Master's thesis in

Modelling of Carbamazepine and Diclofenac in a River Network

–

Photolytic Degradation in Swiss Rivers

submitted to the
Swedish University of Agricultural Sciences, Uppsala

by
Klaus Vochezer

August, 2010

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Degree project in Environmental Science
Master's thesis, 30 HEC

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Key words:
micropollutants, pharmaceuticals, Carbamazepine, Diclofenac, direct photolysis, photolytic degradation, stream network

Abstract

Micropollutants from urban or agricultural sources, for example pharmaceuticals or pesticides, are facing increasing public awareness. In the last years, many studies reported on the occurrence of micropollutions in different water samples, including drinking waters. Moreover, harmful effects could be detected on fish where micropollutants act as endocrine disruptors.

Micropollution measurements of a national water-quality inventory in Switzerland (NADUF) indicate a relatively constant load pattern for Carbamazepine (650 g/week ±190 g/week) at chosen river sections throughout the year. This backs up the hypothesis that Carbamazepine is persistent. For Diclofenac the load pattern of the same river was fluctuating to a larger extent (640 g/week ± 400 g/week). Especially during dryer time periods in summer the loads were significant lower than the average. One explanation for the fluctuation in Diclofenac loads is a variation in the input loads to the rivers, another is degradation by photolysis in the river network.

To prove this, one method was to analyse the measurements statistically and the other method was to set up a one-dimensional model of the fate of this pharmaceuticals in a pre-alpine river catchment ($1750\,km^2$) in Switzerland. The analysis of Diclofenac measurements on two distinctive sites showed the same drop in the mean loads during the summer. This indicates that fluctuations in the input loads occurred.

In the model the pharmaceutical input is calculated on the base of yearly sales per capita, a constant yearly consumption and waste water treatment plants as point pollution sources. The model indicated that up to 28 % of the seasonal variation in Diclofenac loads could be explained by direct photolysis. In truth both hypotheses have to be combined to fully explain the drop. Additionally, when consulting hourly simulations we found that the environment is harmed from human pharmaceuticals to a large extent were critical environmental values are exceeded up by to 80 % of the time. In future the model should be extended to non-point source pollution from agriculture for instance.

Acknowledgement

My special thanks go to Lars Sonesten for the examination, to Kevin Bishop from the Swedish University of Agricultural Science and to Thilo Streck from the University Hohenheim for the supervision.

I thank the whole team of UCHEM at the Eawag, especially to Jürgen van der Vöt for the evaluation on the NADUF data, to Martin Frey for the help with Aquasim and R-Project, to Heinz Singer for helpful discussions, to Irene Wittmer as well as to Ruth Scheidegger, Hans Peter Bader and Rosi Siber also from Eawag.

Further I thank the people that provided me with necessary data from FOEN, WSL, Canton Thurgau, Canton St. Gallen and AWEL.

My largest thanks go to Christian Stamm for supervising me at Eawag and to Paul Vochezer for the critical review of the thesis.

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1 Introduction

Micropollutants are industrially synthesised chemicals that are used as biocides, herbicides, pharmaceuticals or used in other industrial applications. They are found in natural water bodies like lakes, rivers, ground waters and to some extent even in drinking water in a concentration range of a few $\frac{ng}{l}$ to $\frac{\mu g}{l}$ [3], [4]. Micropollutants can act as endocrine disruptor and may affect health and reproduction of man and animals [5].

Buffering of large water amounts in lakes can lead to significantly retarded or time shifted micropollutant concentrations in rivers and lakes compared to the inputs of micropollutants. The actual concentrations in lakes are low compared to streams and rivers, due to dilution [6]. In rivers however, high concentrations occur where comparable higher loads enter small streams. Therefore critical concentrations for the environmental system are exceeded and certain aquatic organisms can suffer ecotoxicological effects [7]. Such a critical threshold is the pollution non effect concentration (PNEC), for instance.

To quantify the concentration of micropollutants and their effects several factors have to be considered [3].

- Measurements have to be sensitive enough.
- The fate of each compound has to be analysed, with respect to the pollution source, the pollution load, and the behaviour in the water bodies.
- The harm to the environment and threshold values of the concentrations have to be evaluated.

Generally, the source of pollution differs between point and diffuse source. The pollution load depends on the consumption, on the release and on degradation processes before the compound enters the water body.

In Switzerland, the "National Long-term Surveillance of Swiss Rivers" (NADUF) conducts the surveillance and evaluation of the chemical–physical state of Swiss rivers. The partners involved are the Swiss Federal Office for the Environment (FOEN), the Swiss Federal Institute of Aquatic Science and Technology (Eawag) and the Swiss Federal Institute for Forest, Snow and Landscape Research (WSL). The NADUF was initiated in 1972 and focused mainly on nutrients and heavy metals. Since micropollutants can be detected in water bodies the NADUF is focusing more on the quantification of micropollutants. In 2009 the NADUF launched a measurement campaign, which measured the concentrations of selected micropollutants at five river sites in the northern part of Switzerland. To account for the variety of micropollutants the analysed substances belong to the groups of biocides, herbicides, pharmaceuticals or industrial used compounds.

An examination of the first NADUF measurement campaigns show high fluctuations of concentrations and absolute loads in time [8]. These findings are in line with the expectations, because the selected compounds belong to different groups and have therefore different sources as well as different environmental properties. To address the cause of these variations one has to focus on specific compounds for which the use and the environmental properties can be quantified. Then, we can analyse the seasonal variations of the selected compound and compare the trends between the compounds. Furthermore, hypotheses on the environmental fate can be formulated. To test these hypotheses a model is a powerful tool, especially when the modelled results are validated with measurements.

In this work measured NADUF data of the Thur catchment are evaluated. The Thur catchment is located in the north-east of Switzerland. We will focus on the human pharmaceuticals Carbamazepine (CBZ) and Diclofenac (DCF) because of two reasons. First, the NADUF measurements for Carbamazepine show a relatively constant load pattern through the whole analysed period, whereas diclofenac loads show significant lower loads in the summer season [8]. Second, Carbamazepine and Diclofenac have the same source and the quantity of pollution can be estimated [9].

Moreover, studies show that Carbamazepine and Diclofenac are widely detected in various water bodies. Herberer et al.(2002) indicate that pharmaceutical residues are found worldwide in environmental systems. For example Carbamazepine and Diclofenac could be detected in the effluent of waste water treatment plants (WWTPs), in surface waters, in ground water and in drinking water [10], [3], [11] and [4]. Zang et al. (2008) concluded that Carbamazepine and Diclofenac concentrations have rather chronic than acute toxic effects in a world wide view. At regional scale critical environmental concentrations are most likely exceeded in small streams [2].

Carbamazepine is an anti-epileptic drug used to control seizures. Diclofenac is an important arylacetic acid non-steroidal anti-inflammatory drug used in human medical care as an analgesic, anti-arthritic and anti-rheumatic compound [1]. The PNEC of Carbamazepine is $500\,\frac{ng}{l}$ and of Diclofenac $100\,\frac{ng}{l}$ [9]. In Table 1.1 the properties of both compounds are summarised.

The source of pollution by human pharmaceutical can be attributed to the effluent of WWTPs [12], [13], [1],[11] [14]. With respect to this study Carbamazepine and

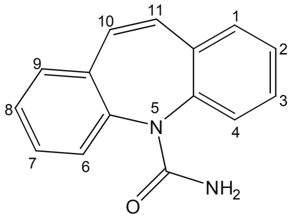
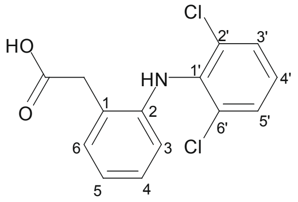
	Carbamazepine (CBZ)	Diclofenac (DFC)
Pharmacology		
Structure, formula, CAS No. and molecular weight		
	$C_{15}H_{12}N_2O$ 298-46-4 236.27 g mol^{À1}	$C_{14}H_{11}Cl_2NO_2$ 15307-86-5 296.16 g mol^{À1}
Usage	Analgesic, antiepileptic	Analgesic, anti-inflammatory
Water solubility[a]	17.7 mg L^{À1} (25 °C)	23.73 mg L^{À1} (25 °C)
Log P (octanol–water)[a]	2.45	–
Henry's Law Constant[a]	1.09 Â 10^{À5} Pa m^3 mol^{À1} (25 °C)	4.79Â10^{À7} Pa m^3 mol^{À1} (25 °C)
pKa	neutral[b]	4.15[a]
Elimination half-life[c]	25–65 h	2 h
Excretion[d]	72% of oral dosage excreted in urine, 28% in faeces	Biliary excretion: 65% of oral dosage excreted in urine
Metabolites in urine (% of oral dosage)	CBZ, CBZ-epoxide, CBZ-diol, CBZ-acridan, 2-OH-CBZ, 3-OH-CBZ[e]	DFC, 5-OH-DFC, 4^0-OH-DFC, 3^0-OH-DFC, 4^0-5-diOH-DFC, 4^0-OH-5-Cl-DFC, 3^0-OH-4^0-CH_3O-DFC[f]
Dosage[g]	Maintenance usually 800–1200 mg daily.	75–150 mg daily
Other Information	Autoinduction, i.e., long term applications increase its metabolism[d]	Dermal applications available

Figure 1.1: Physical, chemical and pharmacological properties of Carbamazepine and Diclofenac. The figure is taken from Zhang et al. 2008 [1]. The indices indicate the source of the data that is listed in the original literature.

Diclofenac pollution occur also through WWTPs, because:

- Carbamazepine and Diclofenac are mostly used in human applications,
- humans do not metabolise Carbamazepine and Diclofenac completely and excrete them into the sewer system,
- common WWTPs degrade Carbamazepine and Diclofenac only partly,
- with the effluent of the WWTPs they reach the water network.

Ort et al. (2009) assumed in an input scenario that for both compounds a constant pollution load from WWTPs can be expected and that both compounds are persistent within rivers. On one hand, other studies highlighted as well the environmental long term persistence of Carbamazepine [11], [1]. On the other hand, several studies indicated that Diclofenac degrades in lakes due to direct photolysis during the summer season [12], [15], [13]. In the literature it is also indicated that for Diclofenac other degradation processes that are of chemical or biological origin or adsorption onto sediments can be neglected [12].

Due to that, we can distil two sources that could explain the seasonal variations in Diclofenac loads. The first source of seasonal variations could be due to variations in the load input to the river. This could be attributed to consumption patterns and elimination rates by humans and by WWTPs. The second source of seasonal variations is affected by processes within the river. As motivated before, we will only consider direct photolysis that could affect the fate of Diclofenac within the river.

In conclusion we formulate three possible hypotheses that could explain the observed patters of Carbamazepine and Diclofenac load.

1. Carbamazepine pollution loads are constant through the season.
2. Diclofenac pollution loads have seasonal variations that leads to a seasonal load variation in the river.
3. Diclofenac is degraded by direct photolysis as it is transported downstream that leads to a seasonal load variation in the river.

The first and the second hypotheses can be tested by analysing the measurements in detail, because they are affiliated to sources outside the river. In hypothesis three direct photolysis is dependent on time and on the water depth [13], [14]. The time dependency is due to fluctuations in light energy at the earth surface (irradiance) within a daily and seasonal scale. The water depth in rivers is varying dependent on the discharge and geometry of the river bed. The total amount of a compound that is degraded within a river network is dependent on the residence time of the compound in the stream network. This dependencies can not be analysed with measurements. Therefore we construct a model that calculates the flow and degradation properties of the compounds in the stream network. The results of this model can be validated and the influence of the direct photolysis in respect to Diclofenac can be quantified.

Conclusively, the goals of this study are, first, to set up a model that describes the fate of Carbamazepine and Diclofenac within the Thur catchment. Second, to test the hypotheses formulated with the measured NADUF data and with the model results. Third, to validate the model with measured data for the sites Frauenfeld-Murg and Andelfingen-Thur. Finally, to detect critical sites where concentrations of micropollutants are harmful to the environment.

2 Methods

2.1 Study Area

The study area is the Thur watershed, which depicted in Figure 2.1. The area is situated in the north-eastern part of Switzerland with a size of 1 750 km^2. The river Thur has a length of 127 km with the major tributaries Murg, Sitter, Glatt and Necker. The elevation ranges from 350 m at the measurement site of Andelfingen to the mountain area Säntis with a peak of 2 502 m. In average the elevation of the catchment is 774 m above sea level. Five kilometre downstream of Andelfingen the Thur discharges into the river Rhine. Secondary tributaries are the river Lützelmurg that flows into the river Murg and the river Urnäsch that flows into the river Sitter. Figure 2.2 shows all analysed rivers with their length, altitude and location of discharge into the main river Thur.

In the northern part the land use is predominated by arable land. Due to the rising altitudes in southern direction forest-, pasture- and meadow-, and barren-areas become more important (Figure 2.1). Agricultural land (arable land, alpine pastures and meadows for feeding cows) accounts for 60 %, forests 25 %, urban areas 8 % and the remaining 7 % are barren areas or surface waters. In the whole catchment living about 360 000 inhabitants. The distribution of inhabitants shows accumulation of inhabitants around the cities Frauenfeld, Weinfelden, Wil and St. Gallen. In the elevated area, in the South East of the catchment, the population density is much lower.

The structure of the landscape reaches from a hilly dissected terrain, in the North, to the steep mountainous area in the South. The climate is characterised by a pre-alpine/alpine climate with moderate to cold winters and relative high summer-temperature fluctuations. This temperature variations are most pronounced in the alpine area. The mean annual precipitation is 1460 mm for the whole catchment. Generally most precipitation falls during the summer months. The alpine area receives more than 2000 mm precipitation per year, whereas the lower sub-mountain area receives only 1000 mm per year. Of the whole catchment the mean annual temperature is 7.5 °C with a range from 0.2 °C at the Säntis to 15.1 °C at Tänikon [16].

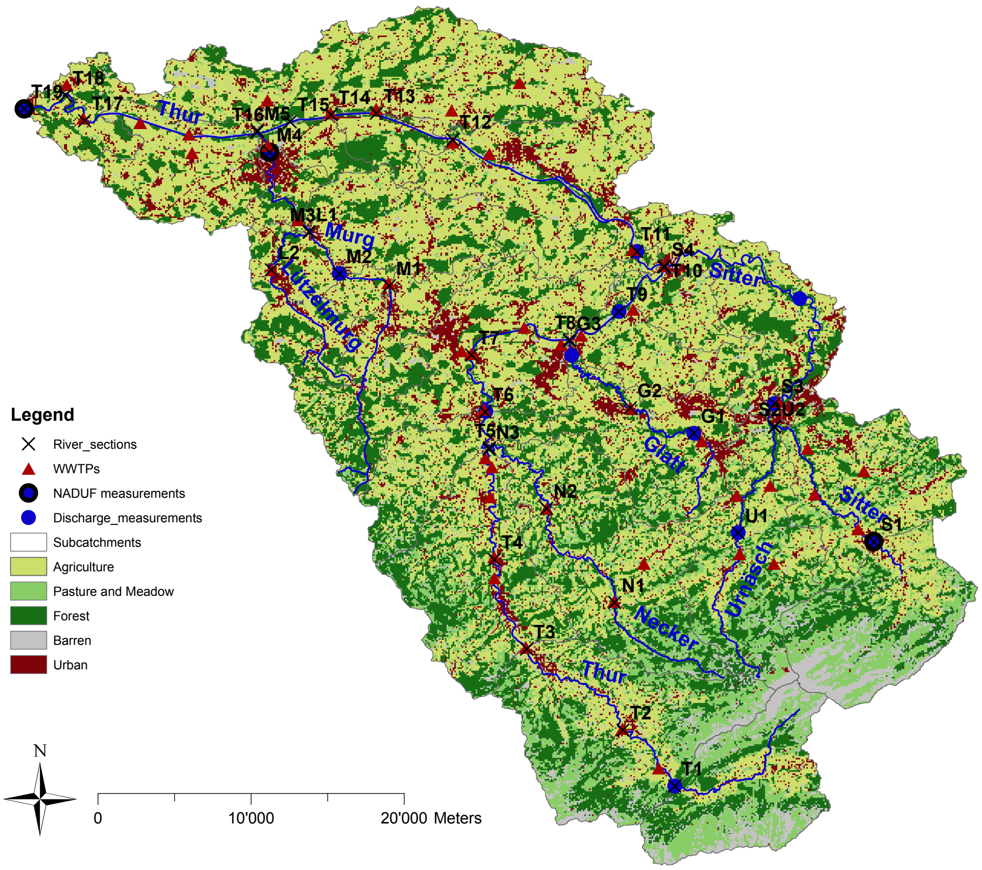


Figure 2.1: Thur catchment with landuse, locations of WWTPs, locations of NADUF measurement sites, additional discharge measurement sites and the modelled river sections. Map reproduced with allowence from swisstopo (JA100119).

