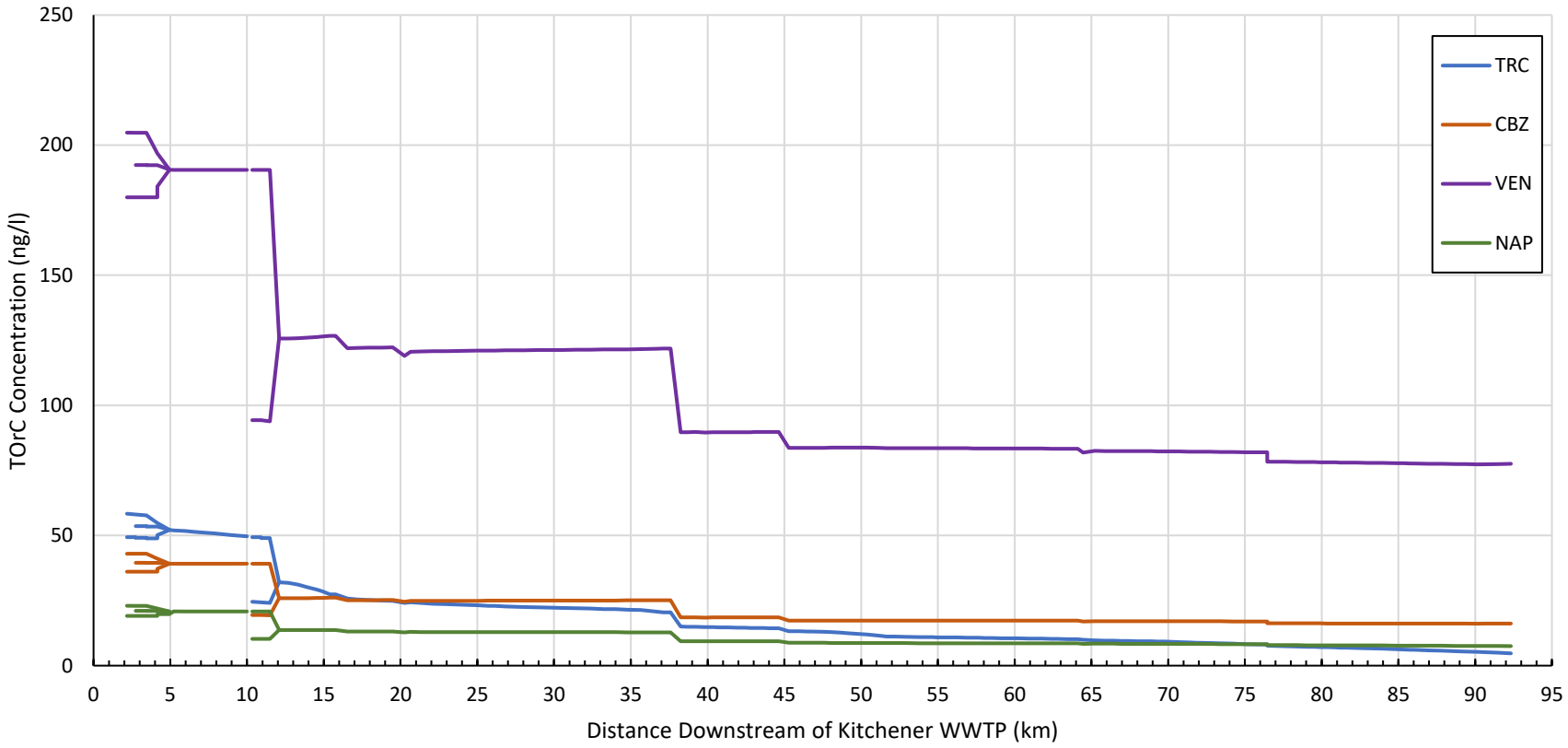

Figure 17: Modeled concentration profile in Grand River downstream of Kitchener-Waterloo for 2015 October 12th.

Contaminant loadings from the Waterloo and Kitchener WWTPs were included and these became mixed within the first 5 km of the river model. Downstream of this, the simulated TOrC concentrations are reduced through dilution and degradation. From these plots, it is apparent that the greatest reductions in concentration come from dilution at various points in the Grand River. Sites of interest, including WWTP outfalls and river confluences, are listed in Table 20 below

Table 20: Urban areas and River Confluences along the Grand River WASP model

Site	River km
Waterloo WWTP	0
Kitchener WWTP	2.17
Schneider Creek	4.16
Speed River	10.43
Preston WWTP	11.50
Mill Creek	16.53
Galt WWTP	20.27
Nith River	38.24
Paris WWTP	39.81
Whitemans Creek	45.29
Brantford WWTP	64.45

River confluences manifested in the model results as dramatic drops in concentration, with the largest occurring at the Speed River and Nith River. The impacts of dilution were removed by expressing the model results as mass-flows which are shown in Figure 18 and Figure 19.

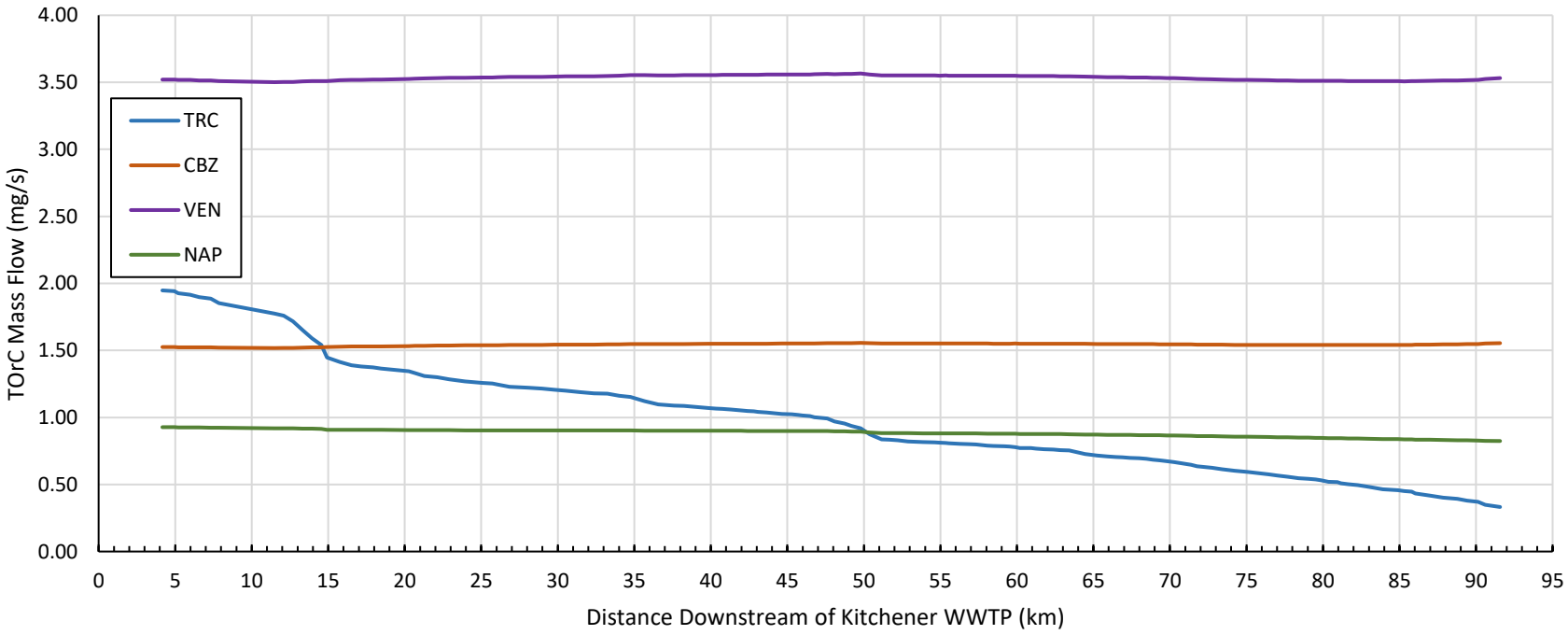

Figure 18: Modeled mass flow profile in Grand River downstream of Kitchener-Waterloo for 2008 June 5th.

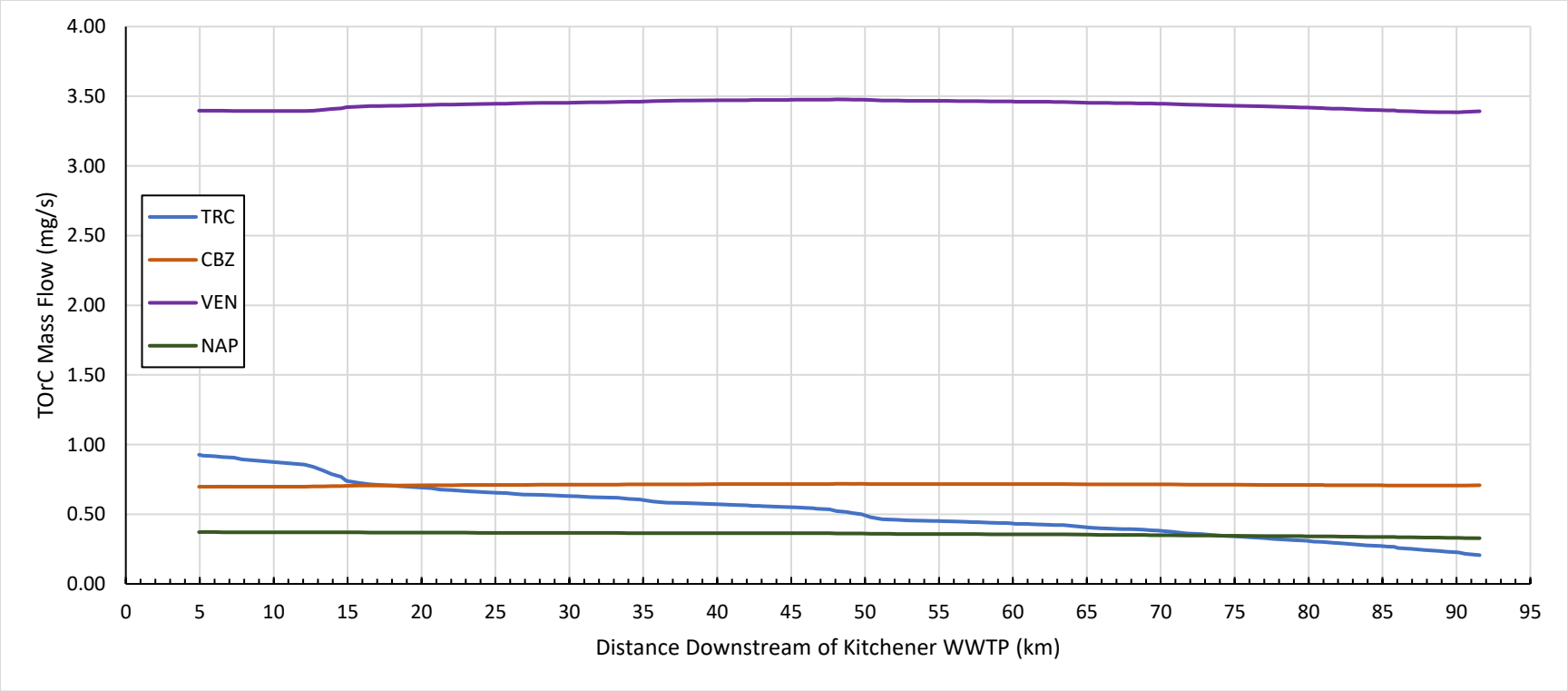

Figure 19: Modeled mass flow profile in Grand River downstream of Kitchener-Waterloo for 2015 October 12th.

Examining mass-flow eliminates the effects of dilution, leaving only the effects of phototransformation and biodegradation on the model. In particular, TRC appeared to degrade by approximately three quarters of its original concentration, while the other TOrCs appear to remain fairly conservative. The default values of degradation coefficients are re-stated in Table 21.

Table 21: Default degradation coefficients used in river model.

Contaminant	Biodegradation Coefficient [1/day]	Phototransformation Coefficient (wavelength 1) [(1/day)(W/m2)]
TRC	0.5	0.08
CBZ	0.0001	0.0001
VEN	0.0054	0
NAP	0.0256	0.036

The higher biodegradation and photolysis coefficients of TRC relative to the other rates align with the observed model results. Naproxen, with the second highest phototransformation rates, exhibited a similar profile to venlafaxine and carbamazepine. This indicates that phototransformation at the rates simulated did not have a sizeable impact on the modeled river concentrations relative to dilution and biodegradation. The relative impacts of biodegradation and phototransformation are explored further in Section 4.4.

Comparing model results for TOrC concentrations in the Grand River to observed data was challenging as there were limited points in the river where TOrC concentrations have been measured. Observations mainly exist close to Kitchener-Waterloo, upstream of the Speed River confluence. This made it difficult to distinguish between potential errors in the WASP TOrC transport model and any error inherited from the WWTP and source models.

Measurements of TOrC concentration in the Grand River did not align in time with model runs. Due to data limitations, results from the pre-upgrade model (2008-2009) were compared with measurements taken in the spring of 2010, while results from the post upgrade model (2015) were compared with measurements taken in the fall of 2017. The measurements were taken at the Kitchener WWTP outfall

near the start of the river model and at Blair, a site 7.86 km downstream of the model start. These measurements are compared with the mean modeled concentrations in Table 22.

Table 22: Comparison of mean observed and modeled TOrC concentrations pre- and post- WWTP upgrades, at the Kitchener WWTP outfall and at Blair.

a)

Pre-Upgrade WWTP	Modeled (2008)	Observed (2010)
TRC	129.63	164.33
CBZ	88.74	126.67
VEN	257.10	294.67
NAP	51.53	91.07

b)

Pre-Upgrade Blair	Modeled (2008)	Observed (2010)
TRC	124.23	76.65
CBZ	88.02	43.85
VEN	254.92	68.90
NAP	51.02	56.85

c)

Post-Upgrade WWTP	Modeled (2015)	Observed (2017)
TRC	52.16	19.63
CBZ	43.05	68.37
VEN	192.67	22.47
NAP	23.13	9.53

d)

Post-Upgrade Blair	Modeled (2015)	Observed (2017)
TRC	49.63	4.92
CBZ	42.66	16.73
VEN	190.87	6.10
NAP	22.87	5.69

The modeled concentrations appear to behave differently from the observed concentrations. In both model outputs, concentrations were similar for Kitchener and Blair. Only minor losses were predicted over this distance. This was not supported by observations, which showed more dramatic losses in all cases. Overall, it appears that the model failed to appropriately describe the translation of TOrC concentration between Kitchener and Blair.

There are a few possible explanations as to where the model may be falling short. Firstly, the removal mechanisms of biodegradation and phototransformation rate constants were too low. The rate constants used to describe these mechanisms were assumed from literature, and were not tested or verified as part of this study. It is also possible that there may be other mechanisms at work which contribute to TOrC removal. Settling and resuspension were not considered for this model, but could be relevant for a TOrC with a high sorption coefficient such as triclosan. In addition, groundwater exchange could dilute flow of

contaminants. These are all factors which were assumed to be negligible in the creation of the model, but which may impact TOrC transportation and removal in reality.

Another discrepancy exists between modeled and observed data in how the WWTP upgrades affected river concentrations. Even immediately downstream of the WWTP outfall, the observed TRC concentrations fell drastically from their pre-upgrade levels (~50-90%), in contrast to the milder drops in predicted concentrations (~33-50%). It can be assumed that this is at least partially a case of inherited error, as the same phenomenon was observed in the WWTP model output for VEN and TRC. However, this does not account for the under-estimation of NAP by the model. One possibility is that the interface between the WWTP river models does not appropriately represent loading of TOrCs into the river. This interface was implemented as a fixed-concentration boundary condition, with flow rates into the river taken from GRCA flow data rather than from WWTP measurements. If the model over-estimates the rate of flow from the WWTP boundaries into the river, it would cause an increase in the mass of contaminant being predicted in the river. The drop in observed concentration of TOrCs in the river could be indicating that these substances are being diluted to a greater degree than the model predicts.

Alternative approaches include using WWTP flow data or using a mass-flux boundary condition. Both of these approaches would allow for the model to better represent the system, and could potentially lead to predicts concentration profiles to behave more similar to observed trends.

4.4. Sensitivity Analysis

A sensitivity analysis of the TOrC fate parameters was performed. Eight coefficients from the WWTP and River models were analyzed one at a time, while all other coefficients were held constant. The relative impacts of these changes were gauged at the downstream end of the river, to evaluate the relative impacts of both WWTP parameters and river parameters. Relative impacts were expressed as normalized root-mean-squared differences (NRMSD), as explained in Section 3.5.2. The factor space and analysis scheme used can be found in Appendix F. The results of this analysis are shown in Table 23.

Table 23: Results of sensitivity analysis.

Coefficient		Contaminant Response (normalised)			
		TRC	CBZ	VEN	NAP
WWTP Model	Sorption	7.32E-03	5.30E-03	7.29E-03	5.30E-03
	Autotrophic biodegradation	9.09E-01	8.37E-01	6.27E-01	1.12
	Heterotrophic biodegradation	7.11E-01	1.61E-02	2.01E-01	1.61E-02
	Biodegredation	1.11	4.73E-03	4.64E-02	3.85E-01
River Model	Phototransformation (1)	8.03E-03	8.08E-05	8.07E-05	8.04E-03
	Phototransformation (2)	9.54E-02	1.01E-03	0	9.55E-02
	Phototransformation (3)	0	0	0	5.13E-01
	Phototransformation (4)	0	0	0	6.48E-01

Comparing normalized RMS differences reveals the relative impact of each parameter on TOrC concentrations when compared to the base case. These differences were normalized using the standard deviation, meaning that values greater than 1 indicate RMS differences greater than the standard deviation. This occurred in two cases: the autotrophic biodegradation of naproxen, and the biodegradation in the river of triclosan. Other parameters with relatively high (greater than the mean of 0.3) NRMSD values were the heterotrophic biodegradation of triclosan, river biodegradation and phototransformation of naproxen, and autotrophic biodegradation for all TOrCs.

The observation that all TOrC concentrations were sensitive to autotrophic biodegradation implies that changes to WWTP processes can have sizeable impacts in the Grand River, even far (>90km) downstream. However, it must be noted that this observation hinges upon the values of biodegradation used in analysis. These values were obtained from manual calibration of WWTP model predictions with synthetic inputs to observed data from a different year. As such, the conclusion that autotrophic biodegradation is strongly linked to TOrC concentrations in the river needs further verification. These results are, however, consistent with the observations of (Olumuyiwa O. Ogunlaja & Parker, 2018) that demonstrated concentrations of TOrCs were more sensitive to removal by autotrophic bacteria than by heterotrophic organisms, and also with the observed drop in TOrC concentrations in the Grand River after WWTP upgrades (M.J. Arlos et al., 2015). Further investigation with a more refined model and more

frequent measurements can better quantify the sensitivity of ecosystem TOrC concentrations to autotrophic biodegradation.

The levels of TOrC modeled in the river were relatively in-sensitive to changes in phototransformation at the lower wavelengths. Since most contaminants modeled do not experience phototransformation at the higher wavelengths, this in effect meant that changes in phototransformation coefficients had little to no impact on model results. The exception was naproxen, which was found to be more sensitive at higher solar wavelengths (315-354 nm). This increase in sensitivity occurred despite the fact that NAP phototransformation coefficients (and ranges for sensitivity analysis) became smaller as the wavelengths increase. This implies that phototransformation for lower wavelengths (< 315 nm) do not have a noticeable impact on modeled TOrC concentrations, even at higher coefficient values.

5. Conclusions

An integrated source-to-fate model of TOrCs which is more grounded in physical processes than previous models (Arlos et al., 2014; Hosseini, 2011) was developed. The consumption-excretion method used to simulate TOrC loadings on wastewater had the advantages of being relatively simple and based on reliable data. It has been used successfully in prior studies and is considered reliable on these grounds. However, this source model should be calibrated and validated with data on TOrC concentrations in WWTP influent. This would enhance the reliability of source model predictions going foreword, and also allow for an isolated calibration of the WWTP model without inherited error from the raw wastewater data.

The WWTP model developed in this study was unique in its approach to calculating TOrC biodegradation. The use of autotrophic and heterotrophic bacteria concentrations to estimate TOrC removal appears to have been effective, although the results could not be verified with a measurable degree of certainty. Predicted effluent concentrations were in the same general range as observed values (~100 to 700 ng/l pre-upgrades and ~30 to 300 ng/l post-upgrades), but the data describing observed concentrations was of insufficient frequency to establish correlation. It is recommended that additional data on TOrC concentrations in the WWTP influent and effluent be gathered over a greater length of time. This would allow for calibration and validation of the mechanistic removal coefficients in WWTP processes independent of other model compartments. It is also recommended that, when possible, the model be updated with actual values of aeration basin volume, rather then the estimates used at some places in this study.

The river model appeared to under-estimate TOrC removal in the river, based on observations between the WWTP outfalls and the Speed River confluence. This could be due to low values for the biodegradation and photolysis rate constants that were assumed from the literature. Alternatively, it could be that other mechanisms are impactful which were not accounted for in the model. Gathering time-

profile observations of TOrC concentration at multiple points in the river would allow for the calibration of removal rate constants. In particular, measurements from farther downstream (such as around Brantford) could enable more reliable calibrations of removal rates in the river than comparing data over a relatively small distance, such as within the Kitchener-Waterloo area. Modeling of other mechanisms, such as settling and resuspension or dilution from groundwater exchange, would require extensive data on the Grand River beyond what was used to assemble this model. Adding this functionality would be a challenge, but it may be the only way to effectively model substances like TRC which are more susceptible to adsorb onto solids. Additionally, certain mechanisms may be present in the downstream reaches of the Grand River, where the river is wider and the flow rate is slow. Settling and resuspension may be important enough to be worth modeling under these conditions, and anoxic biodegradation may be present at greater depths.

The combined model framework was analysed to determine the sensitivity of TOrC responses to select removal mechanism rates at the end of the model, near Ohsweken. It was found that TRC concentrations were sensitive to changes in the heterotrophic biodegradation rate and river biodegradation rate constants, and NAP was sensitive to phototransformation rate constants in the river. All TOrCs were sensitive to changes to the autotrophic biodegradation rate constant in WWTPs. Phototransformation appeared to only be a relevant factor at higher bands of solar wavelength (>315 nm). In the WWTP, autotrophic biodegradation rates were found to be a larger factor in determining TOrC concentrations than heterotrophic biodegradation rates, despite the larger concentrations of heterotrophic biomass. However, it is worth noting that these results are based on a manual sensitivity analysis using only five different values of each rate constant. In future studies, updates to WASP 8 may enable a fully automated sensitivity analysis to be run, allowing for a more detailed and thorough analysis of the impacts of different removal mechanisms on TOrC levels in the ecosystem.

The framework used for combining models made use of a combination of file-based and database storage for data. Moving foreword, converting the framework to make better use of databases would make it

simpler and more intuitive to download, alter, and use the combined model. Converting the source model from a spreadsheet to a script is another change that would make it easier to use and alter the model. Both of these measures would make for a more robust integrated model, making it easier to add additional TOrCs or WWTPs to the project in the future.

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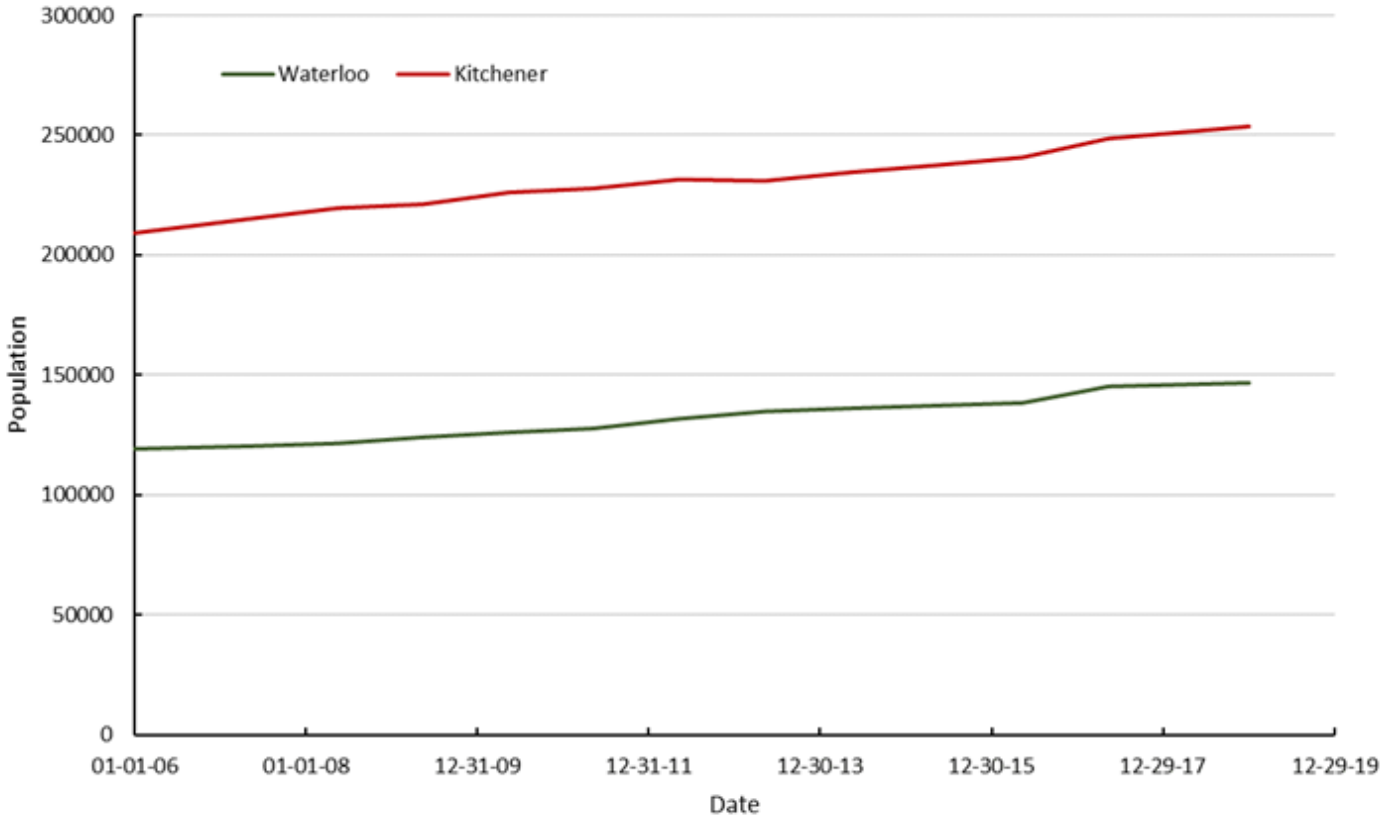
APPENDICES

APPENDIX A

Population data and projections and interpolations.