2.2 Measurements

Six locations in the Northern part of Switzerland were selected from the NADUF measurement campaign of micropollutants. This are from East to West Appenzell on the river Sitter, Frauenfeld on the river Murg, Andelfingen on the river Thur, Freienstein on the river Töss, Rheinsfelden on the river Glatt and Rekingen on the river Rhine. The Murg and the Sitter are tributaries to the Thur. Thur, Töss and Glatt are tributaries

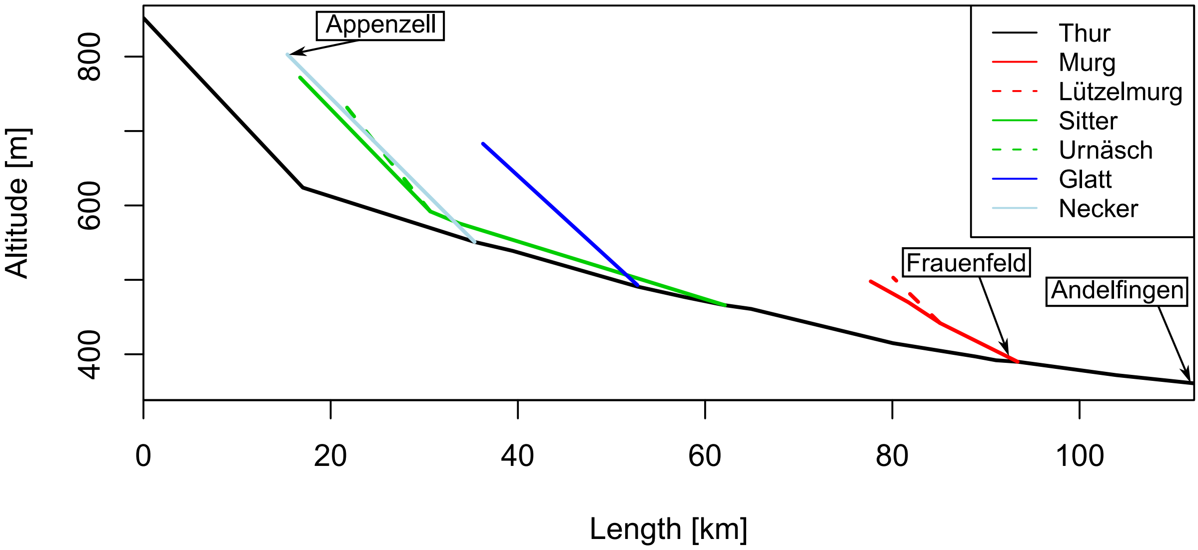


Figure 2.2: Altitude and length of the modelled rivers. Named are the NADUF micropollution measurement stations within the modelled Thur catchment.

to the Rhine. The site Appenzell-Sitter is chosen to get an estimate of the background pollution of an alpine area without WWTPs or agricultural sources for micropollutants like pharmaceuticals and pesticides. The stations Frauenfeld-Murg, Andelfingen-Thur, Freienstein-Töss and Rheinsfelden-Glatt are located at the confluences. The site Rekingen-Rhine is downstream of each tributary of the mentioned rivers.

On each site, mixed discharge proportional water samples over a weekly or biweekly time period are taken automatically. The samples are stored over the sampling period at the sampling station in a fridge at around 4 °C. The analysis of this samples was done by mass spectroscopy at the Eawag for the compounds 5-Methyl-Benzotriazole, Atrazine, Atrazin-Desethyl, Atrazin-Hydroxy, Benzotriazole, Carbamazepine, Carbendazim, Diclofenac, Diuron, Isoproturon, Mecoprop, Metolachlor, N4-Acetylsulfamethoxazol, Sufamethoxazol and Terbutryn. The procedure is described in [17]. The limit of detection (LOD) and the limit of quantification (LOQ) are between 1 and 10 $\frac{ng}{l}$.

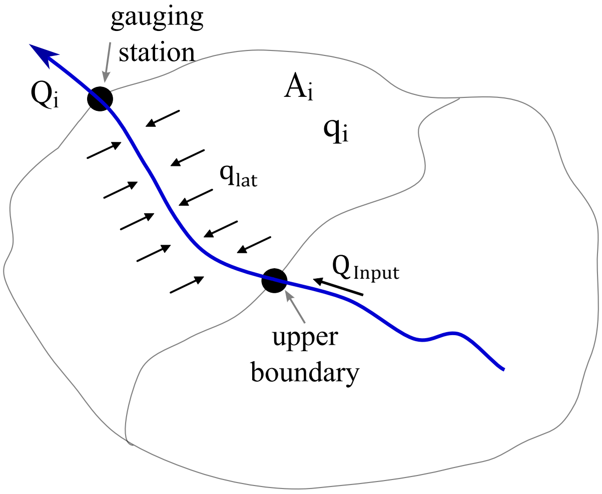


Figure 2.3: Hydrological setup of the model. Hydrological input to the model is indicated with Q_{Input} and q_{lat}. Q_{Input} and q_{lat} are denoted by input discharge and lateral discharge along the river stretch.

2.3 Model implementation

2.3.1 River routing model

To set up the river routing model measurements of the discharge are used as the hydrological input to the system (Figure 2.3). In order to calculate Q_{Input} and q_{lat} a specific discharge (q_i) is calculated for each river section.

$$q_i = \frac{Q_i}{A_i} \tag{2.1}$$

The measured discharge is indicated with $\mathrm{Q_i}$ and the corresponding drainage area is indicated with $\mathrm{A_i}$. For the routing we used a one dimensional approach that describes changes in discharge along the river. Along the cross section averaged values of discharge and compound concentrations are assumed. The model is implemented in the computer program Aquasim 2.1 that identifies and simulates aquatic systems in nature, technical plants and laboratories [18].

For the description of the discharge in the channel the "St. Venant" approach is used. This approach consists of the equations for continuity (Eq. 2.2) and motion (Eq. 2.3). The equation of continuity describes the law of conservation of mass and the equation of motion describes the change of discharge over time, while taking the influence of gravity and friction into account.

$$\frac{\partial A_{adv}}{\partial t} = -\frac{\partial Q}{\partial x} + q_{lat} \tag{2.2}$$

$$\frac{\partial Q}{\partial t} = \frac{\partial}{\partial x}\left(\frac{Q^2}{A_{adv}}\right) - gA_{adv}\left(\frac{\partial z_0}{\partial x} + S_f\right) \tag{2.3}$$

where

t : time $[s]$
x : horizontal coordinate in flow direction $[m]$
A_{adv} : wetted cross section $[m^2]$
Q : discharge $[m^3 s^{-1}]$
q_{lat} : lateral flow per flow length $[m^3 s^{-1} m^{-1}]$
z_0 : water level hight $[m]$
S_f : flow-friction, dimensionless fraction of friction and weight
g : gravitational acceleration $(9.81)[ms^{-2}]$

The cross section of the river is assumed as a simple rectangle and therefore the wetted cross section is calculated from the product of the river bed width ($\mathrm{w_{bed}}$) and the water depth (z) (Eq. 2.4).

$$A_{adv} = w_{bed} \cdot z \tag{2.4}$$

To calculate the flow-friction in Eq. 2.5 we used the approach by Strickler 1923 [19].

$$S_f = \frac{1}{K_{st}^2}\frac{1}{R^{4/3}}\frac{Q^2}{A_{adv}^2} \tag{2.5}$$

where

R : hydraulic radius $\left(R = \frac{A_{adv}}{P}\right)$ $[m]$
P : wetted perimeter $[m]$
K_{st} : Strickler coefficient $[m^{-\frac{1}{3}} s^{-1}]$

The Strickler coefficient can be calculated with Eq. 2.6 where the median grain size of the river bed ($\mathrm{d_m}$) has to be known.

$$K_{st} = \frac{21.1}{{d_m}^{\frac{1}{6}}} \tag{2.6}$$

The dead band approach from Meier (2002) takes the occurrence of pools and riffles in the riverbed into account. This has the effect that the travel times and the longitudinal dispersions are higher. For a rough estimate this effect can also be attributed to a higher friction coefficient [20]. This was done by using Eq. 2.6, because this equation was elaborated on rivers that had also pools and riffles.

2.3.2 Transport and reaction model

The change in time of the concentrations of solute compounds can be described by Eq. 2.7.

$$\frac{\partial(A_{adv}C_{adv})}{\partial t} = -\frac{\partial(QC_{adv})}{\partial x} + \frac{\partial}{\partial x}\left(A_{adv}E_{adv}\frac{\partial C_{adv}}{\partial x}\right) + A_{adv}r_{adv} + q_{lat}(C_{lat} - C_{adv}) \quad (2.7)$$

where

$$\begin{aligned} C_{adv} &: \text{mean compound concentration over cross section } [gm^{-3}] \\ E_{adv} &: \text{dispersion coefficient } [m^2 s^{-1}] \\ r_{adv} &: \text{net transformation rate } [gm^{-3}s^{-1}] \\ C_{lat} &: \text{compound concentration of lateral inflow } [gm^{-3}] \end{aligned}$$

The first term on the right side indicates the advective transport, the second the longitudinal dispersion, the third the reaction and transformation and the forth the lateral inflow. In our case we assume that Diclofenac is only transformed due to direct photolysis. Other transformation processes of Diclofenac and Carbamazepine can be neglected as motivated in the Introduction. Therefore,

$$\begin{aligned} r_{adv\_CBZ} &= 0 \\ r_{adv\_DCF} &= \bar{r}_{photo} \end{aligned}$$

where the indices CBZ and DCF stand for Carbamazepine and Diclofenac, respectively. The net transformation rate of Diclofenac is due to direct photolysis. This net transformation rate is also the net photolysis rate ($\bar{r}_{photo}$).

To calculate $\bar{r}_{photo}$ the following assumptions are made. The actual rate of photolysis (r) at a given water depth is proportional to the irradiance due to the solar radiation, called insolation (I). The intensity of the insolation decreases exponentially with water depth, as stated by the Beer-Lambert law. The rate of photolysis depends on the time, because of two reasons. Fist, the insolation is time dependent due to variations in the day length, and second, the water depth of rivers varies with time due to fluctuations in the discharge. In conclusion, the actual rate of photolysis will show a exponential decrease with the water depth ($l(t)$) [14], [15] and is dependent on time (t) (Eq.2.8).

$$r(l,t) = r_0(t) \cdot e^{(-c \cdot l(t))} \tag{2.8}$$

Here $r_0(t)$ is the photolysis rate at the water surface ($[d^{-1}]$) and c is the absorption coefficient of insolation in water ($[m^{-1}]$). The potential daily average insolation follows a sinusoidal function within a year due to solar altitude and is limited by actual weather conditions [12].

The photolysis rate over the water depth $l(t)$ is the integral of $r(l,t)$ from the water surface ($l = 0$) to the water depth $l(t)$ (Eq. 2.9).

$$r_{photo}(z,t) = \int_0^{z(t)} r(l,t)dl = \frac{r_0(t)}{c}\left(1 - e^{(-c \cdot z(t))}\right) \tag{2.9}$$

The average photolysis rate over the water depth $z(t)$ is given by:

$$\bar{r}_{photo}(z,t) = \frac{1}{z(t)}\int_0^{z(t)} r(l,t)dl = \frac{r_0(t)}{z(t) \cdot c}\left(1 - e^{(-c \cdot z(t))}\right) \tag{2.10}$$

2.3.3 Model parametrisation

Spatial set up

As mentioned in the Introduction the goal of this study is to assess the pollution situation of the pharmaceuticals Carbamazepine and Diclofenac in rivers. We assume that the only pollution pathway is through the WWTP effluent, because humans consume these pharmaceuticals, excrete a part of them into the sewer system and WWTPs cannot eliminate them completely. Therefore the input of Carbamazepine and Diclofenac is treated as a point source pollution, as shown in Figure 2.4.

System boundaries

The study period of the model is the year 2009 in hourly time steps. The lower spatial boundary in the model is the gauging station Andelfingen. To include all WWTPs in the model the upper spatial boundaries are indicated by either the location of the WWTP or the location of the gauging stations, as it is illustrated in Figure 2.4. When a gauging station is higher up the river than the upper most WWTP, this gauging station defines the upper spatial boundary. If this is not the case, which mean the gauging station is below the upper most WWTP, the location of the upper most WWTP defines the upper

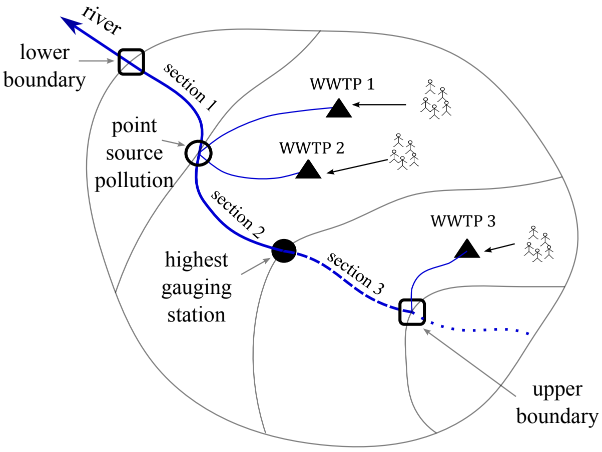


Figure 2.4: Scheme of the spatial set up, with boundaries, WWTPs and river sections.

boundary. The stream from the WWTP to the modelled river is not considered. In most cases the WWTP are located relative closely to the rivers, but some occasion exists with up to 5 km long waste water stream. In order to analyse the spatial conditions the computer program ArcGIS was used and the data in form of maps were provided by swisstopo [21].

River morphology

The morphology in terms of river width and median grain size is described for each river separately. The data are taken from a report of the bedload situation in the Thur catchment from the year 2005 (ger.:"Geschiebehaushalt Thur und Einzugsgebiet") [22]. An overview of the morphological structure of each modelled river is shown in Table 2.1.

Hydrology

Discharge measurements (Q_i) and the corresponding drainage areas (A_i) are provided by the Swiss Federal Office for the Environment FOEN for the stations Jonschwilen, Herisau, Appenzell, St. Gallen, Halden, Wängi and Andelfingen and by the Canton St.Gallen for the Stations Stein/Illishag, Niederbuhren, Wittenbach, Oberbühren and Hundwil. The discharge data have hourly resolutions.

Table 2.1: Morphological structure of the modelled rivers.

River	Modelled length [km]	River bed width [m]	Median grain size [cm]
Thur	112	15 - 72	3.5 - 12.5
Murg	16	7.5 - 15	3.5 - 7
Lützelmurg	5	4	3.5
Sitter	45	16 - 38	8 - 12
Urnäsch	10	5 - 30	8
Glatt	17	5 - 30	8
Necker	20	5 - 30	8

Input of pharmaceuticals

The loads in the WWTP effluents are assumed to be proportional to the number of inhabitants connected and constant values for the excretion rate by humans and degradation rate of each WWTP where assumed further (Table 2.2).

Table 2.2: Sales and degradation rates of Carbamazepine and Diclofenac before the loads enter the rivers.

	Unit	CBZ	DCF	Source
Sales in Switzerland	kg a^{-1}	4100	5540	IMS Health Ltd. (2007-2009)
Sales per capita	mg $capita^{-1} d^{-1}$	1.5	2.0	number of capita [23]
Excretion rate	%	10	16	Ort et. al 2009
WWTP elimination	%	0	25	Ort et. al 2009

The consumption rates per capita are based on yearly sales statistics. The sales data include sales through hospitals, pharmacies, drug stores and doctors. The location where the WWTP effluents reach the rivers and the numbers of inhabitants connected to each WWTP are gained from geographical data, provided by swisstopo [21].

For the transport of the compounds within the river we assume that the compounds dissolve completely. In longitudinal direction dispersion is considered, as indicated in

Eq. 2.7. The dispersion coefficient was taken from a previous study of the river Thur [24].

Direct photolysis

Carbamazepine is assumed to be persistent within the river. For Diclofenac we assume a first order transformation process driven by direct photolysis [13], [15] and [12]. Potential net photolysis rates for Diclofenac are provided by a previous study of Lake Greifensee (Tixier et. al (2003)). These provided potential photolysis rates are daily sums of the net photolysis rates from the period 12. July 1999 to 1. November 1999. They are calculated with the computer program GCSOLAR [25]. GCSOLAR account not for radiation attenuation by clouds, fogs and particles within the atmosphere, which lower the incoming solar radiation. The potential net photolysis rates are from the Lake Greifensee, which is about 35 km West and 10 km South of the geographical mid-point of the Thur catchment. The potential net photolysis rates are integrated values for the top 0.5 m of the water column per day.

Since the time period in this study is a whole year, the provided potential net photolysis rates over the whole year were fitted with a sine function that has constant minimum values for the first and last 30 days (left graph of Figure 2.5). This can be done because the insolation follows a sine function as mentioned before.

In order to calculate the attenuation coefficient in Eq. 2.8 we assume that at a water depth of 0.5 m the photolysis rate is 1 % of the rate at the water surface. This assumption can be made because within the study Tixier et al. (2003) it was seen that photolysis can be neglected at water depths deeper than 0.5 m (Heinz Singer, Eawag). Thus, we can formulate

$$r(0.5, t) = r_0(t) \cdot e^{(-c \cdot 0.5)}$$
$$r(0.5, t) = r_0(t) \cdot 0.01$$

comparing both equations one gets

$$0.01 = e^{(-c \cdot 0.5)} \tag{2.11}$$

what results in a absorption coefficient of $c = 9.2\,m^{-1}$.

As mentioned the provided potential net photolysis rates are integrated values from the surface to a water depth of 0.5 m. In our purpose we need net photolysis rates over a specific water depth, since the water depth of the river is changing with time. Therefore, the potential actual photolysis rate at the water surface has to be calculated for the whole year. This is done by solving Eq. 2.9 by the photolysis rate at the water surface ($r_0(t)$)

$$r_0(t) = \frac{1 - e^{(-c \cdot z(t))}}{c \cdot z(t) \cdot r_{photo}(z,t)} \tag{2.12}$$

where $r_{photo}(z,t)$ are the provided photolysis rates calculated over the top $0.5\,\mathrm{m}$ of the water column from Lake Greifensee. The decrease of the potential actual photolysis rates with water depth is presented in the right graph of Figure 2.5.

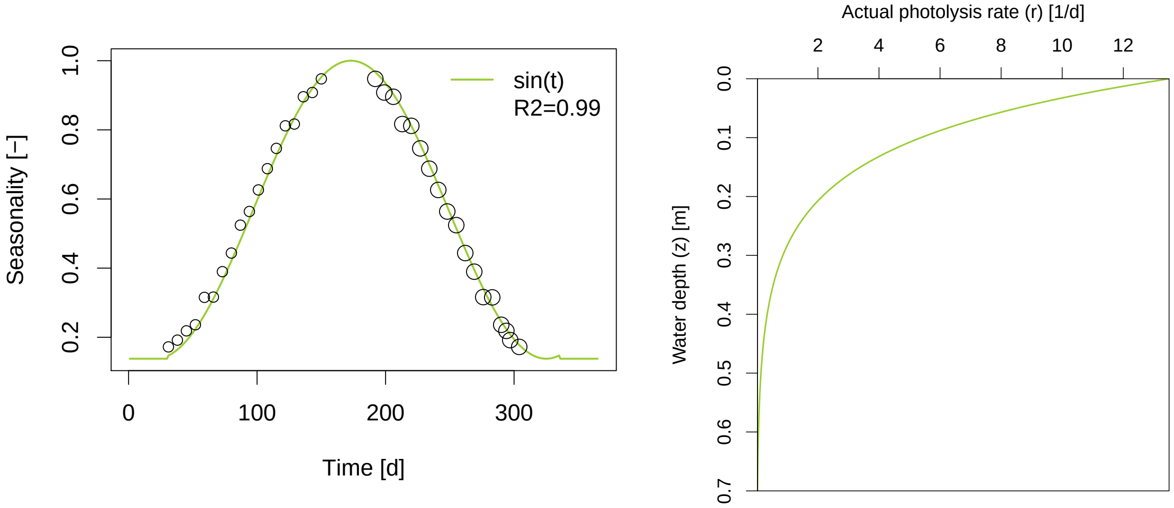


Figure 2.5: The left graph depict the seasonal pattern of the photolysis rates. Large dots indicate provided data from the study of Tixier et al. (2003), small dotes indicate converted data to the first half-year from the provided data in the second half-year. The right graph depict the exponential decrease of the potential actual photolysis rate at the longest day (($t = 171$)), calculated after Eq. 2.8.

Different water properties of the Lake Greifensee and the studied rivers that influence the potential photolysis rates are not taken into account. To assess the reflection and scattering of incoming solar radiation, the potential net photolysis rate is multiplied by a radiation attenuation rate $k(t)$. The radiation attenuation rate is the fraction of incoming solar radiation (E_{mea}) and potential incoming solar radiation (E_{pot}), in daily means. Data for the measured incoming solar radiation are taken from the station

Tänikon (Appendix Figure 7.1). In Tixier et al. (2003) data from the same station were used.

By accounting for the radiation attenuation Eq. 2.10 is reformulated to

$$\bar{r}_{photo}(z,t) = \frac{r_0(t) \cdot k(t)}{c \cdot z(t)} \left(1 - e^{(-c \cdot z(t))}\right) \tag{2.13}$$

The half-life time ($t_{1/2}$) is the time when the concentration of a compound is 50 % of the initial concentration. It can be calculated as follows,

$$t_{1/2}(z,t) = \frac{ln(0.5)}{-r_{photo}(z,t)} \tag{2.14}$$

Eq. 2.13 is implemented in the model. Since the model is in hourly time steps, $r_0(t)$ is converted into hourly values by dividing the daily photolysis rates with the number of hours per day. We assumed that within a day the rates are constant what means we ignored the daily insolation pattern.

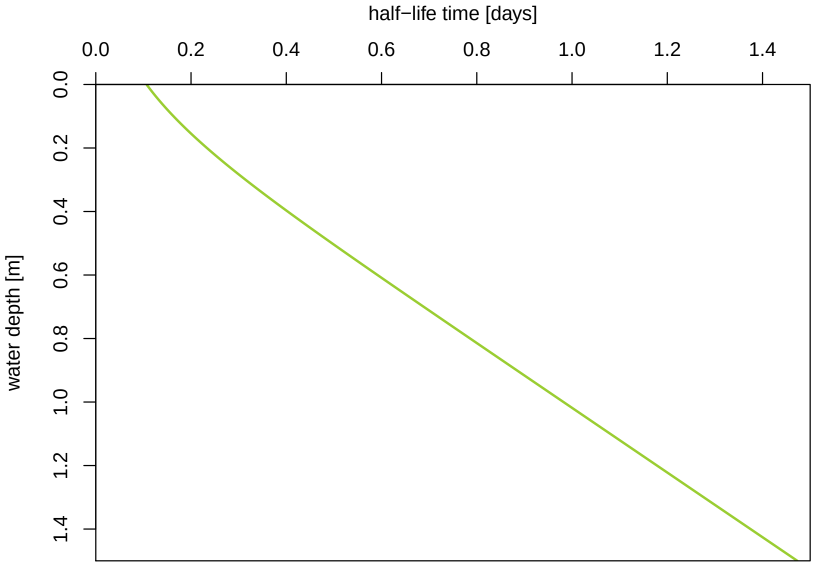


Figure 2.6: Estimated half-live time when degradation rates are highest.

In Figure 2.6 the estimated half-life time when highest daily insolation values are expected, is calculated by Eq. 2.14. Insolation is highest at the longest day of a year and it is proportional to the photolysis rates at the water surface. Therefore the half-live time has its lowest values at the longest day of a year. The net photolysis rate ($r_{photo}(z,t)$) is calculated by Eq. 2.13. There the potential surface photolysis rates are calculated by the potential net photolysis rates of Tixier et al. (2003) (Eq. 2.12) and the annual mean radiation attenuation rate of 0.5.

2.3.4 Model evaluation

To test the hydrological model the Nash-Sutcliffe model efficiency coefficient (NAS) [26] and the coefficient of determination (R^2) are calculated. The NAS is defined as

$$NAS = 1 - \frac{variance\ of\ the\ residuals}{variance\ of\ the\ measurements} \tag{2.15}$$

NAS can range from $-\infty$ to 1, where 1 indicates the perfect fit. A negative coefficient means that the measurements are a better predictor than the model. The NAS as well as R^2 are also used to test the applied compound model.

3 Results

3.1 Measurements

To test the first and second hypotheses, of constant Carbamazepine loads and seasonal variability in Diclofenac loads, the measured pharmaceutical data are evaluated. At the measurement site Appenzell-Sitter concentrations of Carbamazepine and Diclofenac were below the LOD. This means for the measurements at the downstream sites Frauenfeld-Murg and Andelfingen-Thur that they are not affected from environmental background pollution and the origin of the compounds can be addressed to site specific sources. In Figure 3.1 weekly or biweekly loads and weekly discharge measurements at the stations Frauenfeld-Murg, Andelfingen-Thur and Rekingen-Rhine are presented. Gaps in the weekly or biweekly time series correspond to periods without measured data.

The discharge patters at Frauenfeld-Murg and Andelfingen-Thur show a similar trend, because the drainage area of the station Frauenfeld-Murg is situated within the drainage area of the station Andelfingen-Thur. This means the precipitation patterns are similar. In addition, the properties of the drainage areas are also very similar, without any lakes, which buffer precipitation. Snow and ice leads also to a buffering of precipitation, what can be seen in the low discharge at Frauenfeld-Murg and at Andelfingen-Thur in the first 3 weeks of the measuring year. Melting snow and ice cause high discharge peaks from week 10 to 15 in the Murg and in the Thur.

In the Rhine we have to consider the Lake of Constance as a buffer, which is located within the drainage area of the station Rekingen-Rhine. The discharge of the Rhine is directly linked to the water level of the Lake of Constance. Tributaries to the lake and the water capacity of the lake control the water level within the lake. During winter time the water level of the lake decreases due to water storage in form of snow and ice. When snow and ice melt the discharge to the lake increases, and the water level starts to rise. But the water capacity of the lake buffers the response of the discharge at Rekingen-Rhine and thus the increase is less pronounced than at the stations Frauenfeld-Murg and Andelfingen-Thur. During summertime the discharge at Rekingen-Rhine reaches a maximum. The sharp minima in discharge are remarkable in week 3 and week 41. As mentioned above the minimum in week 3 can be linked to a storage in the form of snow and ice. The minimum in week 41 is obviously due to a long temporal dry period at a large spatial scale.

The load of Carbamazepine at Rekingen-Rhine is significantly linearly correlated with the discharge. The Pearson-correlation coefficient (ρ) is 0.95 with a p-value of < 0.01.

The load pattern of Diclofenac at Rekingen-Rhine shows clearly lower values in the summer period with a negative linear correlation (ρ = -0.44, $p < 0.05$). At Frauenfeld-Murg and Andelfingen-Thur the correlation between Carbamazepine loads and discharge is not significant. However, the correlation of Diclofenac loads and the discharge are highly significant with $\rho = 0.7$ and 0.5, respectively and p-values < 0.01. At both stations Diclofenac loads are higher than Carbamazepine loads during the first quarter and last quarter of the year. In the summer period Dilofenac loads are lower than Carbamazepine loads.

The Kendall rang correlation analysis (τ) between the loads of Carbamazepine and Diclofenac show at Frauenfeld-Murg and Rekingen-Rhine no significant correlation (p-values > 0.05). At Andelfingen-Thur a weak rank correlation could be detected with τ = 0.27 and a p-value of 0.04. A significant correlation in loads indicates that characteristics of the compounds are similar. Thus with a significant correlation it is likely that the compounds have the same source of pollution and that they behave similar in the river.

We assess the load patterns within the winter and the summer seasons separately and calculated a seasonality factor (Eq.3.1), to test if there is a seasonal variation in the pollution loads possible.

$$f_{season} = \frac{\bar{M}_{highrad}}{\bar{M}_{lowrad}} \tag{3.1}$$

There it is distinguished between the season where high photolysis rates and the season where low photolysis rates can be expected. $\bar{M}$ are the measured mean load. The high radiation season is between week 20 and week 40. The low radiation season consists of the first 10 weeks and the last 10 weeks of a year. To account for the variability of the seasonality factor a range of f_{season} is calculated (Eq.3.2).

$$range_{f_{season}} = \left(\frac{\bar{M}_{highrad} - \sigma_{M_{highrad}}}{\bar{M}_{lowrad} + \sigma_{M_{lowrad}}} \text{ to } \frac{\bar{M}_{highrad} + \sigma_{M_{highrad}}}{\bar{M}_{lowrad} - \sigma_{M_{lowrad}}} \right) \tag{3.2}$$

where σ indicates the standard deviation.