Table 24: Annual populations in Kitchener and Waterloo (Region of Waterloo, 2018)

Year	Waterloo Population	Kitchener Population
2008	121413	219596
2009	124006	221223
2010	126029	226106
2011	127688	227761
2012	131776	231488
2013	134851	230922
2014	136179	234466
2015	137322	237417
2016	138464	240669
2017	145381	248481
2018	146288	251544


300000
250000
200000
150000
100000
50000
0
Population
Waterloo
Kitchener
01-01-06
01-01-08
12-31-09
12-31-11
12-30-13
12-30-15
12-29-17
12-29-19
Date

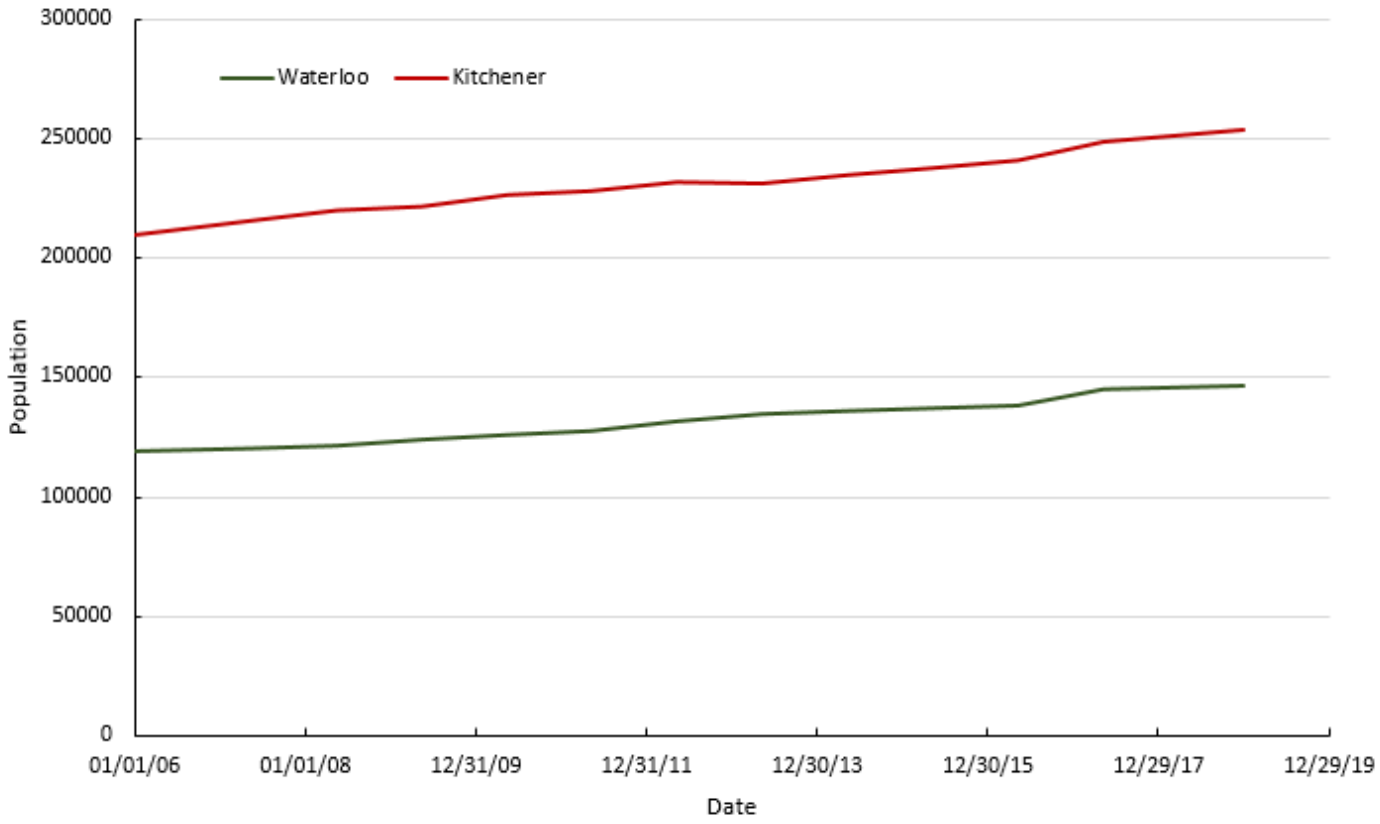


Figure 20: Daily population projections based on annual values for Kitchener and Waterloo

APPENDIX B

The WWTP model was calibrated first for conventional parameters, then for TOrC decay rates. Calibration of conventional parameters was performed through OSTRICH, minimizing RMSD between modeled and observed MLSS profiles as a target variable. This was performed using the model of the Kitchener WWTP train "A" for the pre-upgrade time period. The parameters modified are summarized in Table 25.

Table 25: Summary of calibration of WWTP model conventional parameters

Parameter	Description	Initial Value	Lower Bound	Upper Bound	Optimized
Y_H	Heterotrophic biomass yield coefficient (-)	0.5	0.4	0.6	0.3831
Y_A	Autotrophic biomass yield coefficient (-)	0.12	0.01	0.3	0.12
K_S	bCOD half rate coefficient (mg/l)	15	5	30	6.563
K_N	Ammonia half rate coefficient (mg/l)	0.5	0.1	5	0.5
k_{d_h}	Heterotroph cell decay rate (/d)	0.09	0.06	0.15	0.09
k_{d_a}	Autotroph cell decay rate (/d)	0.06	0.01	0.15	0.028
Y_k	Heterotrophic yield coefficient (/d)	8	4	12	8
μ	Autotrophic yield coefficient (/d)	0.9	0.4	4	0.9
f_d	Fraction of cells as detritus (-)	0.12	0.01	0.30	0.2793
f_{VSS}	Volatile fraction of suspended solids (-)	0.05	0	0.15	0.132
t_{delay}	Time span used for input-averaging (d)	5	1	30	6

(Metcalf & Eddy, 2014)

The OSTRICH program uses a Ostin.txt file to define the factor space, objective variable, and other factors relevant to the calibration. The text of this file as used in this study is shown below.

```
# Configuration file for OSTRICH
ProgramType       DDS
ModelExecutable         BaseModelOst.m
ModelSubdir             .
ObjectiveFunction WSSE

PreserveModelOutput     no

BeginFilePairs
ParamOst.csv; PharmParamOst.csv
EndFilePairs

BeginExtraFiles
# list output files
K1_OstOutput.csv
```

```
EndExtraFiles

# Parameter Specification
BeginParams
#parameter        init.       low   high  tx_in tx_ost      tx_out
Y_het             0.5         0.4   0.6   none  none        none
Y_aut             0.12        0.01  0.3   none  none        none
K_sub             15          5     30    none  none        none
K_nit             0.5         0.1   5     none  none        none
b_het             0.09        0.06  0.15  none  none        none
b_aut             0.06        0.01  0.15  none  none        none
k_sub             8           4     12    none  none        none
u_aut             0.9         0.4   4     none  none        none
f_decay           0.12        0.01  0.30  none  none        none
f_bio_VSS         0.05        0     0.15  none  none        none
t_delay           5           1     30    none  none        none

EndParams


# list the model configurations you want to run
#BeginInitParams
#

BeginObservations
#observation      value weight      file              keyword           line
      column      token
MLSS_RMSerr 0     1     K1_OstOutput.csv  OST_NULL    0     0     ','
EndObservations
```

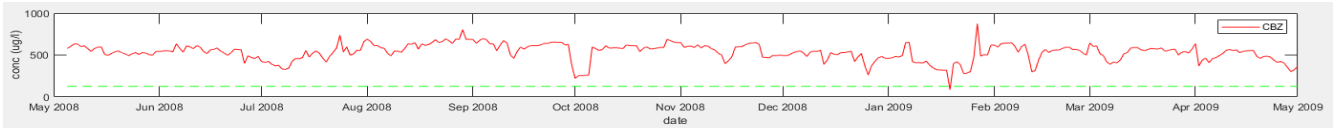
APPENDIX C

The autotrophic biodegradation coefficients (Ka) for each TOrC were calibrated manually to fit modeled TOrC concentrations in WWTP effluent to observed values. This was performed using the model of the Kitchener WWTP train "A" for the pre-upgrade time period. Root-mean-squared difference between modeled and observed concentration in WWTP effluent was used as a gauge of good fit (lower = better). Note that observations are from fall of 2010, whereas the model is generating predictions for summer 2008 to spring 2009. Values highlighted in yellow were selected as optimal.

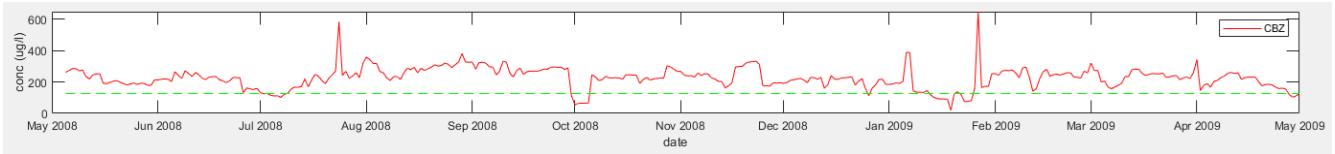
CBZ

Ka = 0
RMS = 725

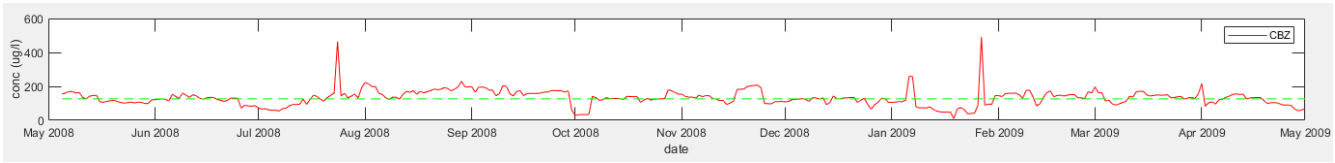
Ka = 1
RMS = 419



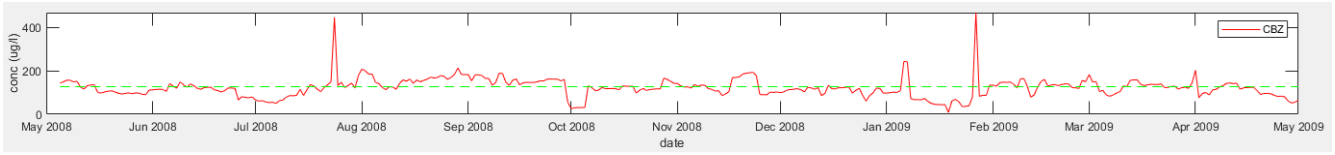
Ka = 5
RMS = 120



Ka = 10
RMS = 47

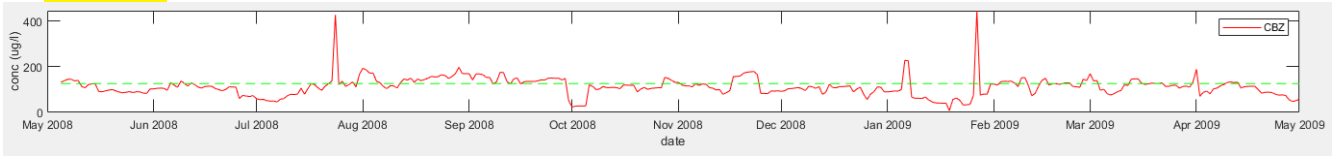


Ka = 11
RMS = 45



Ka = 12

RMS = 44



Ka = 13
RMS = 45

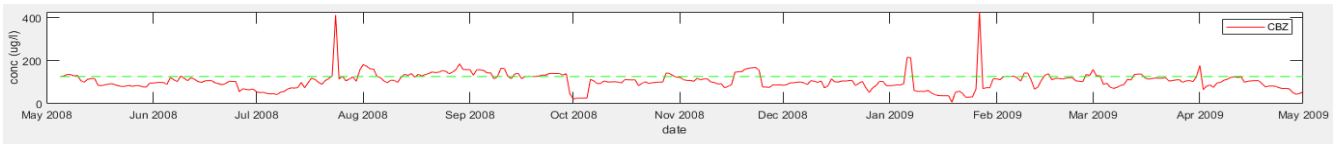
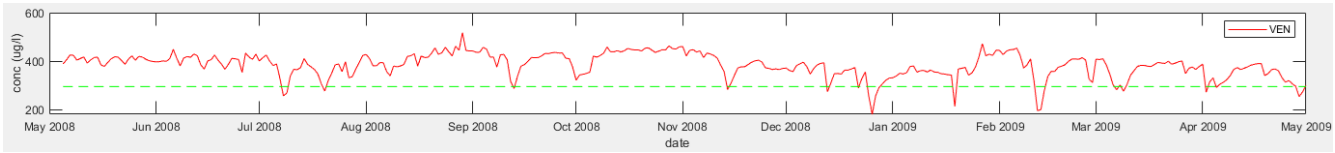


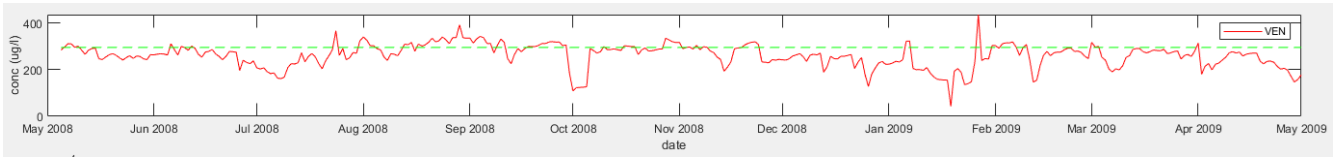
Figure 21.1-7: Modeled CBZ concentration at Kitchener A effluent under different rates of autotrophic biodegradation