With this seasonal differentiation we will now analyse the measured loads at Frauenfeld-Murg and Andelfingen-Thur in more detail. Figure 3.2 depict boxplots of the loads of Carbamazepine and Diclofenac at Frauenfeld-Murg and Andelfingen-Thur separately for the low and high radiation seasons. Carbamazepine loads show no clear seasonal dependence. The medians of Carbamazepine, differ with the radiation season within the 1.5

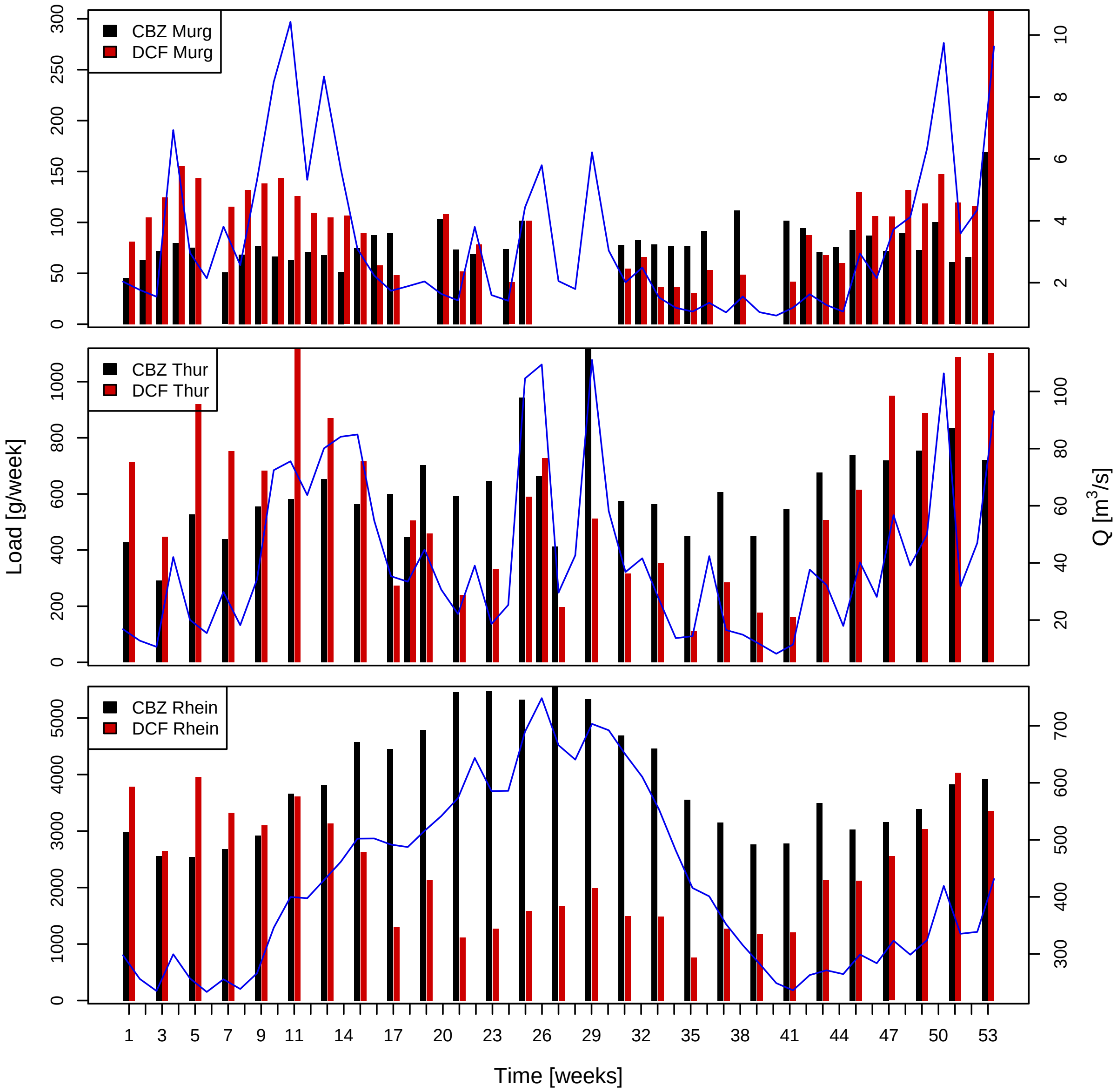


Figure 3.1: Measured loads of Carbamazepine and Diclofenac and weekly average discharge (blue line) at the NADUF measurements stations Frauenfeld-Murg, Andelfingen-Thur and Rekingen-Rhein

inter quantile range (1.5IQR) at both sites. By contrast, Diclofenac shows clearly lower loads during the high radiation season at both sites. The seasonality factor f_{season}, calculated after Eq. 3.2 for the loads at Frauenfeld-Murg is 0.45, ranging from 0.18 to 0.95, and at Andelfingen-Thur is 0.43, ranging from 0.14 to 0.80. This indicates that either the pollution loads of Diclofenac have a seasonal variation or Diclofenac is degraded in the river.

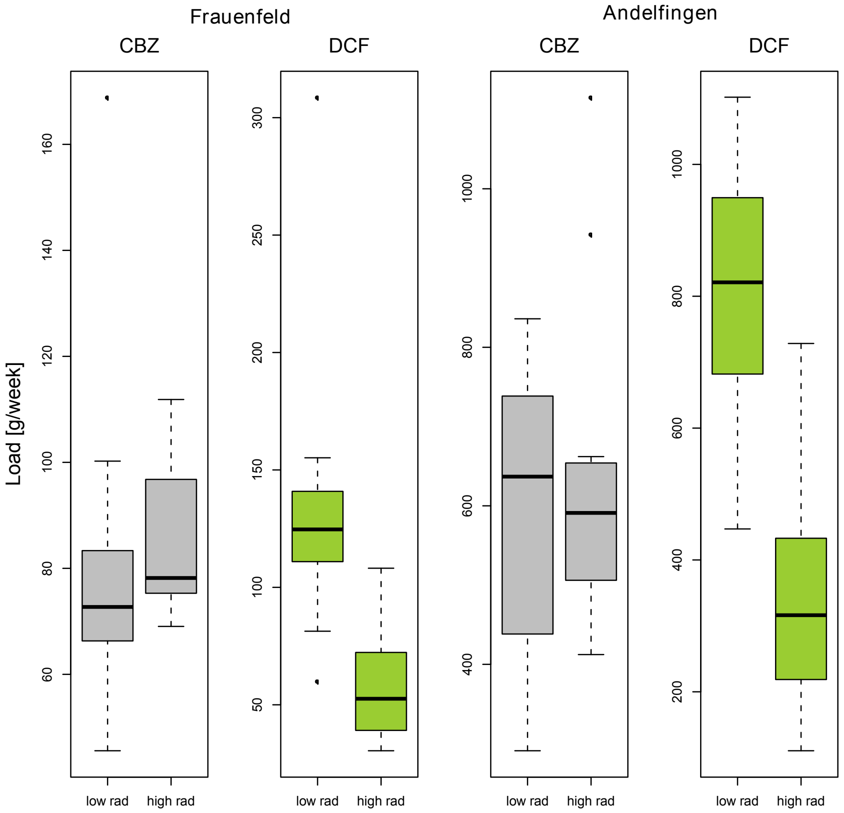


Figure 3.2: Boxplots of Carbamazepine and Diclofenac loads separated for low and high solar radiation periods. Low radiation period from week 1 to 10 and week 44 to 53, high radiation period from week 20 to 40. The boxplots indicate the medians (black line), the 25 % and 75 % quartiles (coloured area), the 1.5 inter quartile ranges (whiskers) and the outliers (points)

3.2 Comparison of measured and estimated compound river input fluxes

Calculated input fluxes of Carbamazepine and Diclofenac based on statistical sales (see chapter 2.3.3) differ from measured mean values. For the estimates of the input fluxes to the model we assumed constant inputs over the year. To compare these estimates with the measurements of Carbamazepine an annual mean load is calculated (Table 3.1). For Diclofenac, the mean loads over the low radiation season are calculated, because we assume that photolytic degradation can be neglected during this period (Figure 2.5). The measured values are of a factor 1.4 to 1.7 higher than the estimated values. The mean factors at both stations are 1.61 for Carbamazepine and 1.47 for Diclofenac. To up scale the estimates a unique correction factor of 1.55 is applied for both substances.

Table 3.1: Measured, estimated and corrected estimates of compound input loads.

Station	**Inhabitants**	**Measurement**			**Estimate**		**Corrected estimate**	
		annual		low-rad				
		CBZ	DCF	DCF	CBZ	DCF	CBZ	DCF
		$\frac{g}{week}$	$\frac{g}{week}$	$\frac{g}{week}$	$\frac{g}{week}$	$\frac{g}{week}$	$\frac{g}{week}$	$\frac{g}{week}$
Frauenfeld	49878	80	98	131	51	83	79	128
Andelfingen	360806	613	572	815	368	599	569	926

3.3 Model

3.3.1 Hydrological model

Both model efficiency tests, NAS and R^2, of the modelled hydrograph at the station Frauenfeld-Murg show the same value of 0.98. In Figure 3.3 the hydrographs of Andefingen-Thur indicate a considerable model overestimations in the period between 2000 and 4000 hours. In this period the discharge is fluctuating in relative short time periods. One big flood occurred in the catchment during the study period at the 18 July 2009 (4764 hours). It had a maximum discharge of 745 $\frac{m^3}{s}$ and lasted over about four days. Statistically such a flood event returns every 5th year [27].

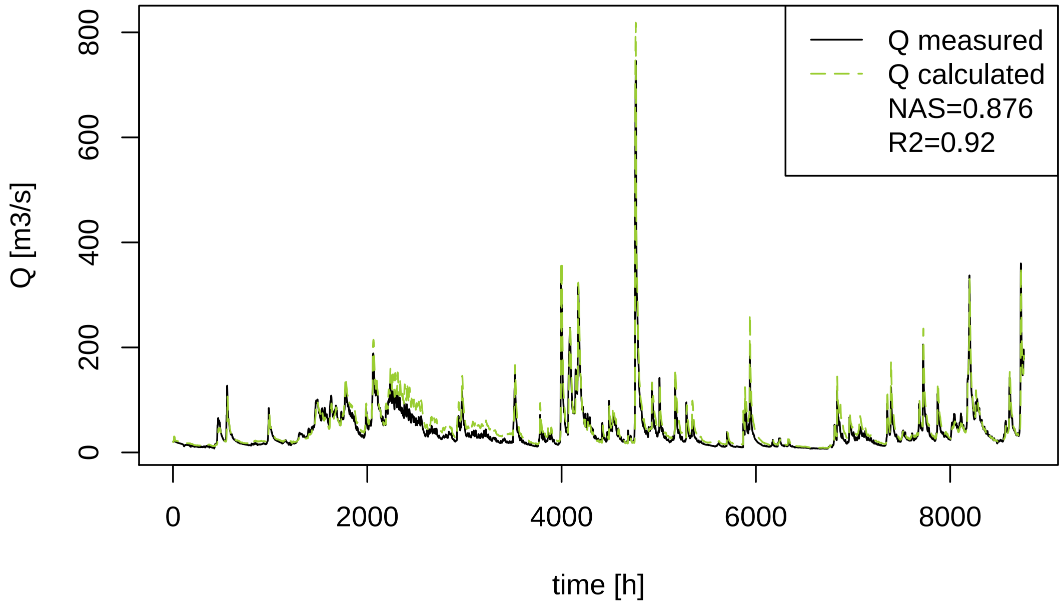


Figure 3.3: Measured and calculated hydrograph at the station Andelfingen-Thur

The next step is to calculate the mean residence time of the compounds and the mean water depth within the river. Both of this factors influence the quantity of photolytic degraded Diclofenac. The maximum residence time at base flow conditions in the Murg is 7 hours considering the flow from Münchwilen (M1) to Frauenfeld (M4). The sites are indicated in Figure 2.1. Base flow ($Q_{95\%}$) is defined as the flow reached or exceeded in 95 % of the time during the studied period. The maximum residence time is extracted from the model. In the Thur the maximum residence time at base flow is 44 hours for the longest distance, which is from Stein (T1) to Andelfingen (T19).

The residence time is dependent on the discharge. With increasing discharge the residence time is decreasing. Therefore events with different discharge values were localised in time. At this times a tracer compound was added at the upper boundaries of the model with a duration of one time step (one hour). The maximum residence time is the time between the initialisation at the upper boundary and the detection of the peak at the lower boundaries (Andelfingen-Thur and Frauenfeld-Murg). Due to dispersion the peak at the lower boundaries has a longer duration than one time step. To account for that the maximum of the peak was taken. To distinguish between the different upper boundary sites the tracers are named different. In the Appendix Figure 7.2 and 7.3 the maximum residence times of the river Murg and Thur are presented.

With the maximum residence time a mean residence time is calculated. The mean residence time is weighted with the residence time from each WWTP (τ_i) and with the quantity of pollution of each WWTP, expressed in Eq. 3.3. The quantity of pollution from each WWTP is proportional to the number of inhabitants connected (N_i).

$$\bar{\tau} = \sum \frac{N_i}{N_{tot}} \cdot \tau_i \tag{3.3}$$

where i indicates the WWTP and N_{tot} the total number of inhabitants within the catchment. This results in a mean residence time of about 5 hours for the Murg and about 22 hours for the Thur.

The hydrological model calculates the water depths, which will be used to estimate a mean water depth for the whole river. The mean water depth ($\bar{z}$) is estimated by first calculating the mean water depth for each river section (i) over the season and second by calculating the mean water depth of the river (Eq. 3.4).

$$\bar{z} = \frac{1}{n} \sum_{i}^{n} \left(\frac{1}{m} \sum_{j}^{m} z_j \right) \tag{3.4}$$

Where z_j indicates the water depth at each hourly calculation step, m is the number of hourly calculation steps and n is the number of river sections. Since the river sections do not have all the same length $\bar{z}$ is not an exact value but it is a good estimate, because the river sections are spread along the whole river network (Figure 2.1).

This results in a mean water depth of 0.14 m for the Murg which ranges from 0.01 m to 1.4 m. For the Thur we can calculate a mean water depth of 0.25 m. The influence of the water depth to the photolysis is discussed in the next section.

3.3.2 Modelling of compound fluxes

Carbamazepine

Figure 3.4 depicts modelled and measured concentrations of Carbamazepine in Andelfingen-Thur. The overall trend indicates relative high model efficiencies, whith are NAS $= 0.58$ and $R^2 = 0.80$. When focusing to the first ten weeks the model overestimates the concentrations, whereas from week 11 onwards a general trend of underestimation is visible. At the station Frauenfeld-Murg the model efficiency is even higher, with values of NAS = 0.90 and $R^2 = 0.91$, the graph is shown in the Appendix Figure 7.4. At both stations the differences between the model and the measurements are in general lower when the discharge is lower and visa-versa.

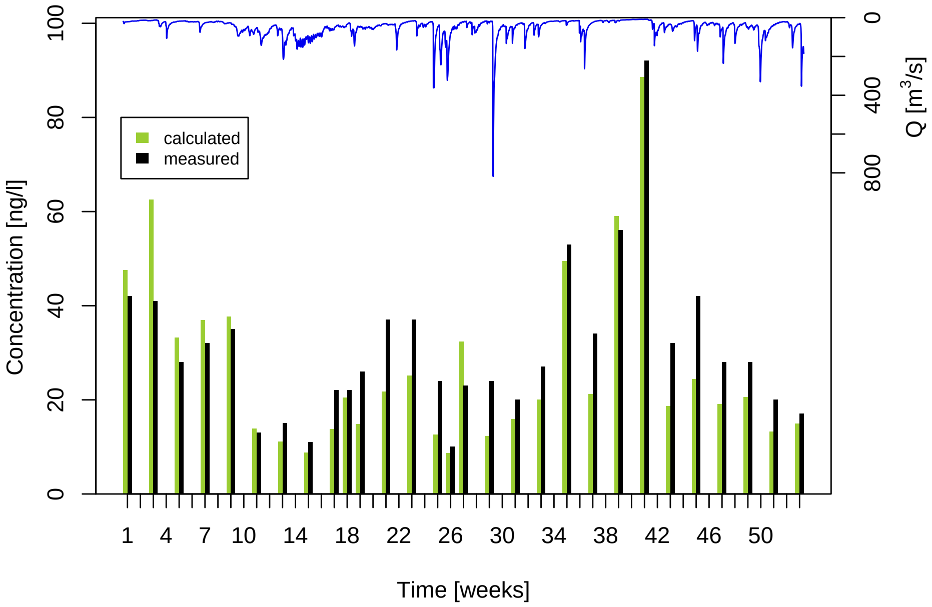


Figure 3.4: Calculated and measured weekly concentration of Carbamazepine and hydrograph at the station Frauenfeld-Murg

Diclofenac

In the model it is assumed that Diclofenac is affected by photolysis. We assumed that the rate of photolysis decreases with water depth (Eq. 2.13). In the literature several photolytic degradation rates of Diclofenac are available. Table 3.2 presents an overview of different photolytic degradation rates. The study by Radke et al. (2010) assessed direct photolytic degradation of the river Roter Main in Germany, the others studied photolytic degradation in the Lake Greifensee, which is located close to the Thur catchment. The data used in this work are data evaluated within the study of Tixier et al. (2003), but these data are not published.

In Table 3.2 the half-life times represent values of different water bodies and over different water depths. Comparing the studies where the values represent a water depth of 0.5 m or greater we see that Buser et al. (1998) and Tixier et al. (2003) are in

Table 3.2: Half-life times of different literature studies, k indicates if radiation attenuation is accounted.

Study	**Period**	**Water column**	**Half-life time [d]**	**Comments**
Buser et al. (1998)	whole season	whole water column	< 8–30	measurements
Poiger et al. (2001)	whole season	water surface	0.3–18	calculated, without k
Tixier et al. (2003)	16 Aug.- 22 Oct.	top 0.5 m	8	calculated, without k
Radke et al. (2010)	22 Aug.- 13 Sept.	1 m river depth	1.8	calculated, with k
present work	longest day	water surface	0.1	calculated, with k
present work	longest day	1 m river depth	1.0	calculated, with k

one range. Neither of them accounted for attenuation of solar radiation by clouds and fogs. As mentioned in chapter 2.3.3 we found in the present study an average value for attenuation of solar radiation of 0.5 over the season, when dividing measured incoming radiation over potential incoming radiation. The half-life time found by Radke et al. (2010) is comparable to the half-life time used in this study. The half-life time at the water surface of the present study is lower as the one presented by Poiger et al. (2001).

The assumptions made about photolysis, load input and transport lead to a specific pattern of Diclofenac loads at the stations Frauenfeld-Murg (Figure 3.5) and Andelfingen-Thur (Figure 3.6). They are presented together with the measured loads. The measured loads are already presented in Figure 3.1. Where weekly measurements are available, weekly modelled values are calculated by weekly sums of hourly model results. For biweekly measurements biweekly sums of the model results are calculated in $\frac{g}{week}$.

In Figure 3.5 the modelled loads at Frauenfeld-Murg show in the first 13 weeks and in the last 13 weeks constant values that are equal to the sum of the input loads of the Murg catchment. Between week 14 and week 40 the modelled loads are below the sum of the input loads with a minimum value of 113 $\frac{g}{week}$ at week 27. The modelled mean for the low radiation season (first and last 10 weeks) is 128 $\frac{g}{week}$ and the modelled mean

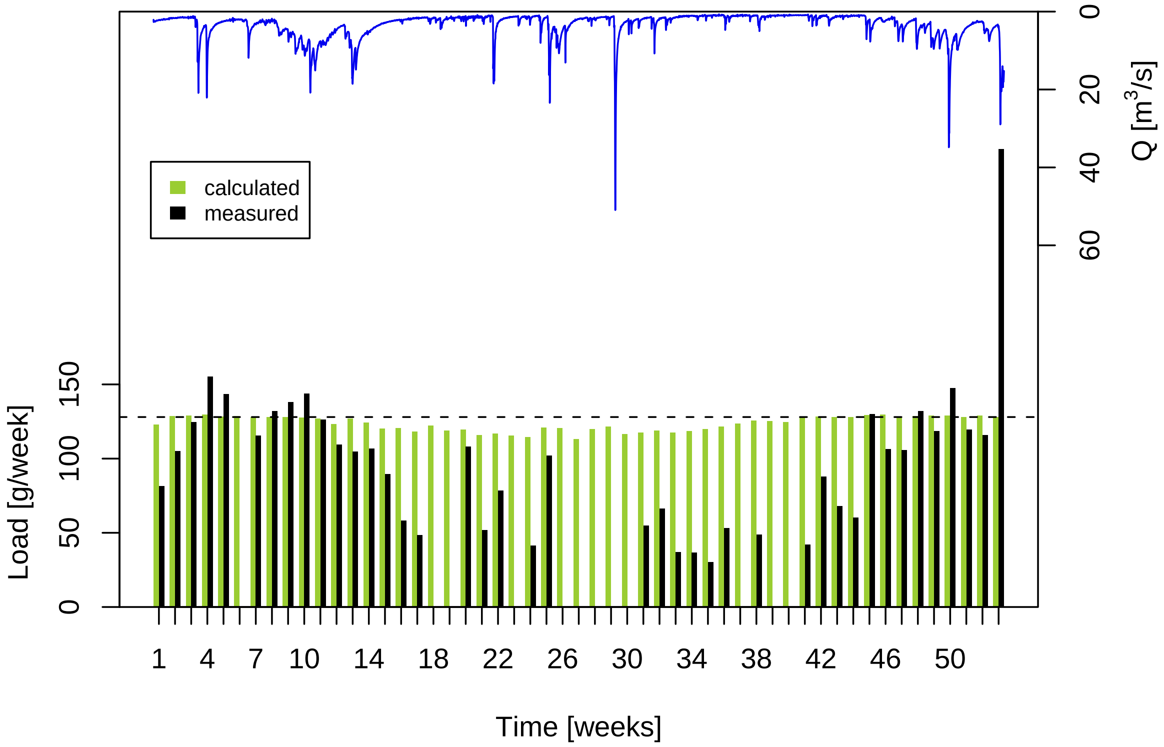


Figure 3.5: Modelled and measured loads of Diclofenac at the station Frauenfeld-Murg. The dashed line indicate the weekly sum of the constant input load and the hydrograph is presented at the top of the graph.

for the high radiation season (week 20 to week 40) is 119 $\frac{g}{week}$. Therefore the seasonal factor of the modelled loads is 0.93. The load-model efficiency at Frauenfeld-Murg is after NAS = -0.18 after $R^2 = 0.34$. The first and the last week of the period have only four days. The measurements take this not into account because the measured period starts some weeks before the year 2009 and was some weeks longer at the end of the year 2009. The model calculates the exact period 2009. Therefore larger differences between the model and the measurements can occur in loads and concentrations. This fact can explain the outlier of the measurements in the last week (Figure 3.5). But in the rest of the winter season the constant assumption fits very well with the measurements. In the summer season the model overestimate the loads to a large extent, especially when the discharge is low (week 34 to week 40).

Figure 3.6 depicts the measured and calculated loads together with the residence time (Tau in the graph and τ in the text) at the station Andelfingen-Thur and the net photolysis rate at the right y-axis. The net photolysis rate is a function of time and water depth, thus the net photolysis rate is plotted exemplar for a water depth of 0.5 m. The residence time is presented in weekly mean values. It is calculated with the weekly discharge. Figure and equations of the dependency of residence time and discharge are presented in Appendix Figure 7.3.

In Figure 3.6 it is shown that the modelled loads are below the sum of the input loads throughout the study period. The mean modelled loads are 864 $\frac{g}{week}$ in the low radiation season and 625 $\frac{g}{week}$ in the high radiation season. This results in a seasonal factor for the modelled loads of 0.72. When comparing the modelled and measured loads in the first 14 weeks, no significant trend of over or underestimation is visible. After week 14 measured and calculated loads are decreasing. But the measurements show lower minimum loads than the calculations. Especially from week 35 to week 41 measurements are lowest, whereas calculated loads are increasing. The model efficiency is NAS = 0.09 and $R^2 = 0.53$ of Diclofenac loads at Andelfingen-Thur.

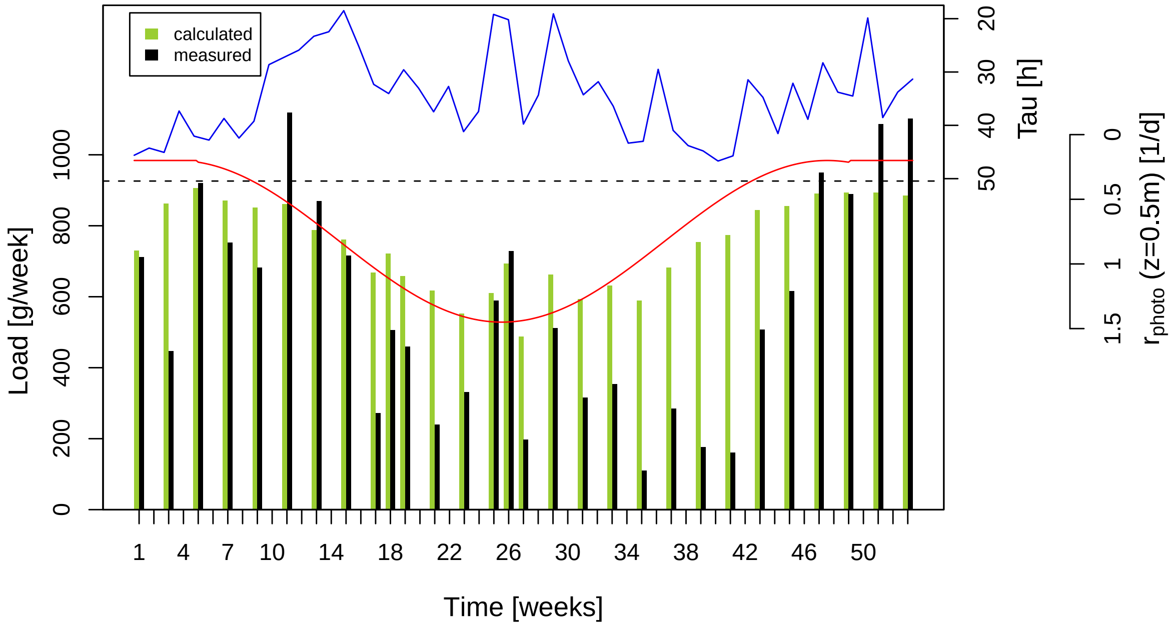


Figure 3.6: Modelled and measured loads of Diclofenac at the station Andelfingen-Thur. The dashed line indicate the biweekly sum of the constant input load. The residence time (Tau) is presented at the top and the net photolysis rate (r_{photo}) for a water depth of 0.5 m in the middle of the graph.

The shape of the net photolysis rate fits into the decrease of measured and modelled loads at Andelfingen-Thur. But the loads are in general overestimated from week 17 to week 45. The overestimations in this period are lower when at the same time the residence time τ is shorter (week 25, 26 and 29). By contrast, the overestimations are largest when τ is highest (week 35 to 41). In Figure 3.6 one can see that the measured loads follow the residence time at least for the period where the photolysis rate is higher. By contrast, the modelled load follow more the net photolysis rate.

The trend of increasing overestimation with increasing residence time can also be seen at the station Frauenfeld-Murg. Figure 3.7 depicts the factor of overestimation and the discharge for the period from week 15 to week 45. The discharge is calculated in weekly or biweekly mean values in correspondence to the loads. If the factor of overestimation is >1 the loads of the model are higher than the measurements, if it is <1 the model underestimates the loads, and values of 1 means the modelled and measured loads are equal.

Discharge and the residence time are reciprocally proportional. In Figure 3.6 we saw the overestimations are increasing when the residence time is increasing. Therefore we expect that with increasing overestimations the discharge is decreasing. This trend is indicative at Frauenfeld and Andelfingen (Figure 3.7).

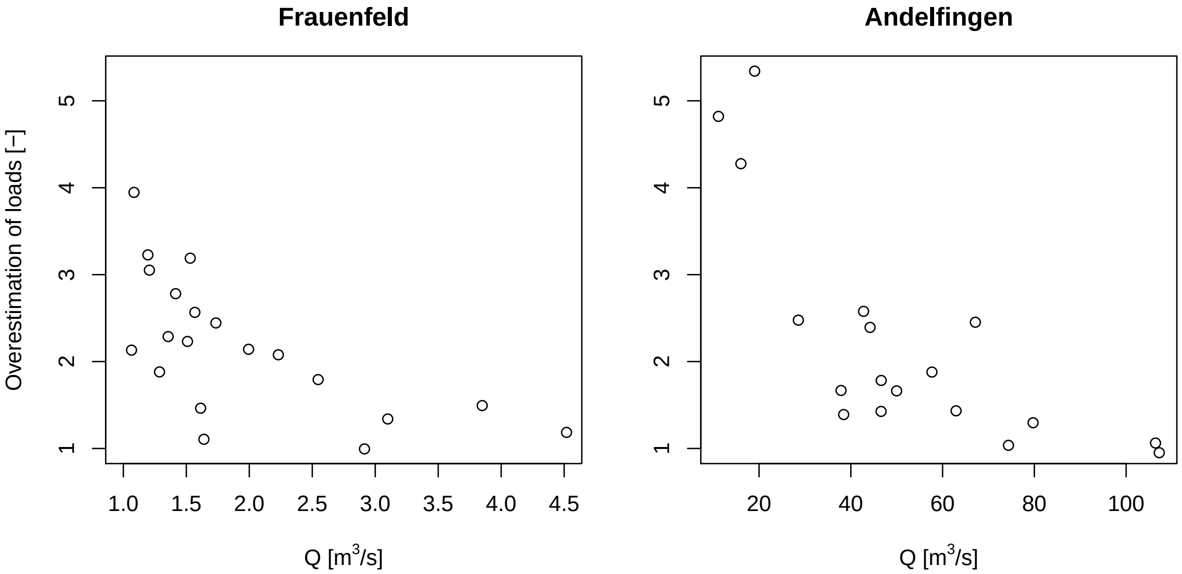


Figure 3.7: Factor of overestimation of Diclofenac loads between week 15 to 45. Abscissa corresponding accumulated weekly or biweekly discharge.

Figure 3.8 depicts modelled and measured Diclofenac concentrations at Frauenfeld-Murg in the upper graph and Andelfingen-Thur in the lower graph. At the site Frauenfeld-Murg the model predicts the measured concentrations very accurate for the first 14 weeks and from week 45 onwards. This period is in line with the low radiation season (week 1 to 10 and week 44 to 53) when week 44 is excluded. The efficiency values of the low radiation season without week 44 are then comparable high with $\mathrm{NAS} = 0.77$ and $R^2 = 0.87$. In the summer season, when high photolysis rates occur, the model overestimates the measurements. The overall model efficiency is comparable low, due to the large overestimations ($\mathrm{NAS} = -3.37$ and $R^2 = 0.34$). Especially between week 30 and 44, where discharge is low. The overestimations in the Diclofenac concentrations are up to a factor of four at week 35 at Frauenfeld-Murg.

At the station Andelfingen-Thur the overestimations are less frequent (lower graph in Figure 3.8). In the general pattern the model predicts the measurements very well over the whole season. Where the model is overestimating the concentrations a view outliers are visible. That are at the weeks 3, 27, 35, 39 and 42. At week 3 the model overestimates also the loads to the same extent (Figure 3.6). In addition, at week 3 the discharge shows very low values. This has the effect that with constant loads, as it is assumed in the model over this period, a decrease in the discharge results in a reciprocally proportional increase in the concentrations. The other large overestimations are also occurring when discharge is low. The model efficiency is $\mathrm{NAS} = -0.96$ and $R^2 = 0.35$, because of the few but large overestimations.

Hourly model results

The model calculates the concentrations in hourly time steps. Thus we can analyse if a high temporal resolution shows the same ranges of concentrations and loads than the weekly or biweekly sums. When looking at the hourly resolution of the modelled concentrations the ranges of the concentrations are much higher than in the weekly sums. This is shown in Figure 3.9 for Carbamazepine concentrations at the site Andelfingen-Thur. There the boxplots of measured and modelled biweekly concentrations have similar 1.5 inter quantile ranges and similar whiskers. The hourly concentrations are varying more, have larger 1.5 inter quantile ranges have, larger whiskers and have more outliers at high concentrations.

Especially the extreme values and the high frequency in the number of outliers motivates to analyse the modelled hourly time series more in detail. In the Appendix Figure 7.6, boxplots of modelled Carbamazepine concentrations at the start (upper boundary) and end location of each modelled river section (see Figure 2.1), together with the predicted no effect concentration (PNEC), are presented. As mentioned in the Introduction the PNEC for Carbamazepine is 500 $\frac{ng}{l}$ [2].

At most sites the concentrations are far below the PNEC. The median concentrations for the sites at the Glatt are the highest in the whole catchment. Outliers exceed the PNEC at the upper boundary site of the Urnäsch and at the start and end of the Lützelmurg. Highest concentrations were modelled for the upper boundary site of the Lützelmurg which are more than of factor six higher as the PNEC.

Boxplots of the modelled Diclofenac concentrations are presented in the Appendix Figure 7.6. As mentioned in the Introduction the PNEC of Diclofenac is 100 $\frac{ng}{l}$ [2]. Outliers of modelled concentrations exceed this value at most sections. Outstanding is that the median of all sites at the Glatt and at the Lüetzelmurg are above the PNEC and that the median concentrations of all sites at the Murg are around the PNEC. Highest concentrations are again at the upper boundary site of the Lützelmurg with maximum values up to 50 times over the PNEC.

Comparing the concentration ranges of Carbamazepine and Diclofenac, a general pattern of higher Diclofenac concentrations is noticeable. Furthermore, at sites where Carbamazepine concentrations are elevated, Diclofenac concentrations are also elevated.

Overall the highest concentrations could be detected where the rivers are smaller, which means at the upper boundaries of the model. The ratios of exceeding PNEC concentrations are presented in Figure 3.10. They are calculated according to the boxplots in the Appendix Figure 7.6. Generally the ratios are at the upper boundaries of each river highest. For Carbamazepine the PNEC is exceeded at two sites with an maximum temporal extent of 2 % at the upper boundary site of the Urnäsch. For Diclofenac the PNEC is exceeded at the upper boundary sites of the rivers Lützelmug (L1) with 93 %, Murg (M1) with 57 %, Glatt (G1) with 83 % and Urnäsch (U1) with 43 %.