VEN

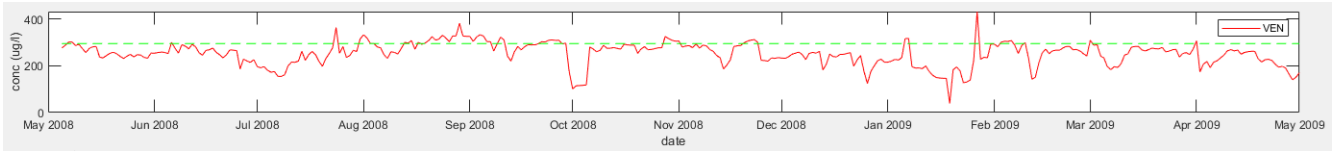
Ka = 0.1
RMS = 101



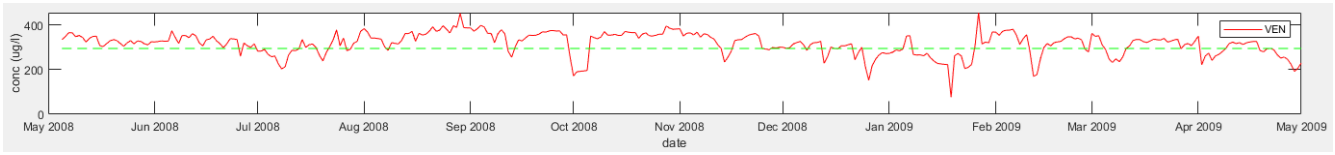
Ka = 1
RMS = 60



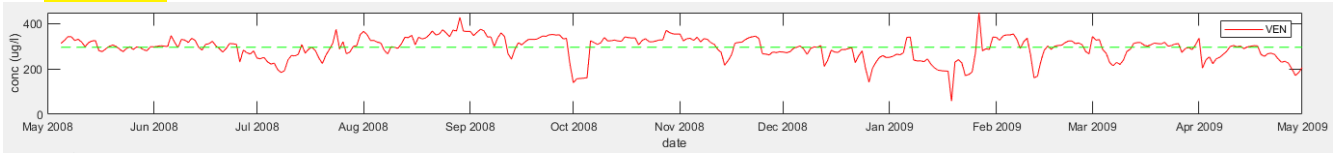
Ka = 1.1
RMS = 65



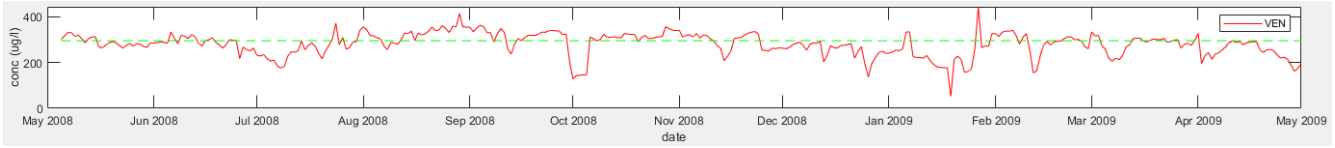
Ka = 0.5
RMS = 54



Ka = 0.7
RMS = 50



Ka = 0.8
RMS = 52



Ka = 0.6
RMS = 51

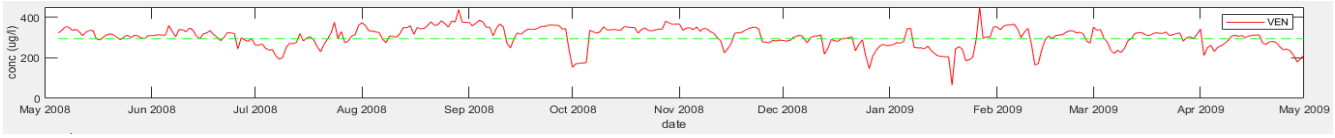
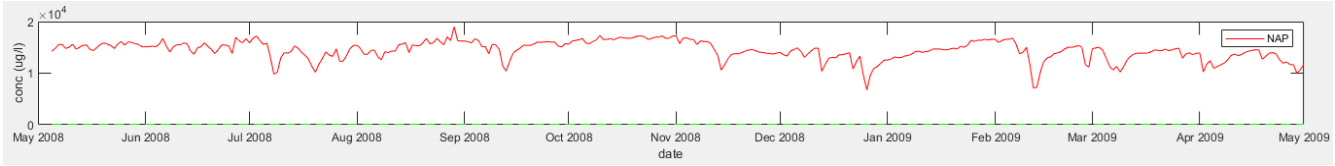


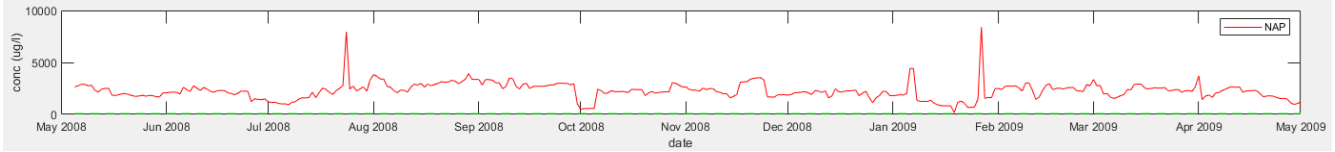
Figure 22.1-7: Modeled VEN concentration at Kitchener A effluent under different rates of autotrophic biodegradation

NAP

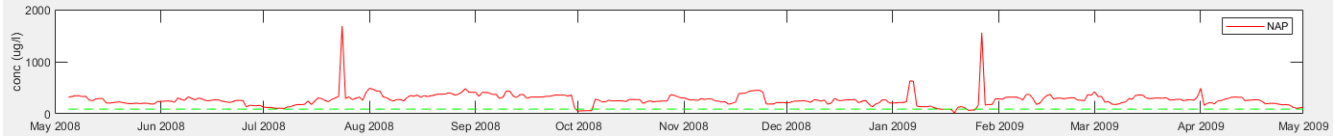
Ka = 0
RMS = 14,467



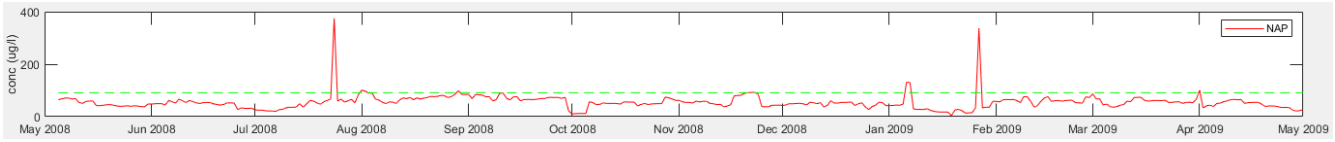
Ka = 10
RMS = 2,319



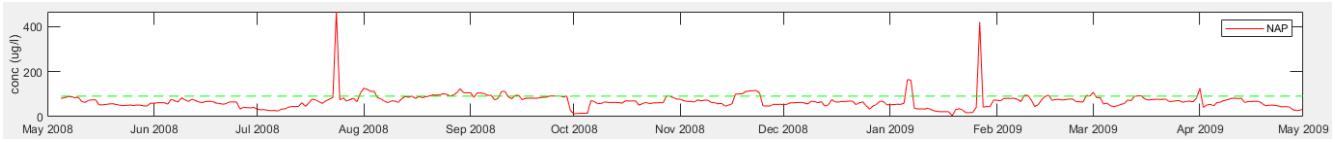
Ka = 100
RMS = 225



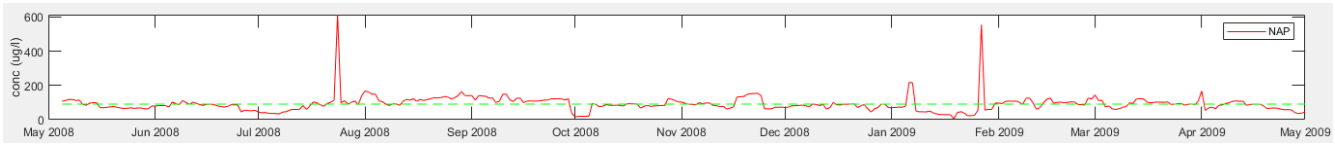
Ka = 500
RMS = 46



Ka = 400
RMS = 42.4



Ka = 300
RMS = 48



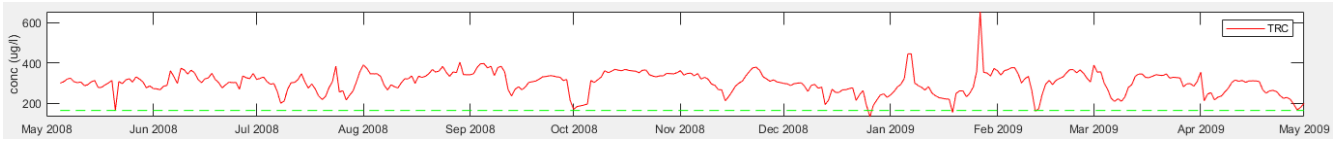
Ka = 390
RMS = 42.3

Ka = 410
RMS = 42.6

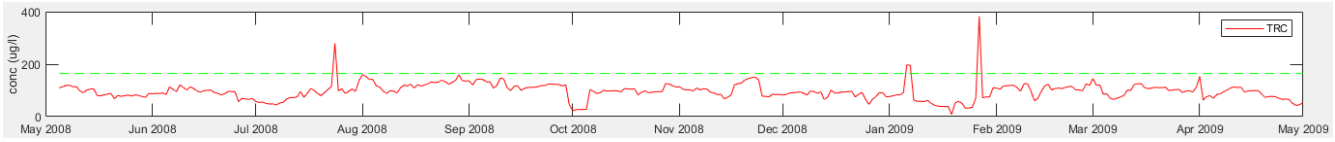
Figure 23.1-6: Modeled NAP concentration at Kitchener A effluent under different rates of autotrophic biodegradation

TRC

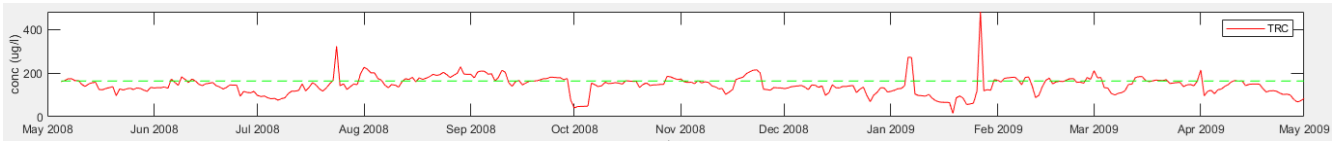
Ka = 0
RMS = 149



Ka = 10
RMS = 74

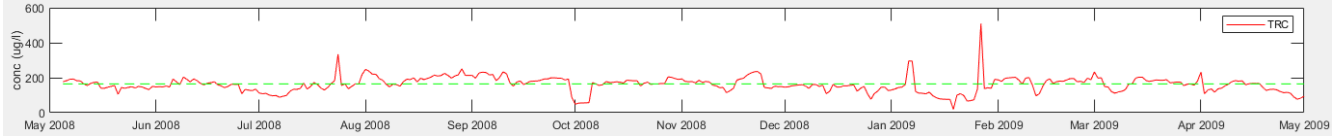


Ka = 5
RMS = 46



Ka = 6
RMS = 51

Ka = 4
RMS = 44



Ka = 3
RMS = 50

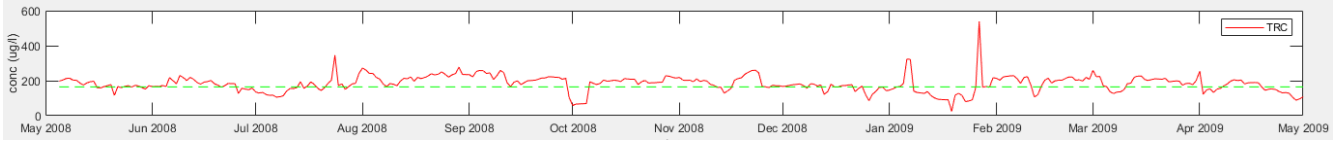


Figure 24.1-5: Modeled TRC concentration at Kitchener A effluent under different rates of autotrophic biodegradation

SUMMARY

CHEM	Ka	RMS-Error
CBZ	12	44.1
VEN	0.7	50.5
NAP	400	42.4
TRC	4	44.4

Notes:
Results after quick manual-visual calibration. Literature values assumed for heterotrophic consumption and sorption. Data used for calibration: 2010 fall data from Servos Lab.

More accurate numbers can be obtained by: using 2008 data, using more frequent observed data, using calibrated values for heterotrophic consumption and sorption.

More precise numbers can be obtained by: using automated calibration methods, using more frequent observed data.

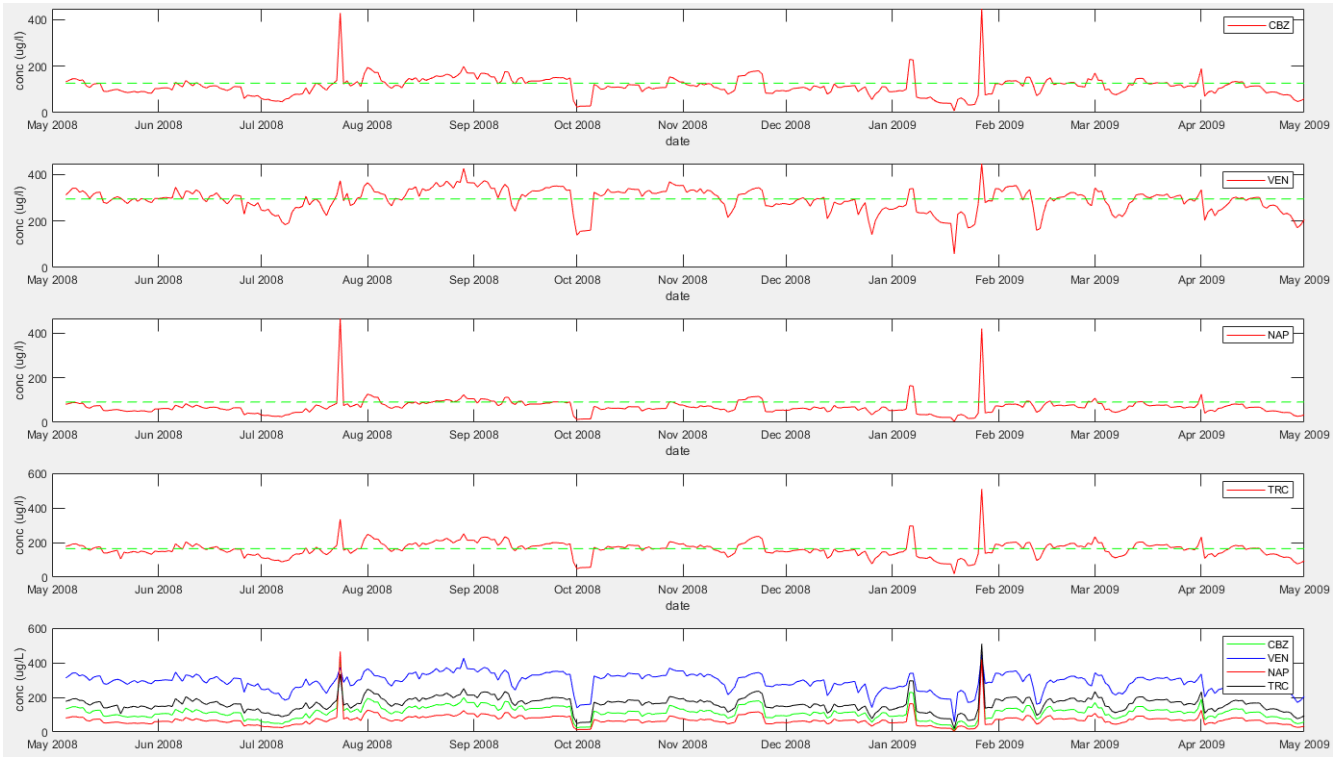


Figure 25: Modeled TOrC effluent curves for Kitchener A pre-upgrades using calibrated autotrophic biodegredation