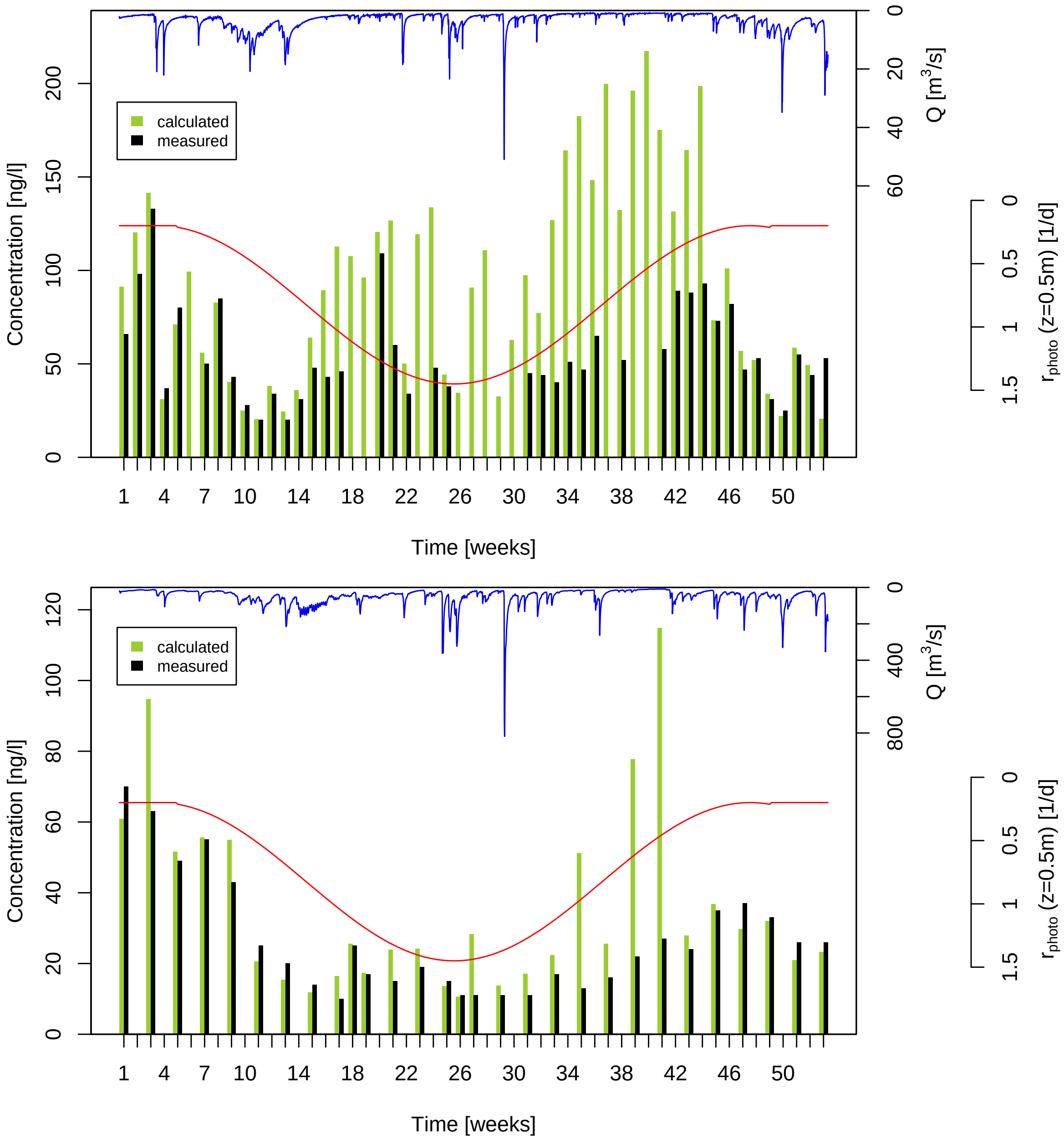


Figure 3.8: Modelled and measured concentrations of Diclofenac at Frauenfeld-Murg in the upper graph and at Andelfingen-Thur in the lower graph. The hydrographs are presented at the top of each graph.

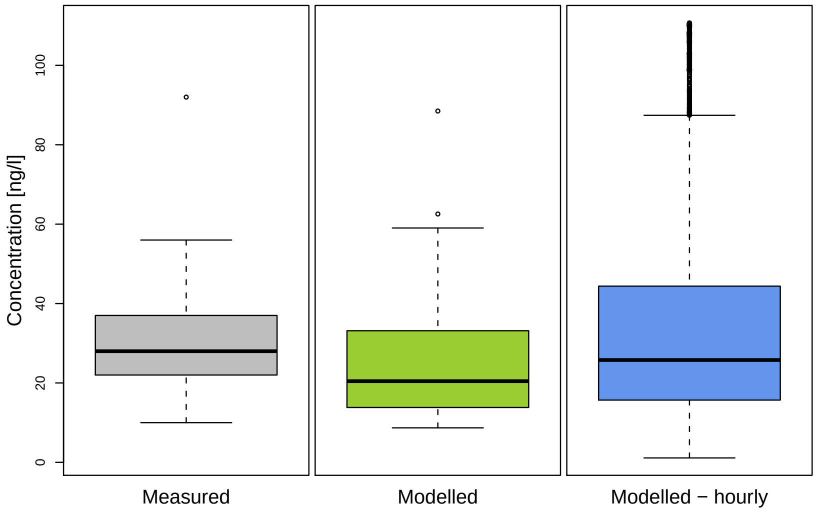


Figure 3.9: Boxplot of measured-biweekly, modelled-biweekly and modelled-hourly Carbamazepine concentrations at the station Andelfingen-Thur.

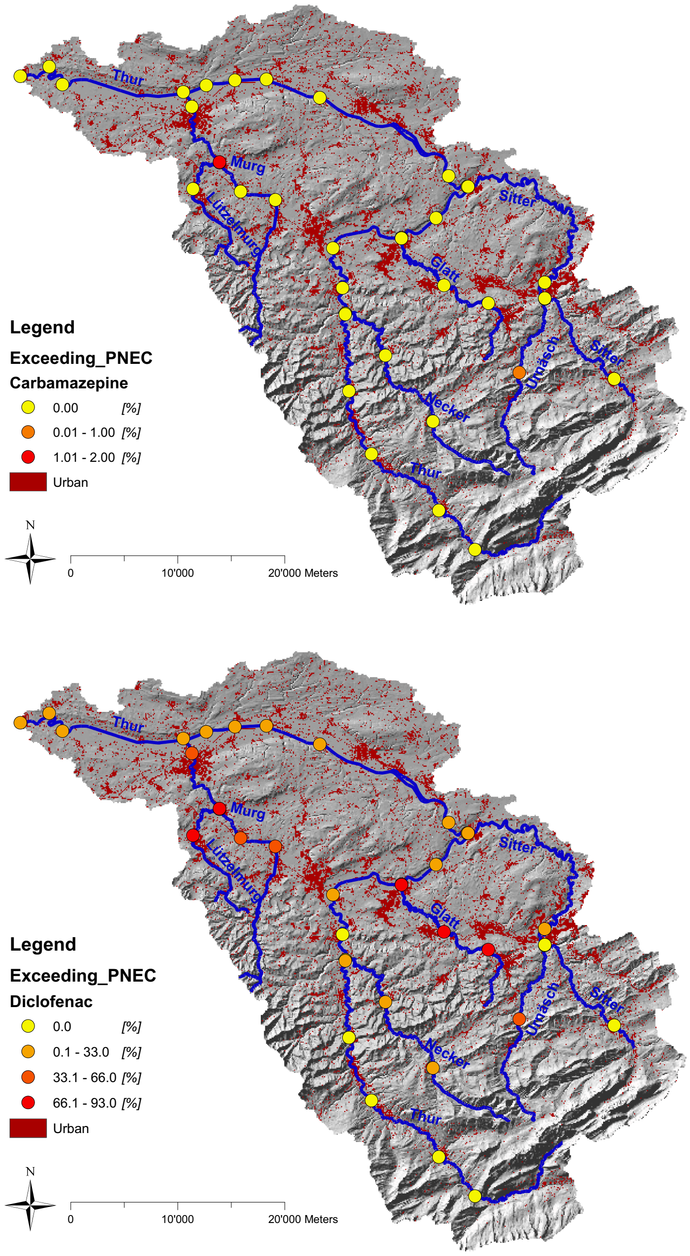


Figure 3.10: Exceeding PNEC concentrations in spatial and temporal scale at each modelled river section. In the upper graph the situation of Carbamazepine (PNEC = 500 $\frac{ng}{l}$) and in the lower graph of Diclofenac (PNEC = 100 $\frac{ng}{l}$).

4 Discussion

The intention of this study is to analyse the source of Carbamazepine and Diclofenac pollution and the fate of these pharmaceuticals within a river network. The first hypothesis stats that the pollution loads of Carbamazepine are constant for the whole season. The second hypothesis states that Diclofenac input loads have seasonal variations and the third hypothesis states that Diclofenac is degraded in the river due to direct photolysis. The purpose of the following discussion is to point out if the results strengthen or reject these hypotheses.

At the beginning we want to interpret the results of the NADUF micropollution measurements with respect to Carbamazepine and Diclofenac. In general these show clearly different patterns at the stations Frauenfeld-Murg, Andelfingen-Thur and Rekingen-Rhine. Discharge, load and concentration pattern are similar for Frauenfeld-Murg and Andelfingen-Thur, but clearly different at Rekingen-Rhine. This can be attributed to the characteristics of the corresponding drainage areas.

Having a closer look at the station Rekingen-Rhine one notes that the Lake of Constance is situated within the drainage area of Rekingen-Rhine. Therefore Lake of Constance is acting as a buffer system for discharge and concentrations. The residence time of Lake of Constance is 4.3 years, what is long enough to dampen sharp fluctuations [28]. Therefore the concentration pattern of persistent compounds like Carbamazepine is relatively constant over the season at Rekingen-Rhine. Constant concentrations in the Lake of Constance cause significant positive linear correlation between discharge and loads at the station Rekingen-Rhine (Appendix Figure 7.5). If the assumption of constant pollution inputs is true for Carbamazepine and Diclofenac we would expect to get the Carbamazepine-load correlation pattern also for Diclofenac loads. For Diclofenac the discharge and loads are correlated, however the correlation is negative. That can be explained by photolytic degradation of Diclofenac in the Lake of Constance [29]. In conclusion, direct photolysis of Diclofenac in the Lake of Constance is very significant in the summer season. This pattern could also be seen in other lakes [15], [13].

As mentioned in chapter 3.1, within the drainage areas of Frauenfeld-Murg and Andelfingen-Thur no lakes are buffering the discharge of the Murg and Thur, and the discharge follows at both sites a similar pattern. This means that lakes and other characteristics that could influence the transport of the compounds to a large extent can be neglected. Thus we chose the sites Frauenfeld-Murg and Andelfingen-Thur to test the formulated hypotheses where we compare the measured and simulated loads of Carbamazepine and Diclofenac.

First, we test the hypothesis of constant pollution loads of Carbamazepine over the season. This can be done by analysing the correlation between discharge and Carbamazepine loads and by evaluating seasonal ranges of load fluctuations in the measurements. If we consider a catchment without a lake, we expect no correlation between discharge and Carbamazepine loads, because we assume constant load inputs. In general, a significant correlation between discharge and loads would mean constant concentrations. However, constant concentrations are in contrast with constant loads, since the discharge varies. At the sites Frauenfeld-Murg and Andelfingen-Thur no significant correlation between Carbamazepine loads and discharge can be detected. In addition, the winter and summer seasons indicate no trend in the differences of the load medians. This leads to the conclusion that no seasonal variation of pollution loads by Carbamazepine can be expected. Moreover, factors of consumption, human excretion and WWTP elimination of Carbamazepine can be assumed to be constant throughout the year.

Measured Diclofenac loads show a different pattern to the measured Carbamazepine loads, if we compare the low with the high radiation season. The observed seasonal variations indicate a seasonal factor of 0.45 ranging from 0.18 to 0.95 at Frauenfeld-Murg and a seasonal factor of 0.43 ranging from 0.14 to 0.80 at Andelfingen-Thur.

The hypotheses two and three were formulated to explain these seasonal variations. According to hypothesis two the origin is a seasonal variation in the input loads of Diclofenac. The input loads depend on the compound characteristics of consumption, number of inhabitants connected, human excretion, appropriate human disposal, fate in sewer system and degradation in WWTPs. Each of these factors can contribute to the input loads in different ways.

Consumption was assessed from sales statistics, as mentioned in chapter 2.3.3. Sale statistics do not vary between the quarters of a year, as indicated by data provided from IMS Health Ltd. (2000-2004). The actual consumption is dependent on the fraction of sold and used quantities. Unused quantities can be neglected [9], [30]. An example of unused quantities is inappropriate disposal of pharmaceutical leftovers through flushing in toilets. Due to the relation between actual use and sale quantities we can assume that a seasonal variation is very unlikely [9].

The number of inhabitants connected to each WWTP will not vary within a season, due to considerable stable population trends over several years, in northern Switzerland [23]. The human excretion rate will not vary within a season, because human metabolism does not show a seasonal pattern.

The fate of the compounds in sewer systems is rather unknown. One study indicate that similar predominant microbial processes occur in sewer networks and WWTPs [31]. The amount and rate of possible Diclofenac degradation in sewer networks depends on the microbial community in the sewer network. Factors that affect the microbial community in the sewer network could be the temperature or the composition of the sludge. Regarding the temperature one notes that on one hand, the sewer systems are usually in the soil where the seasonal temperatures are relative stable. On the other hand, the sludge temperatures within a WWTP varies (Eawag, Christian Konrad Abegglen). These temperature fluctuations in the WWTP can be linked to processes within the WWTP itself or to the sludge temperatures of the WWTP inputs from the sewer system. The composition of the sludge may also change seasonally due to a seasonal use of specific products. As a consequence, a seasonal variation in the degradation of Diclofenac in the sewer system is possible, due to temperature variations or variations in the composition of the sludge within the sewer system. In conclusion, a more detailed study about the fate of the compound in the sewer network is necessary.

The literature values of Diclofenac degradation rates show a large variation, which can be traced back to different treatment processes in WWTPs [11]. Hollender et al. (2008) indicated a range of 15 to 40 % for the degradation of Diclofenac with a sludge retention time of 5 to 15 days. Usual sludge retention times of WWTPs are 7 to 13 hours [32]. The degradation rates of Diclofenac in conventional WWTPs of Switzerland are assessed in [32], [29]. Both of these studies were investigated the degradation rates in short time periods before mid May or after mid September. The degradation processes within a WWTP are highly depended on the sludge temperature. Sludge temperature can increase significantly during summer as mentioned above. This period is not covered in the studies [32] and [29]. Thus we can only speculate that the degradation rates could be higher in summer than in winter. This means that the loads of Diclofenac within the WWTP effluent could vary seasonal due to fluctuations in the degradation rates of WWTPs. In conclusion, the load input of Diclofenac into the river can show a seasonal pattern.

As it is discussed above the compound characteristics of consumption, number of inhabitants connected, human excretion and appropriate human disposal are not significantly varying within a year. Conversely, the fate in sewer systems and the degradation in WWTPs are dependent on seasonally changing variables. The most important variable seems to be the temperature. A detailed quantification of the effects to the input loads of the rivers is here not possible. Comparing these conclusions with the measurements we can state that the measured seasonal variations in Diclofenac loads can be attributed to seasonal variations in the input loads to the river. If they can explain the measured lower loads in the summer than in the winter, of about 45 % ($f_{season} = 0.43$ and 0.45), is not clear. Although almost equal seasonal factors for both catchments, Murg and Thur, are a strong indicator that the input loads of Diclofenac are in summer lower than in the winter.

Another possibility to explain the lower Diclofenac loads in summer than in winter is the degradation of Diclofenac by direct photolysis in the river. To test this third hypothesis the process of direct photolysis is implemented in the model. The model shows that direct photolysis reduces the loads in the summer season. At the station Frauenfeld-Murg, the simulated loads are at average 7 % lower in the summer season than in the winter season. At Andelfingen-Thur, the reduction by the model was with 28 % more pronounced. Mean residence time and mean water depth within each catchment are caracteristic for the extent of the photolysis rate. The Murg has a mean residence time of 5 hours and a mean water depth of 0.14 m, the values for the Thur are 22 hours and 0.25 m respectively. This means on one the hand that Diclofenac is exposed longer to the process of photolytic degradation in the Thur than in the Murg. On the other hand, the greater mean water depth leads to less net photolysis rates over the whole water column in the Thur than in the Murg. The simulations indicate a higher effect of photolysis in the Thur (28 %) compared to the Murg (7 %). Therefore in this case the differences in the residence time is more important than the differences in the water depth.

To test the direct photolysis assumption for Diclofenac we compared the observed reductions in the summer season with the modelled reductions in the same season. The measurements are about 45 % lower in the summer than in the winter. In summary, direct photolysis can explain the seasonality in Diclofenac loads to about 15 % at Frauenfeld-Murg and to about 60 % at Andelfingen-Thur. Therefore photolytic degradation alone is not sufficient to explain the seasonal variations in Diclofenac loads in the Murg and in the Thur. In order to match modelled and measured values one has to take seasonal input fluctuations, as in hypothesis two, into account.

Besides testing the hypotheses, another goal of this study is to validate the applied compound model with available measurements at the stations Frauenfeld-Murg and Andelfingen-Thur. Measurements of Carbamazepine loads show a relative constant pattern through the season at both sites. The fluctuations in the loads can not be attributed to seasonal patters. In the model the assumptions of constant pollution load inputs lead to constant simulated loads over the whole season for Carbamazepine. This means the observed variations in the loads of Carbamazepine at both sites can not be described by the model. However, this constant input loads result in a very accurate prediction in the concentrations of Carbamazepine at both sites.

In general, the simulation of Carbamazepine concentrations at Frauenfeld-Murg is more certain than at Andelfingen-Thur. This can be explained by higher efficiencies in the modelled hydrograph at Frauenfeld-Murg ($\mathrm{NAS} = 0.98$) than at Andelfingen-Thur ($\mathrm{NAS} = 0.88$). In the case of Andelfingen-Thur the hydrograph is overestimated by the model during one longer period. As discussed before, overestimations in the hydrograph are leading to a higher dilution and therefore to lower concentrations when assuming constant input loads. In the Results of this work a general trend of underestimation is shown for Carbamazepine concentrations. Modelling efficiency of Carbamazepine concentration is lower at Andelfingen-Thur ($\mathrm{NAS} = 0.58$) than at Frauendeld-Murg ($\mathrm{NAS} = 0.90$). Conclusively, comparable small uncertainties in the hydrological model leads to much larger uncertainties in the concentration model. Nevertheless, the assumptions of a constant seasonal load input and the persistence of Carbamazepine in a stream network are reasonable, in knew of the simulations and the measurements.

For Diclofenac we assumed also constant input loads together with direct photolysis. The direct photolysis shows a seasonal dependence. The constant input assumptions lead to a good prediction of loads and concentrations of Diclofenac in the winter season. In the summer season we saw that the photolysis approach of Diclofenac can not fully describe the observed seasonal variations in Diclofenac loads. Large overestimations of the model occur within the season where photolysis rates are higher. The ratio of the compound that is degraded is not only dependent on the rate of photolysis. Moreover, the discharge of the river has a large influence to the photolytic degradation process, as it is shown in chapter 3.3.2. This is so because the river discharge influences the water depth of the river and thus the residence time of the compound within the river. Further the water depth influences the net photolysis rate directly, means the photolysis rate decreases with water depth. In summary the proportion of Diclofenac that is degraded at a given time, decreases with increasing discharge values. Such a dependency is supported by the measurements, because the trend of Diclofenac loads seem to follow the trend of the residence time.

The modelled data, however, follow more the photolysis rate (Figure 3.6). The model overestimates the loads and concentrations of Diclofenac especially when the residence time is low. The lower the residence time the longer the compounds are exposed to photolytic degradation in the river. The longer the time of exposure the higher is the proportion of the compound that is degraded. As a result, large overestimations during a low residence time indicate that the extent of the photolytic degradation is too low.

In the model a lot of assumptions had to be made in order to keep the model simple or because no data could be acquired from the literature or from other sources. These assumptions have always a certain degree of uncertainty. The overall uncertainty results from a combination of the pollution inputs occurring from WWTPs, the uncertainty of the hydrograph and the uncertainty of the photolytic degradation approach for Diclofenac. This uncertainties will be discussed more in detail, what will also contribute to the question why the model overestimates the Diclofenac patterns during dry periods when discharge is low.

Fist, we will analyse the uncertainties of the constant pollution assumption. As mentioned in chapter 3.2 estimated load inputs of Carbamazepine and Diclofenac had to be corrected by a factor of 1.55. The first estimates of the load inputs were calculated according to Ort et al. (2009). In the same study, the uncertainty of the input-loads calculation was evaluated to ± 64 % in total. It was derived from 10 000 Monte Carlo simulations were uncertainties of ± 20 % for the measurements, ± 50 % for the load to the WWTPs and ± 20 % for the elimination rate by WWTPs were considered. Thus the correction factor (1.55) is in the range of the uncertainty of the estimation procedure of the load inputs (± 64 %). However, we corrected the inputs to be able to compare the model with the measurements. The uncertainties of the load to the WWTP and in the elimination rates of the WWTPs were discussed partly in the previous section with respect to seasonal variations. Now we will continue this discussion to also account for the non seasonal uncertainties.

As mentioned before, the loads to the WWTPs are dependent on the sale statistics, the correlation between the sale statistics and the consumption, human excretion, appropriate disposal and the fate within the sewer system. The variations in consumption and human excretion are considered in the uncertainty of the input to WWTPs (± 50 %) as described by Ort et al. (2009). The influence of different sewer systems is of less importance, because the sewer systems in a smaller region are usually similar (Christian Konrad Abegglen and Ralf Kaegi, Eawag)

Elimination rates by WWTPs can vary highly. Advanced waste water treatment can eliminate Carbamazepine and Diclofenac to up to 95 % [33], [34], but such technology is rarely used. According to several studies usual WWTPs do not degrade Carbamazepine, but degrade Diclofenac of about 15–40 % [32],[34]. Consider the elimination rate of each WWTP individually, by including properties like the type of treatment or sludge age, would be the best practice but the effort would be very high. Therefore the average value of Diclofenac degradation rates for Swiss WWTPs by 25 ± 20 % (Ort et al. (2009)) seems to be acceptable. In the model, the same degradation rate is assumed. It is constant over the season and equal for all WWTPs.

In conclusion, the degradation process before Diclofenac enters the river is highly uncertain. Degradation rates of WWTPs and possible degradation in the sewer system influence directly the input loads to the rivers. The most important influence to the input loads can be addressed to the degradation rates in the WWTPs. Thus seasonal variations in the degradation rate could result in seasonal variations in the input loads. Keeping that in mind the model assumption of constant Diclofenac load inputs is questionable. We can expect that the simulations become more accurate when we apply a seasonal variation of the WWTP degradation rates in the load inputs of the model.

The simulation of transport and degradation of the compounds is highly influenced by the hydrograph, because residence time and water depth depend on it. The hydrological inputs are based on discharge measurements. The model efficiency values indicate that the model is in general accurate enough to model the fate of the compounds in the river. The overestimations by the simulated hydrograph at Andelfingen-Thur between week 12 and 24 influence the simulations of the compounds Carbamazepine and Diclofenac. First, due to dilution an overestimation of the discharge will result in lower concentrations when assuming constant loads. Second, higher discharge leads to greater water depth and therefore to an underestimation of the degradation.

Although the effects of the uncertainties in the hydrograph are low compared to the inaccuracies of the input assumptions. Significantly higher influence to the model have the assumptions of the Diclofenac degradation by direct photolysis.

The process of direct photolysis depends on various factors, for which assumptions had to be made. The assumptions in the process of direct photolysis concerning parameters like photolytic rates, shading by vegetation and the composition of water. They are now discussed in more detail.

In the literature exist various assumptions about the degradation rates of Diclofenac in natural water bodies, as presented in chapter 3.3.2. The rates used in this study are similar to the rates of a comparable river investigated by Radke et al. (2010).

Another factor that influences direct photolysis in rivers is shading by vegetation along the river and aquatic plants within the river. Radke et al. (2010) accounted also for shading of the river by plants with a shading factor between 0.2 and 0.4. Shading factors are dependent on the density of the vegetation along the river, the type of the vegetation, the seasonal growing stage of the plants as well as on the river width. The characteristics of the vegetation can be gained by aerial photographs [14] and by considering of the seasonal dependent leaf area index. A hint for the river width is the size of the catchment area. Radke et al. (2010) investigated the catchment area of the river Roter Main which is 500 km^2 large. Such a size is in between the catchment areas of the river Murg with 200 km^2 and the river Thur with 1 750 km^2. This means, average shading factors along the Murg could be higher and along the Thur lower to that along the river Roter Main. In an other study a shading factor of 0.7 due to aquatic plants is considered for the river Glatt. The Glatt has a catchment area of 400 km^2 and is closely located to the study area [35].

In the model shading was neglected and therefore the photolysis rates were too high. We can expect that this overestimation of the photolysis rates is most pronounced when the rivers are smallest. Applying shading in the model would lead to less degradation of Diclofenac and therefore the differences between simulated and measured values would even be higher.

Another source of uncertainty is the different water composition between the studied stream network and lake Greifensee, from where degradation rates were taken. The composition of the water affects the attenuation of the light intensity with water depth (see chapter 2.3.2). Therefore ones could expect different photolysis rates in the rivers. An indication of the water composition is the dissolved organic carbon (DOC) content. The study by Canonica and Freiburghaus (2001) indicate that the DOC content and the degradation rates are proportional for Dimethoxyphenol [36]. When assuming a proportional relation between Diclofenac photolysis rates and DOC we will now compare the different DOC contents in the waters of interest.

The DOC content in the lake Greifensee is around 4 mg/l [37] and in the river Roter Main it is 8.5 mg/l (supporting information of [14]). For the Thur watershed the DOC ranges between 1.3 mg/l and 2.6 mg/l, where the lower value are found at locations higher up the river and the higher value at the station Andelfingen [38]. Considering the linear relationship between DOC content and photolytic degradation rates ([36]) we can conclude that the degradation rates in this study should be higher than the degradation rates found for lake Greifensee. Comparing the DOC contents in the study area and the DOC content in the river Roter Main we should have also higher degradation rates in this study than in the river Roter Main.

A difference in the DOC content is an indicator for differences in the absorption coefficients of the waters. Therefore we can recommend to estimate the real rate of photolysis. This could be done by measuring the absorption coefficient of the assessed river network. Since the water composition in a river network is site specific, it would be best to measure the absorption coefficient at different sites. With the absorption coefficient of the water a compound specific photolytic degradation rate can be calculated, for example with the computer program GCSOLAR. This would probably lead to higher degradation rates in the assessed rivers as discussed above. As a consequence, the model would show better agreement between measured and modelled values.

5 Conclusion and outlook

To simulate the fate of pharmaceuticals in a stream network a lot of assumptions have to be made. Each assumption has itself a specific degree of uncertainty that can aggregate in the model. Some assumptions have a relative large uncertainty range. For example constant load inputs or the rate of degradation could vary to a large extent. Consequently one can expect large differences between simulated and measured patterns of the pollutants. For all three modelled sites, however, the modelled concentrations and loads of Carbamazepine and Diclofenac are matching the measurements rather well regarding a whole year.

A constant load input assumption over the season is practicable for the pharmaceuticals Carbamazepine and Diclofenac. The first hypothesis saying that Carbamazepine is persistent in water networks could be confirmed. This could be seen in the analysis of measurements and by simulations over one year.

Diclofenac on the other hand shows a seasonal pattern in observations. The reasoning for that is due to significant lower loads of Diclofenac in the summer season than in the winter season. When comparing two different river catchments the Diclofenac loads drop in the summer to the same extend of about 45 %. The analysed sites were at different locations in the same river network. The pattern of the hydrograph was similar, but the average of the discharge and the length of the river were different. Especially the difference in the river length leads to differences in the residence time. Effects other than the input loads would show up in a different load drop in the summer season. Due to the fact that the load drop was the same for both sites one can conclude that the observed seasonal variations of Diclofenac loads at sites downstream the river can be attributed to the input loads. This supports the second hypothesis of this study.

With the third hypothesis the intention was to explain the observed drop in summer loads with photolytic degradation in the river of Diclofenac. Therefore we constructed a model that used the assumption of constant input loads and a degradation process due to direct photolysis of Diclofenac. This was found to be partly true. At the site with a shorter residence time and less discharge the drop of Diclofenac loads in the summer season could be described to about 15 %. At the site with the longer residence time and more discharge the lower summer loads compared to the winter loads could be described to about 60 %. For Diclofenac the applied degradation by photolysis is not sufficient to describe the strong seasonal fluctuations. Therefore we can state that the approach of constant seasonal load inputs and degradation due to direct photolysis can explain to some extent the seasonal variations of Diclofenac loads as well.

In order to match modelled and measured values of Diclofenac one has to take seasonal load input fluctuations and/or higher degradation due to direct photolysis into account. The seasonal load input fluctuations can be caused by seasonal fluctuations in a pre-degradation chain that consist of the human body, the sewer system and the WWTP. Most likely is that the WWTP contribute largest to seasonal variations in this pre-degradation chain, due to fluctuations in the temperature.

The second factor that could explain the overestimation of Diclofenac by the model are higher photolytic degradation rates than the degradation rate used, from lake Greifensee. The key parameter the water composition, for example the DOC content. From a literature review we found that DOC was by a factor two lower in the studied stream network of the river Thur than in the lake Greifensee.

Shading was not accounted for in the photolytic degradation process. Shading is site and season specific due to the characteristics of the vegetation along the river, aquatic plants within the river and the river width. Shading has the effect that the degradation rates are diminished. Generally we expect for our rivers shading factors that are rather in the lower range of the factors mentioned, because the rivers in this study are wider and have less aquatic plants. Which of these two factors, different absorption coefficients or shading, has a larger influence on the photolytic degradation cannot safely be stated.

We summarise that the hypothesis of constant pollution loads of Carbamazepine could be verified. Hypothesis two said that Diclofenac pollution loads have a seasonal variation that leads to a seasonal load pattern in the river. Hypothesis three explains the same seasonal pattern of Diclofenac with direct photolytic degradation in the river network. Each of hypotheses two and tree for itself are true at least to a certain degree. It is likely that Diclofenac patterns are influenced by both, photolytic degradation and a seasonal variation in the input loads.

Finally, with the hourly model results we could contribute to the broader discussion of the assessment of micropollutants in the environment. Critical sites within a river catchment were concentrations of Carbamazepine and Diclofenac reaching values that are harmful to the aquatic environments could be identified. For example the PNEC of Diclofenac is exceeded up to 93 % of the time. Such a hourly temporal resolution show much larger extreme concentrations as common micropollution models of a river network.

The model constructed within this work is already in use to simulate the fate of Carbamazepine and Diclofenac at the other NADUF sites, where measurements to these compounds are available. For more accurate results we can highly recommend to clarify the pre-degradation process and to evaluate the river-site specific degradation rates in respect to Diclofenac. In other words, it should be figured out if the degradation rates in WWTPs are seasonally dependent and if degradation in sewer systems should be taken into account. The site-specific degradation rates in the river should be estimated when measuring the absorption spectrum at some sites along the river. Shading should also taken into account. As a first estimate the shading factors used in Radke et al. (2010) could be taken.