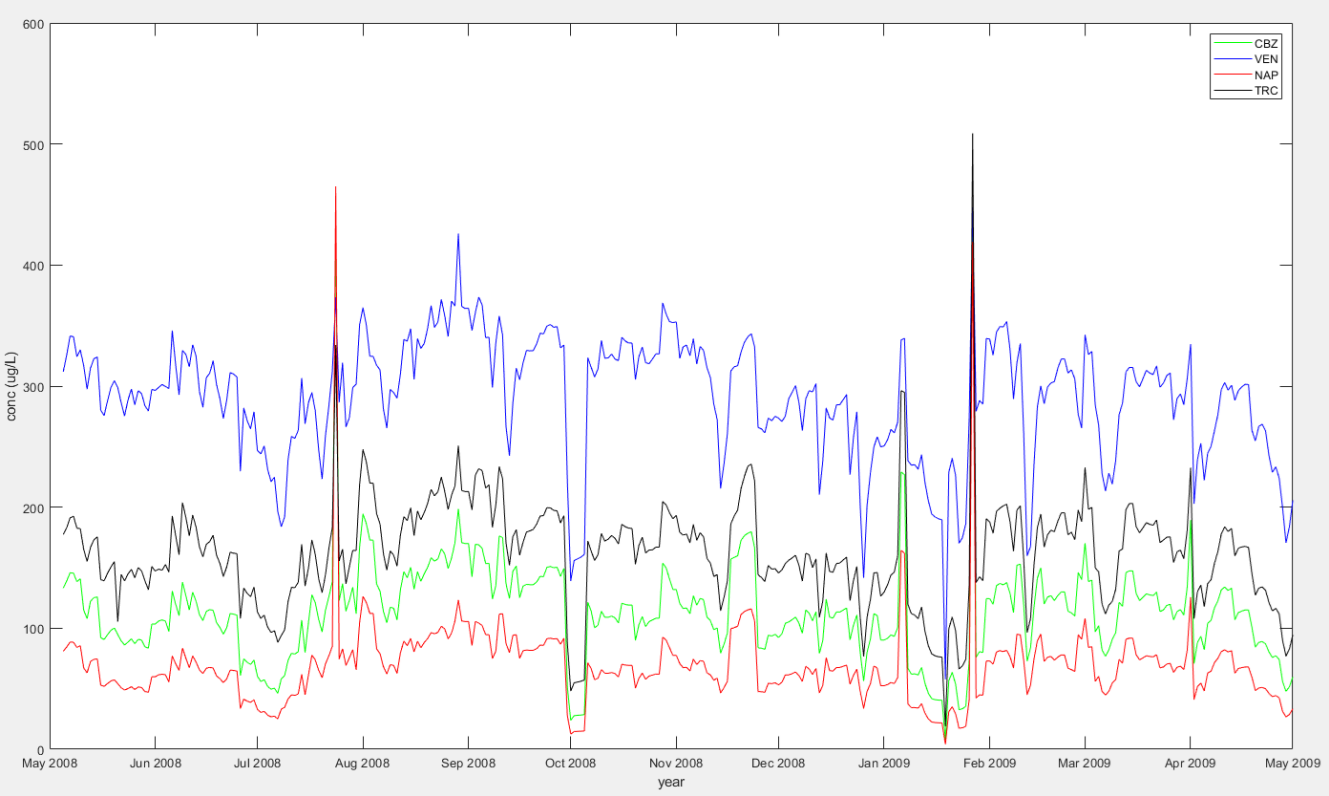


Figure 26: Modeled TOrC effluent curves for Kitchener A pre-upgrades using calibrated autotrophic biodegradation, expanded for clarity

APPENDIX D

The WASP hydraulic model was based on a GRCA HEC-RAS model and was calibrated using flow gauge data from the GRCA.

The model was calibrated for water elevation at the GRCA Galt monitoring station for the year of 2014. This was then validated by comparing modeled results to measured observations for Galt in 2008, and Brantford for 2014.

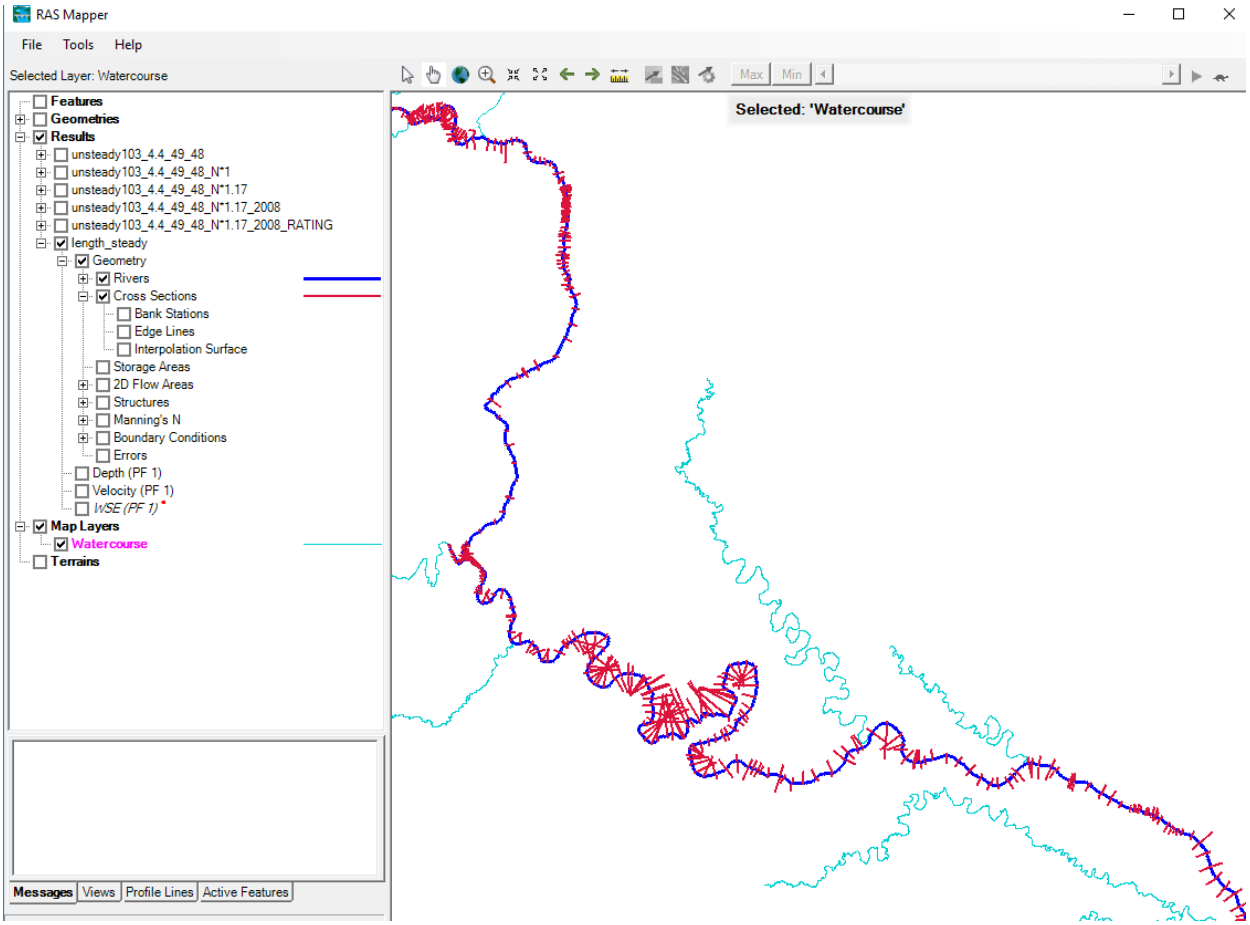


Figure 27: Cross Sections in HEC-RAS

Hydraulic calibration (for Mannings n values) was performed at Galt (HECRAS_Cross Section 322) for 2014. Depths at Galt were converted to geodetic survey of Canada datum by adding 259.08m. Calibrated Manning values are equal to 117% of the GRCA HEC-RAS model values.

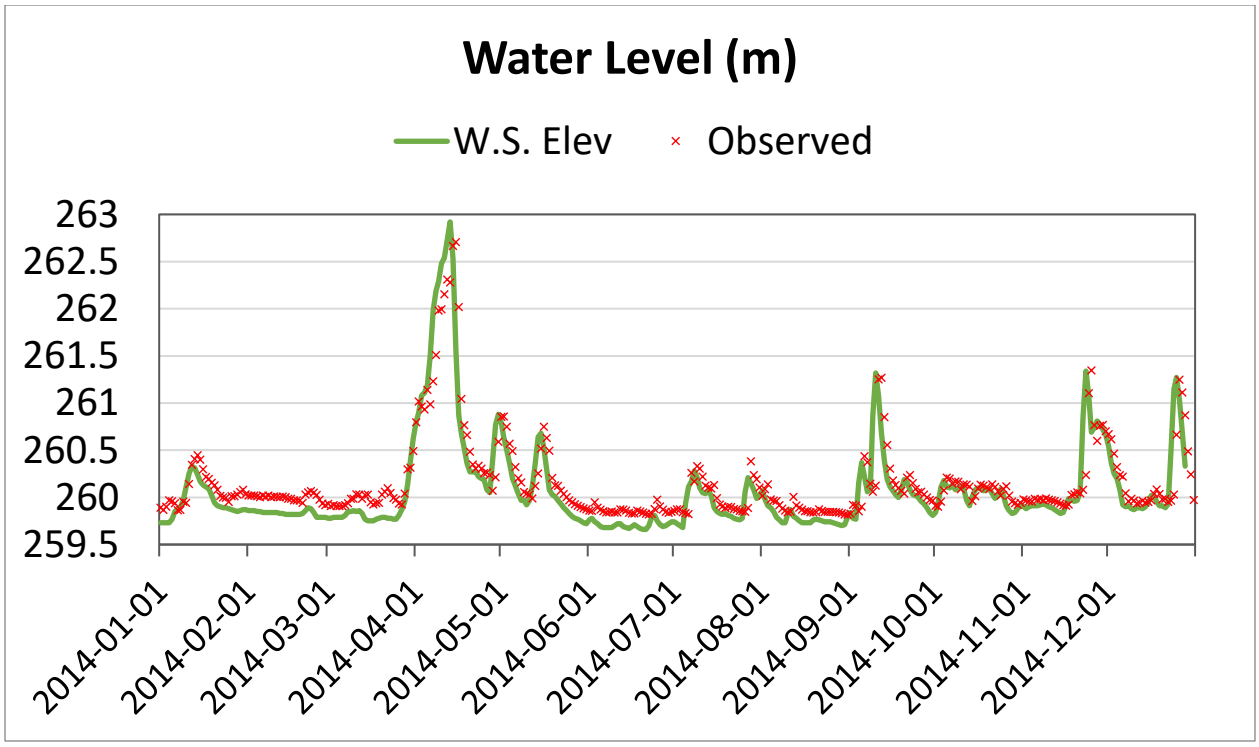


Figure 28: Observed and modeled water level after calibration, Galt 2014

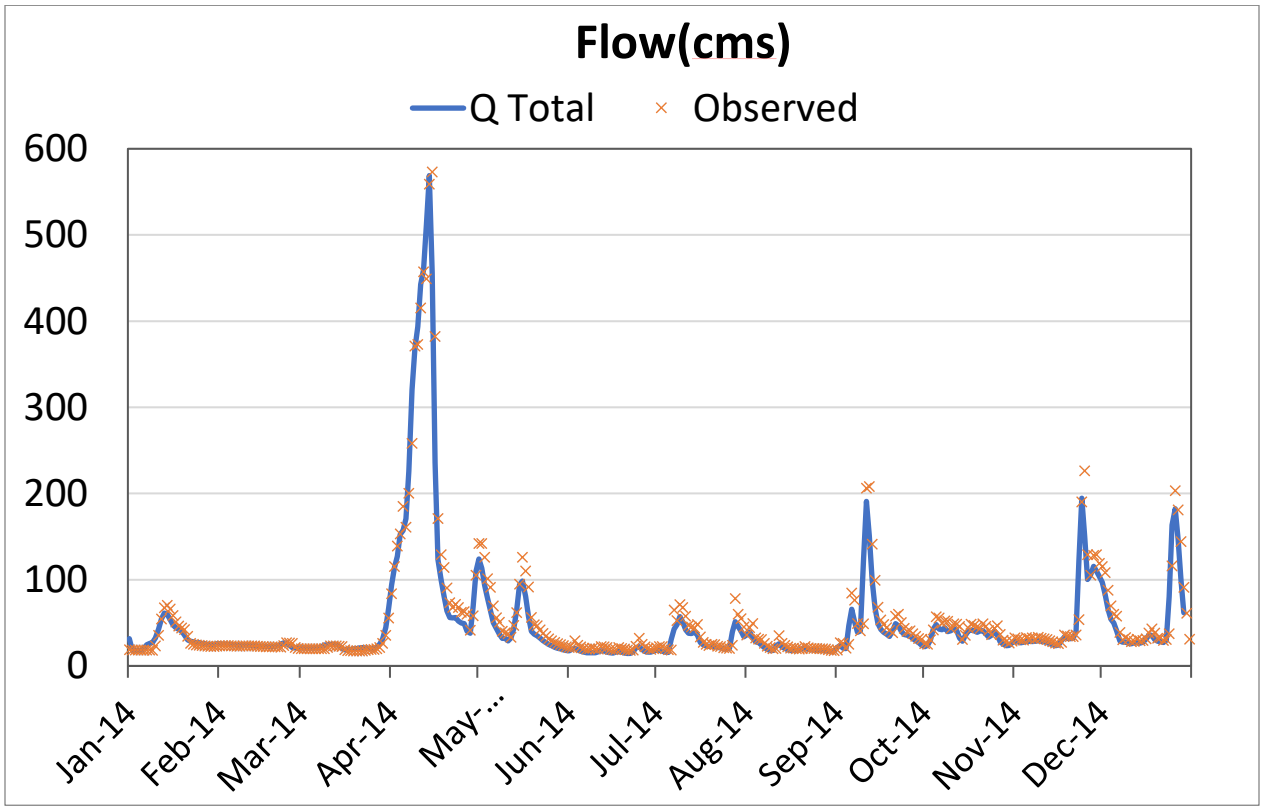


Figure 29: Observed and modeled flow rate after calibration, Galt 2014

Validation at Galt for 2008 and Brantford (HECRAS_Cross Section 201, assumed datum of 195.682m) shown below.

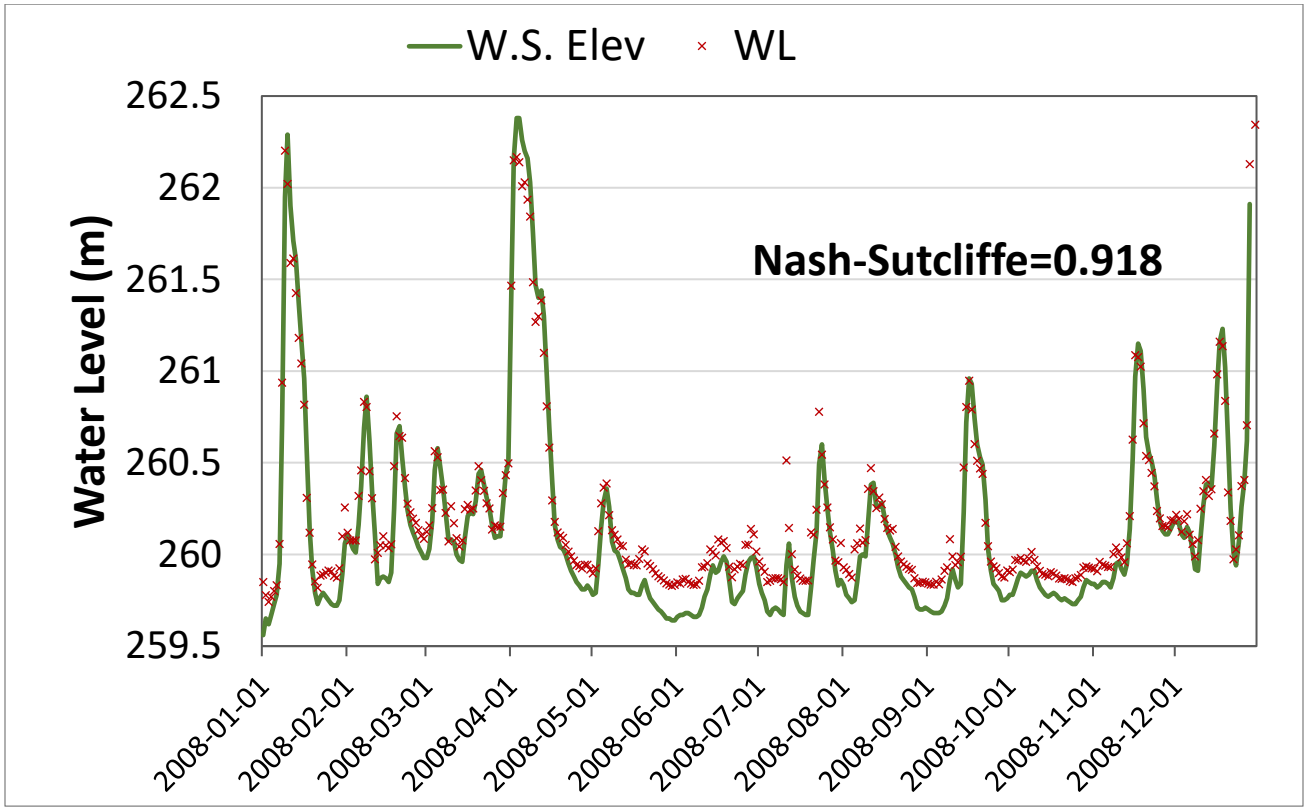


Figure 30: Observed and modeled water level after calibration, Galt 2008

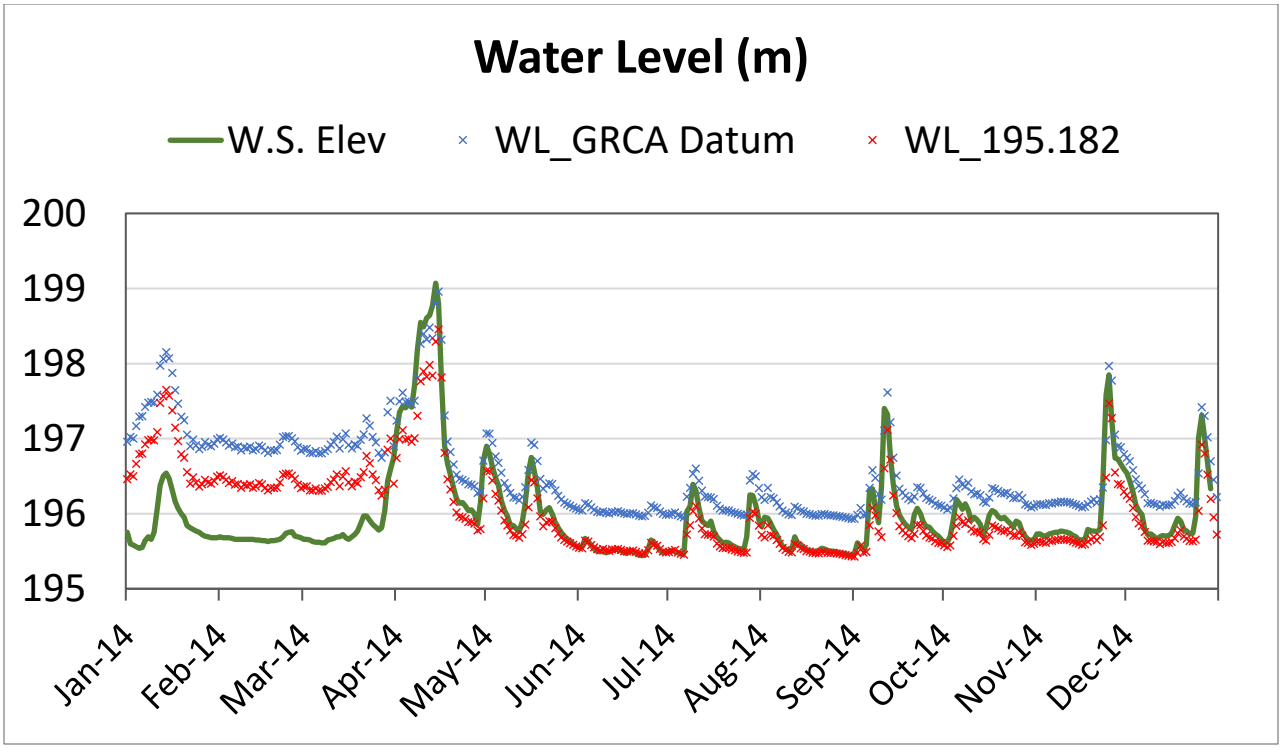


Figure 31: Observed and modeled water level after calibration, Brantford 2014

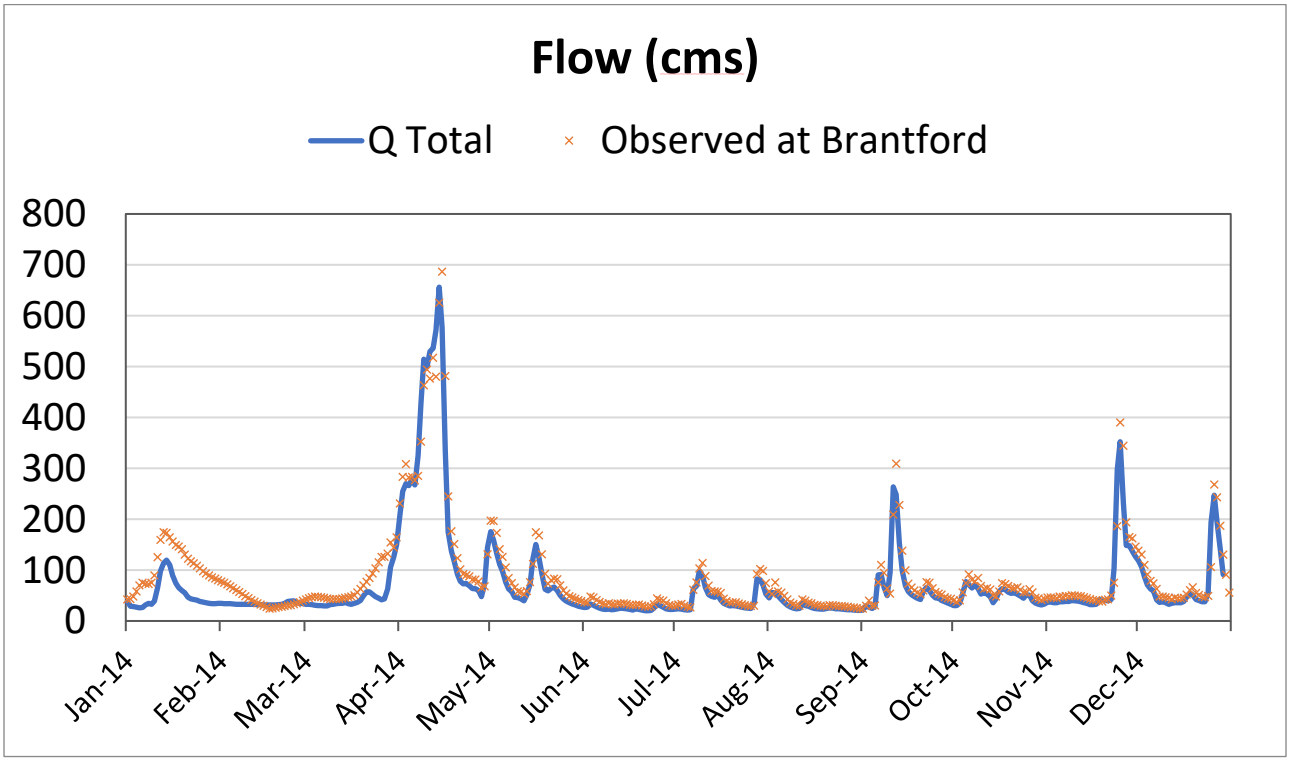


Figure 32: Observed and modeled flow rate after calibration, Brantford 2014

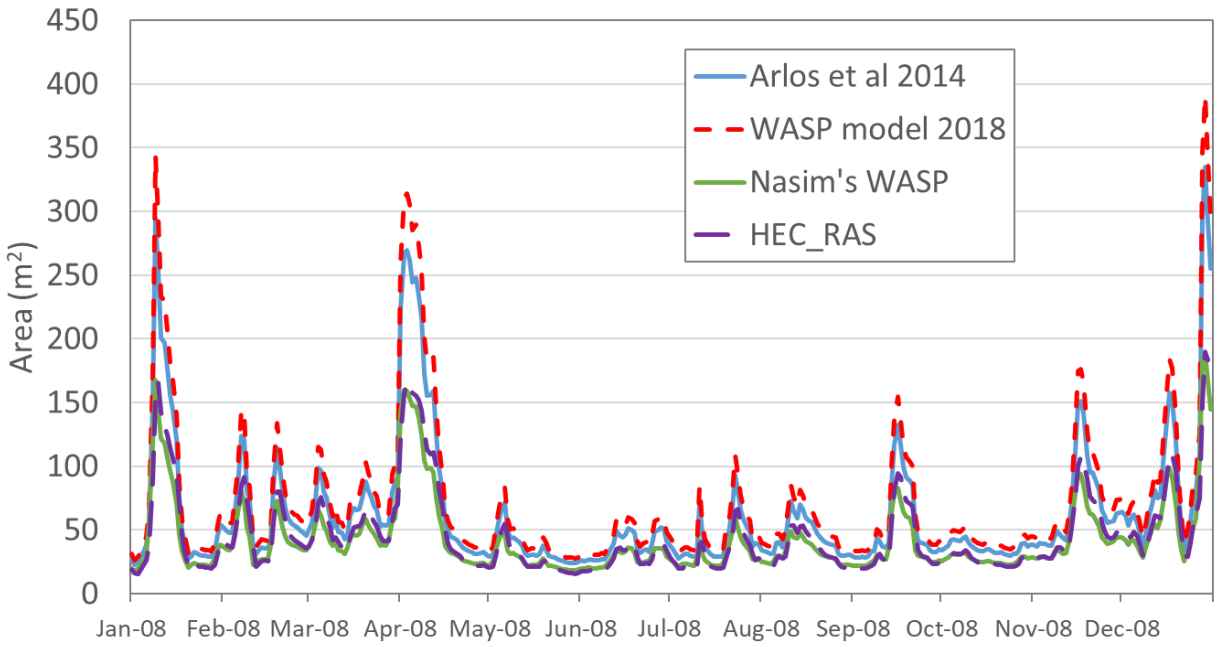


Figure 33: Comparison between WASP models. "WASP model 2018" is model used by (Maricor J. Arlos et al., 2018). "Nasim's WASP" is model used in this study.