Moreover, within the spatial set up, the model should be extended to diffuse pollution from agricultural fields or urban constructions. These could contain specific herbicides or biocides. To account for pollutants from diffuse source like agricultural fields the pathway form application on the field, infiltration into the soil, transport in the soil and leakage into the stream network has to be modelled separately. The output of such a infiltration-leakage model can than be fed in as point or lateral inputs to the constructed model.

At the end, the results of this river routing model can be used to detect in a temporal and spatial scale the extent of harmful effects to the environment. Such investigations should be used further to make recommendations on the appropriate use and treatment of sewage.

6 Bibliography

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7 Appendix

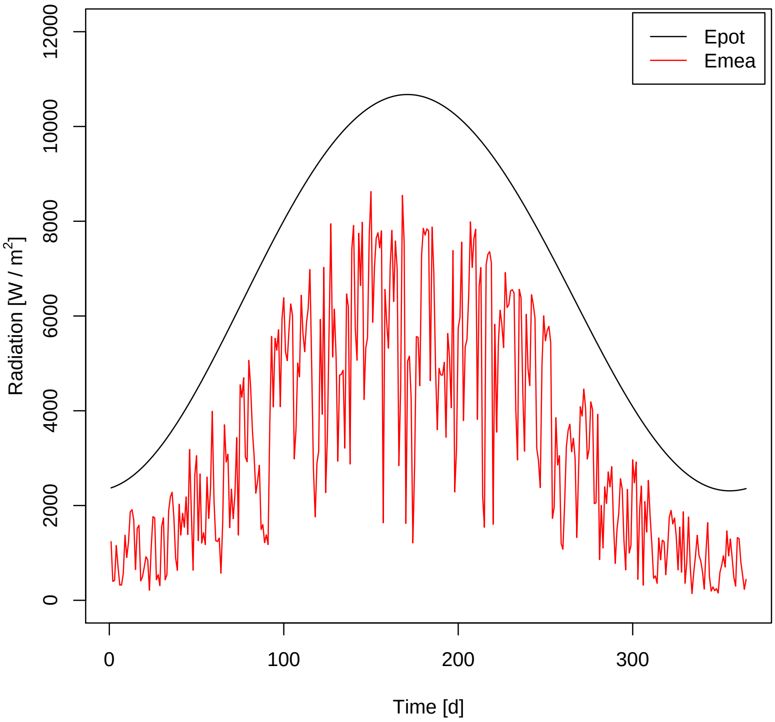


Figure 7.1: Measured and potential solar radiation for the site Tänikon.

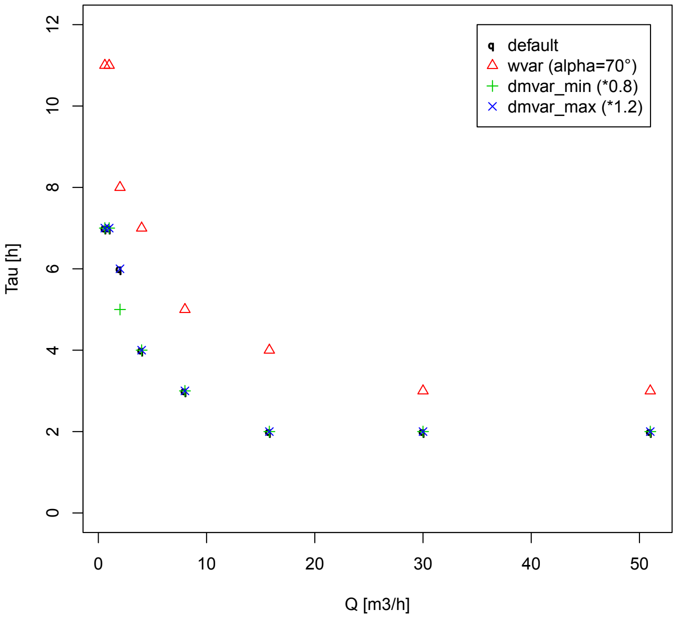


Figure 7.2: Maximal residence time in the Murg from Münchwilen to Frauenfeld. For different simulations.

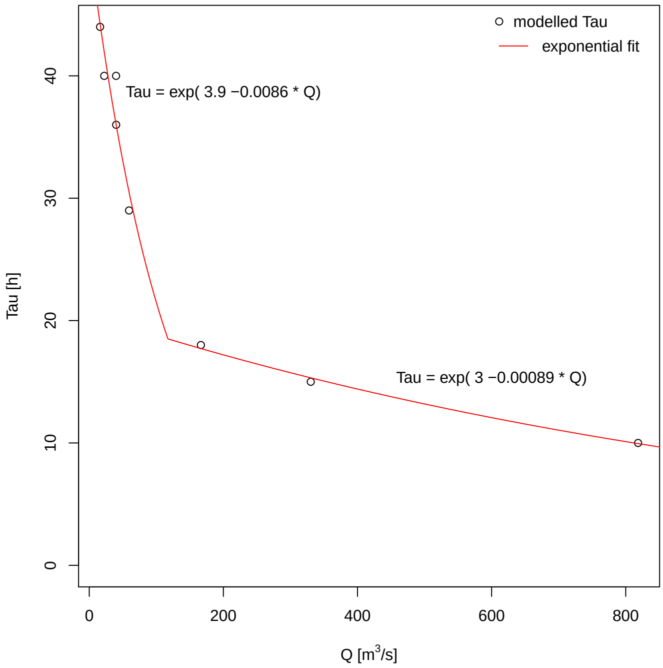


Figure 7.3: Maximal residence time in the Thur from Stein to Andelfingen. With exponential fit.

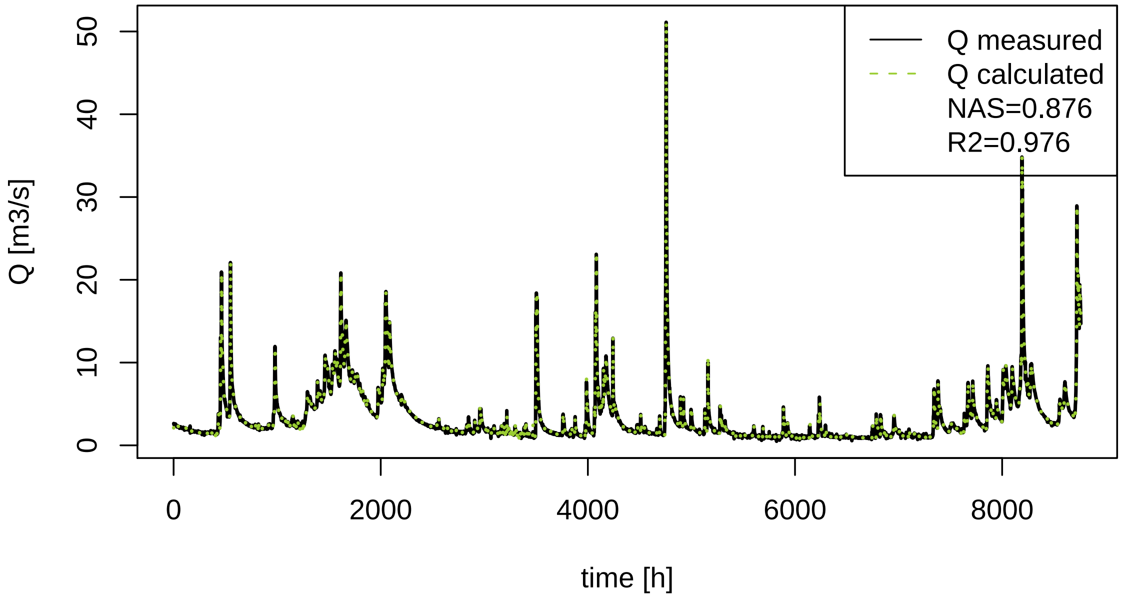
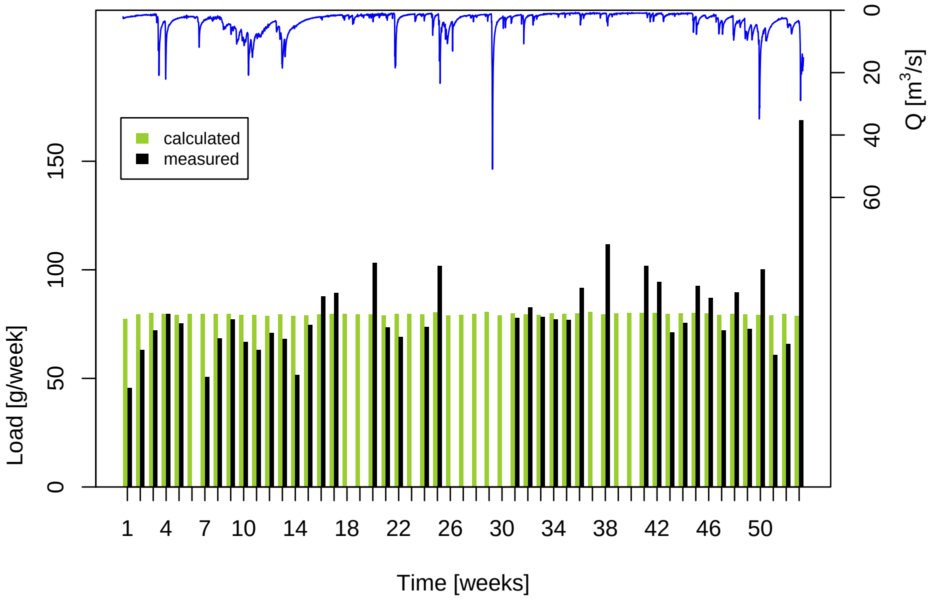


Figure 7.4: Measured and modelled discharge at Frauenfeld-Murg.



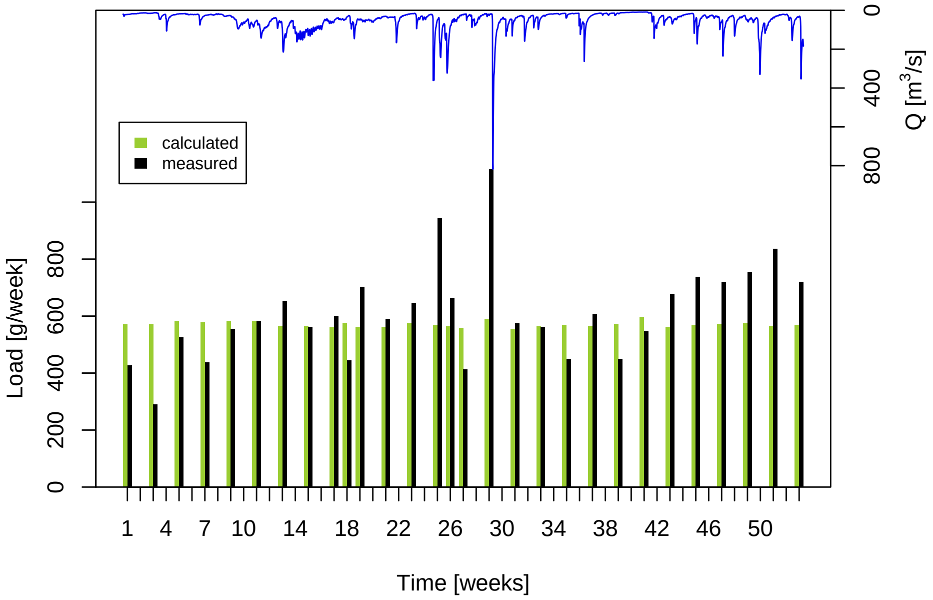


Figure 7.5: Modelled and measured loads of Carbamazepine at Frauenfeld-Murg in the upper graph and Andelfingen-Thur in the lower graph. The hydrographs are presented at the top of each graph.

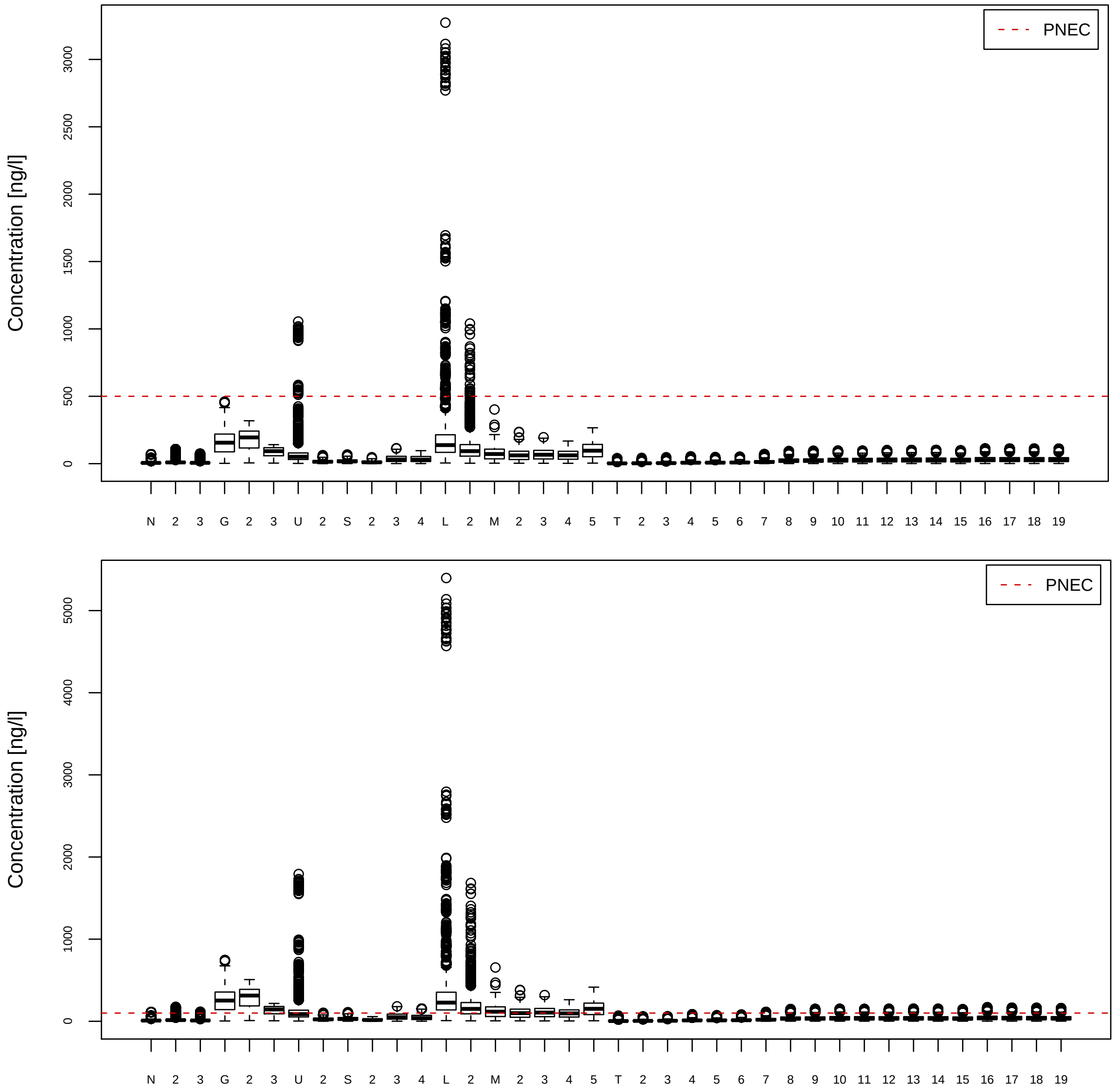


Figure 7.6: Boxplot of Carbamazepine concentrations in the upper graph and Diclofenac concentrations in the lower graph, at the start and end locations of every modelled river section. The boxplots should be read from left to right. The letters stands for the upper boundary sites of each river. The following numbers indicate the section boundaries in downstream direction. Fist the tributaries and than the parent rivers are listed. The dashed line indicates the PNEC of Carbamazepine (500 $\frac{ng}{l}$) and Diclofenac (100 $\frac{ng}{l}$) respectively [2]. (N: Necker, G: Glatt, U:Urnäsch, S: Sitter, L: Lützelmurg, M: Murg and T:Thur)