APPENDIX E

Chloride concentration data from GRCA sampling stations was used to calibrate the WASP model for contaminant transportation.

PWQMN STATIONS
Grand River at Freeport 16018404102
Schneider Creek 16018411702
Grand River at Blair 16018401202
Speed River 16018410102
Mill Creek 16018413102
Grand River at Glen Morris 16018401002
Nith River 16018400902
Withemans Creek 16018410602
Grand River at Brantford 16018402702
Fairchild Creek 16018409302

LGL STATIONS
Kitchener Upstream
Kitchener Downstream Near
Kitchener Downstream Far
Schneider Creek
Preston Upstream
Preston Downstream Near
Galt Upstream
Galt Downstream Near
Galt Downstream Far
Hespeler Upstream
Hespeler Downstream Near
Hespeler Downstream Far

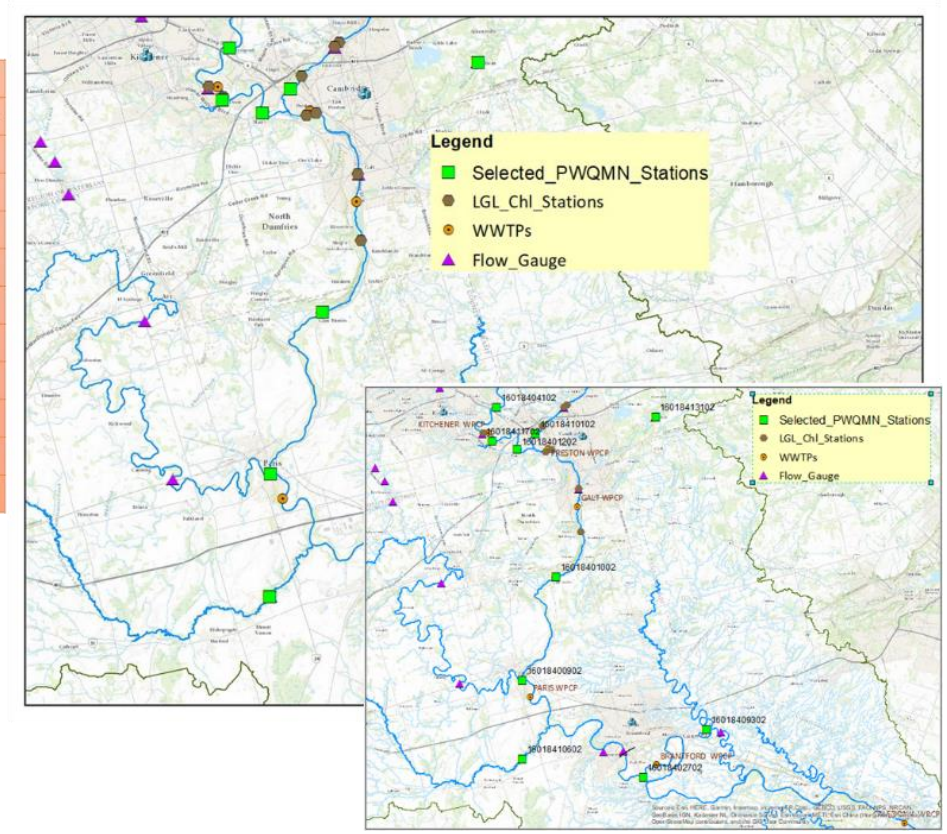


Figure 34: Locations of chloride sampling stations in Grand River

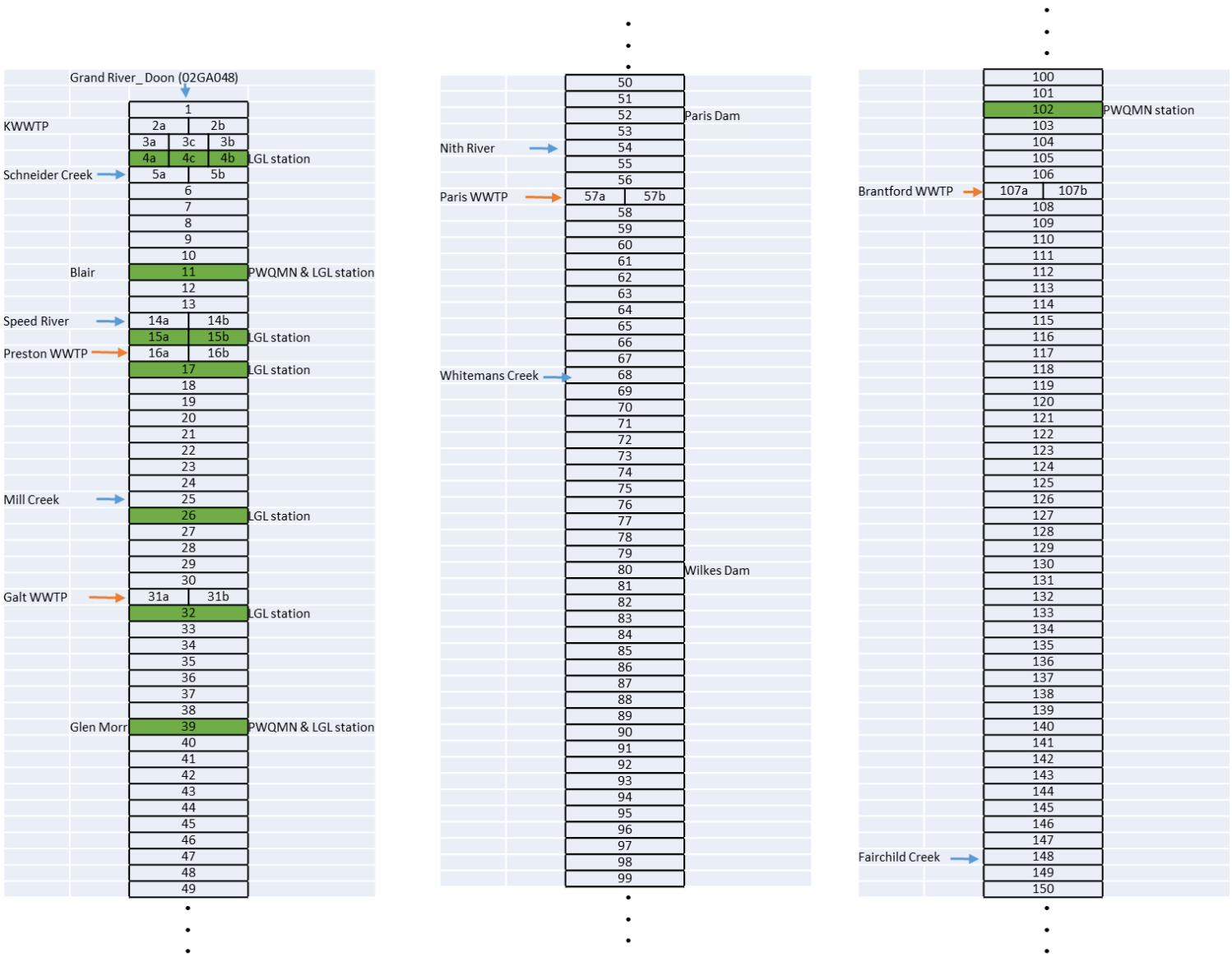


Figure 35: Locations of chloride sampling stations in WASP segmentation

Simulated and measured chloride concentrations were compared at sites throughout the model to determine if correlation was statistically significant ($\alpha = 0.05$).

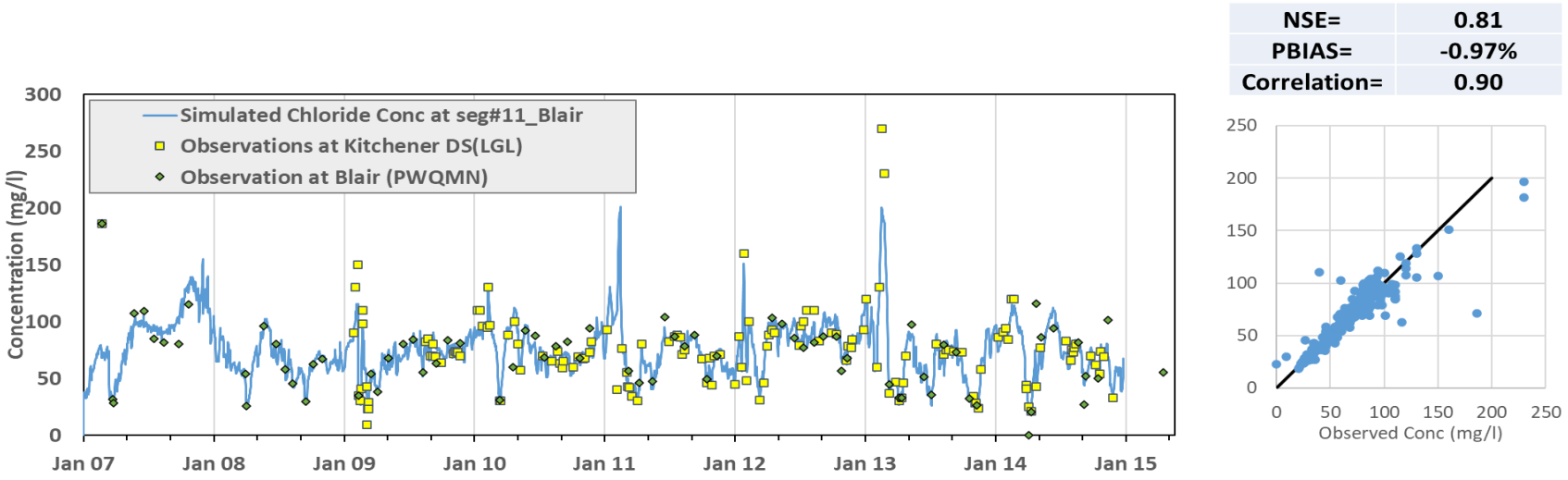


Figure 36: Simulated and measured chloride concentrations at Blair

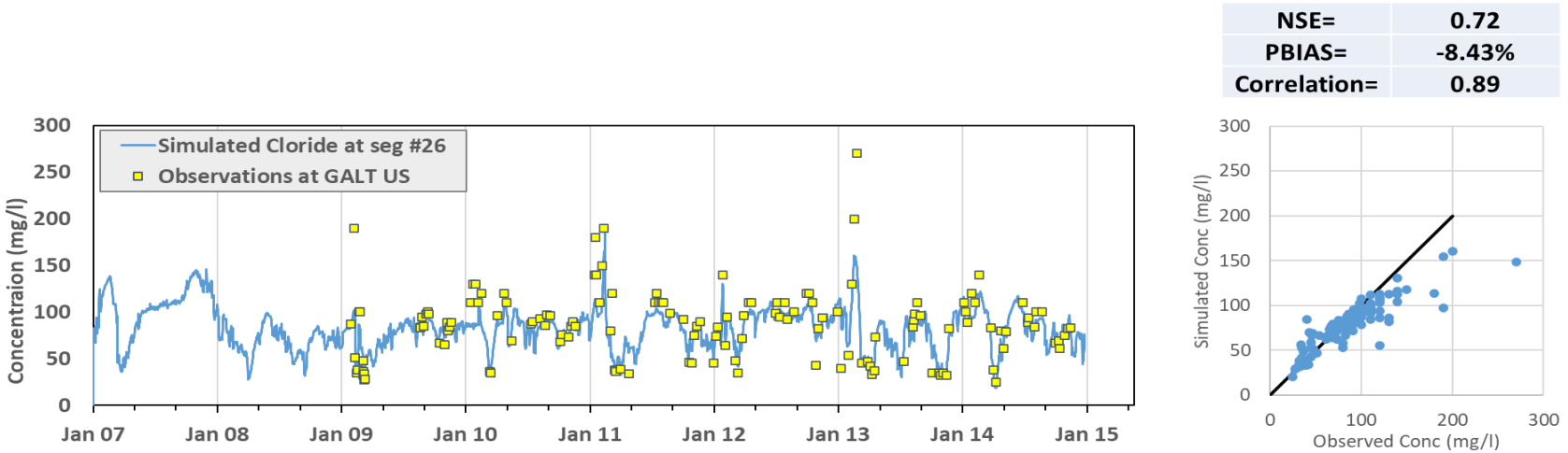


Figure 37: Simulated and measured chloride concentrations at Galt

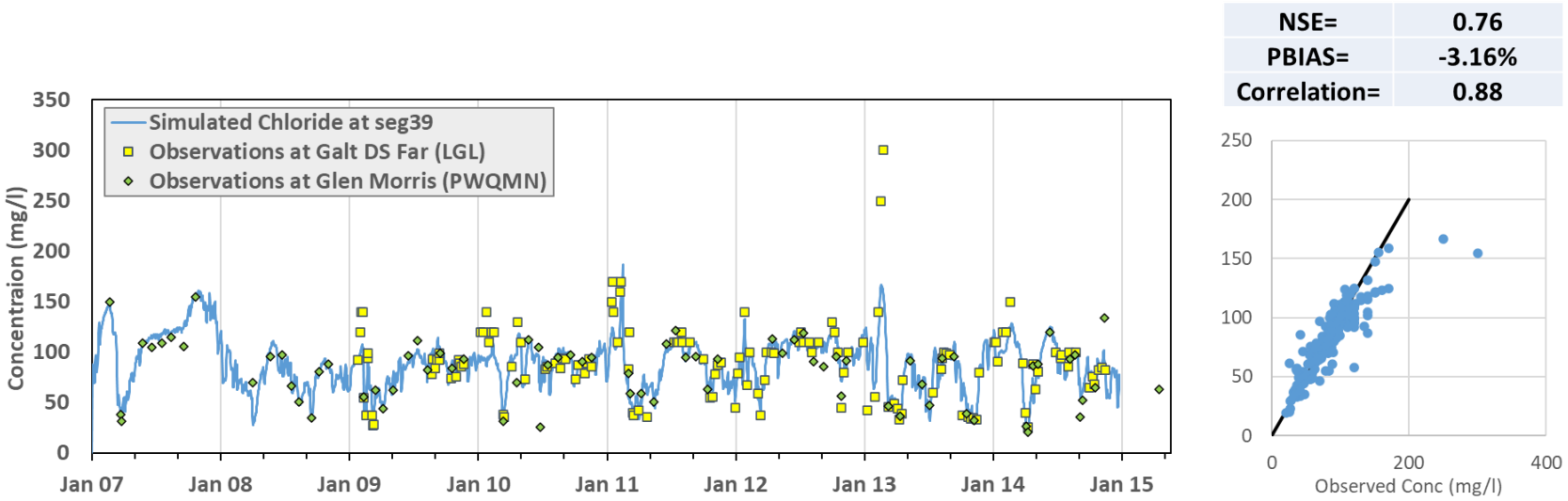


Figure 38: Simulated and measured chloride concentrations at Glen Morris

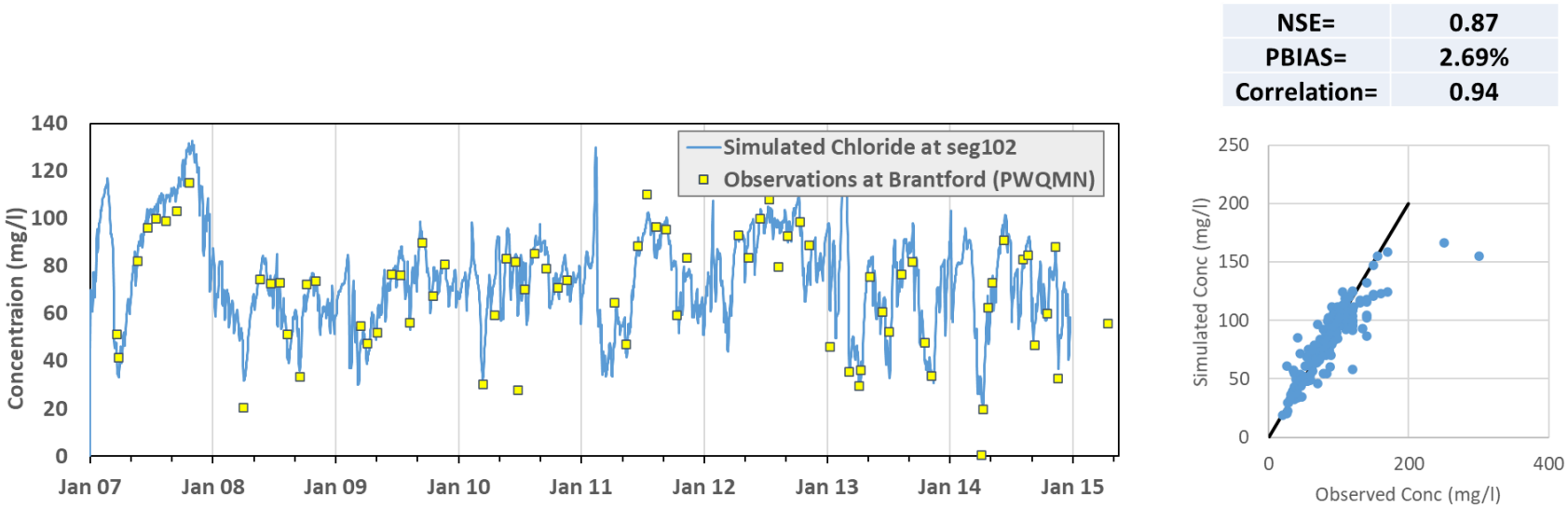
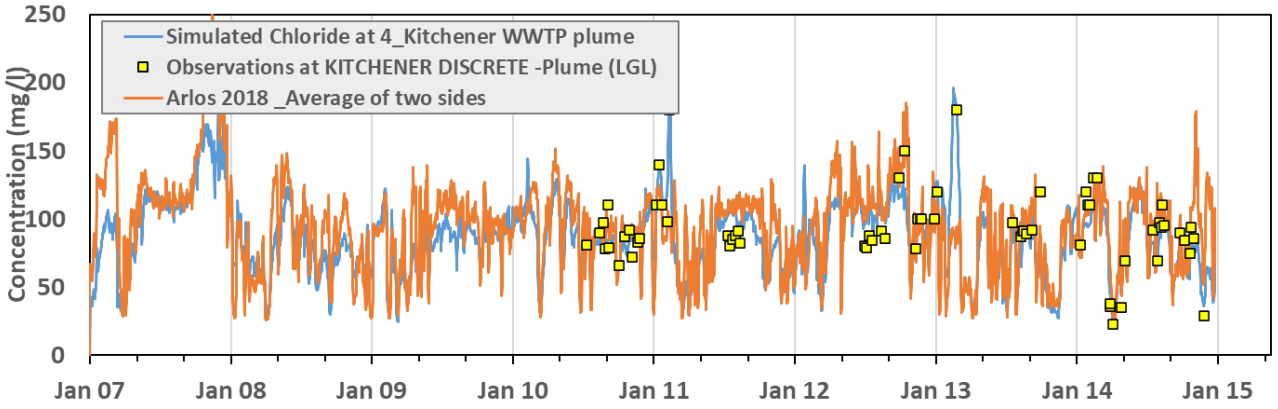
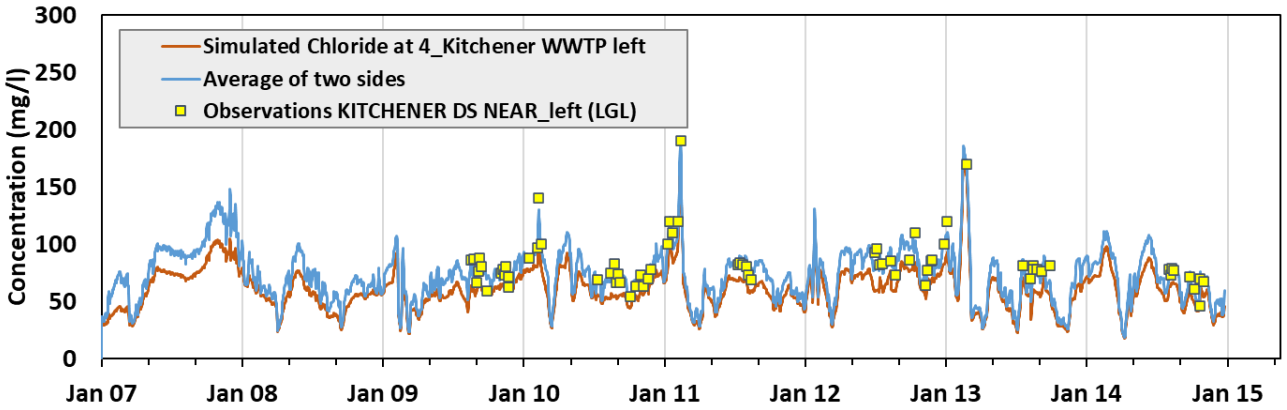


Figure 39: Simulated and measured chloride concentrations at Brantford



NSE=	0.61
PBIAS=	-12.34%
Correlation=	0.88

Figure 40: Simulated and measured chloride concentrations at Kitchener WWTP (plume)



NSE=	0.92
PBIAS=	0.29%
Correlation=	0.96

Figure 41: Simulated and measured chloride concentrations at Kitchener WWTP (near outfall)

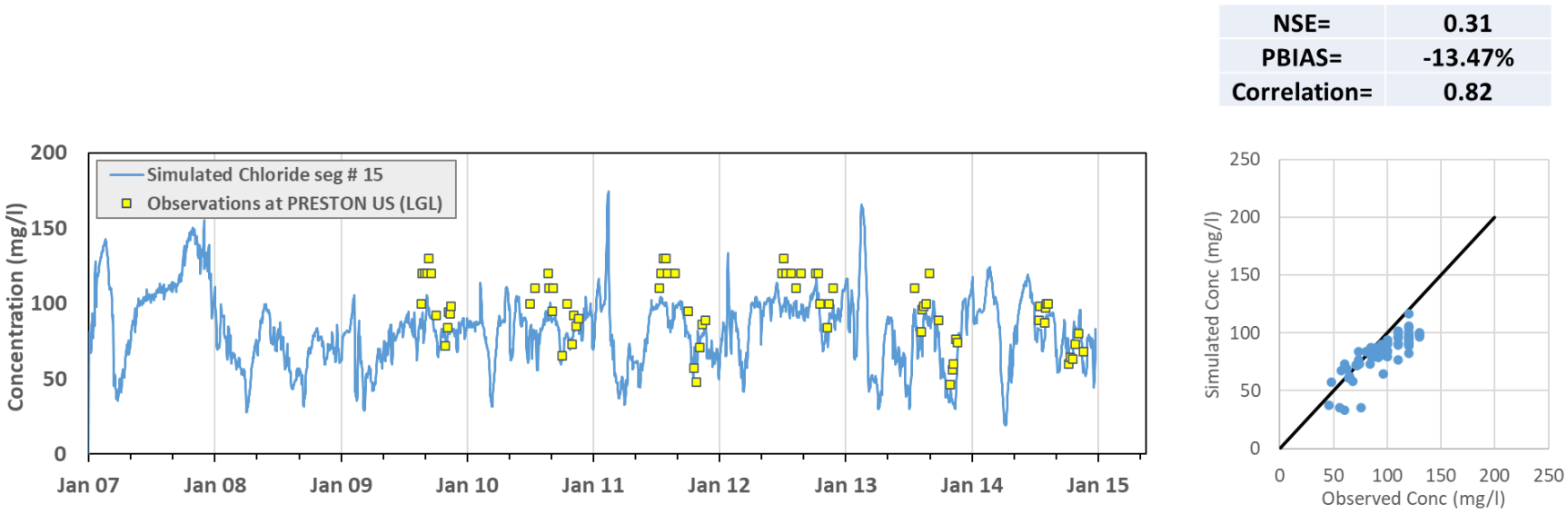


Figure 42: Simulated and measured chloride concentrations upstream of Preston WWT

APPENDIX F

Integrated model sensitivity analysis was performed manually by varying the parameter values for all TOrCs between five values (including the defaults), one parameter at a time. This includes a low, medium-low, medium (i.e. default), medium-high, and maximum value for each of the sorbtion, autotrophic biodegradation, heterotrophic biodegradation, river biodegradation, and four photolysis coefficients. The medium-low and medium-high values were chosen as approximate linear midpoints or logarithmic mid-points between minimum, default, and maximum values. The values used are listed in the Manual Sensitivity Analysis Scheme, presented in

Table 26.1-5: Manual sensitivity analysis scheme for Sorption

min				
Parameter	CBZ	VEN	NAP	TRC
Kd	0	0	0	0
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

mf				
Parameter	CBZ	VEN	NAP	TRC
Kd	0.36	0.05	0.024	6.8
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

mp				
Parameter	CBZ	VEN	NAP	TRC
Kd	0.36	0	0.24	1.8
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

max				
Parameter	CBZ	VEN	NAP	TRC
Kd	0.1	0.1	0.1	10
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

def				
Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

Table 27.1-5: Manual sensitivity analysis scheme for Autotrophic Biodegradation

1 (min)				
Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	1	0.01	1	0
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

2 (mp)				
Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	6	0.35	200	2
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

3 (def)				
Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

4 (mf)				
Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	16	3	450	12
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

5 (max)				
Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	20	5	500	20
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

Table 28.1-5: Manual sensitivity analysis scheme for Heterotrophic Biodegradation

1 (min)				
Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0	0	0	0
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

2 (mp)				
Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.0005	0.005	0.0005	0.17
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

3 (def)				
Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

4 (mf)				
Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.005	0.1	0.01	0.67
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

5 (max)				
Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.01	1	0.1	1
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

Table 29**.1-5:** Manual sensitivity analysis scheme for Biodegradation in river

1 (min)				
Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0001	0.0001	0.0001
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

2 (mp)				
Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0003	0.0027	0.0128	0.25
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

3 (def)				
Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0005	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

4 (mf)				
Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0007	0.0077	0.0628	0.75
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

5 (max)				
Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.001	0.01	0.1	1
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

Table 30.1-5: Manual sensitivity analysis scheme for Phototransformation (235-304nm)

min				
Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0	0	0	0
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

mp				
Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.00005	0	0.0001	0.04
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

def				
Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

mf				
Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0005	0.0001	0.036	0.09
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

max				
Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.001	0.001	0.1	0.1
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

Table 31.1-5: Manual sensitivity analysis scheme for Phototransformation (305-314nm)

min

Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0	0
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

mf

Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.027	0.07
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

mp

Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.001	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

max

Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.1	0.1
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

def

Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

Table 32.1-5: Manual sensitivity analysis scheme for Phototransformation (315-334nm)

min

Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0	0
KP_d	0	0	0.0036	0

mf

Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.05	0
KP_d	0	0	0.0036	0

mp

Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.001	0
KP_d	0	0	0.0036	0

max

Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.1	0
KP_d	0	0	0.0036	0

def

Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0

Table 33.1-5: Manual sensitivity analysis scheme for Phototransformation (335-354nm)

min

Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0	0

mf

Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.019	0

mp

Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0001	0

max

Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.1	0

def

Parameter	CBZ	VEN	NAP	TRC
Kd	0.036	0	0.024	3.61
Kba	12	0.7	400	4
Kbh	0.001	0.01	0.001	0.34
Kb	0.0001	0.0054	0.0256	0.5
KP_a	0.0001	0	0.0036	0.08
KP_b	0	0	0.0072	0.04
KP_c	0	0	0.009	0
KP_d	0	0	0.0036	0