Modeling the Fate of Pharmaceuticals in a Fourth-Order River Under Competing Assumptions of Transient Storage

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Abstract Quantifying the degradation of micropollutants in streams is important for river-water quality management. While biodegradation is believed to be enhanced in transient-storage zones of rivers, it can also occur in the main channel. Photodegradation is restricted to the main channel and surface transient-storage zones. In this study, we propose a transient-storage model framework to address the transport and fate of micropollutants in different domains of a river. We fitted the model to nighttime and daytime measurements of a tracer and four pharmaceuticals in River Steinlach, Germany. We could separate the surface and subsurface fractions of the total transient-storage zone by fitting fluorescein photodegradation at daytime versus conservative nighttime transport. In reactive transport, we tested two model variants, allowing biodegradation in the main channel or restricting it to the transient-storage zones, obtaining similar model performances but different degradation rate coefficients. Carbamazepine is relatively conservative; photodegradation of metoprolol and venlafaxine can be quantitatively attributed to the main channel and surface transient-storage zone; metoprolol, venlafaxine, and sulfamethoxazole undergo biodegradation. We projected a decrease of overall pollutant removal under higher flow conditions, regardless of attributing biodegradation to specific river compartments. Our study indicates that model-based analysis of daytime and nighttime field experiments allows (1) distinguishing photodegradation and biodegradation, (2) reducing equifinality of surface and subsurface transient-storage, and (3) estimating biodegradation in different domains under different assumptions. However, entirely reducing the equifinality of attributing biodegradation to different compartments is hardly possible in lowland rivers with only limited transient storage.

1. Introduction
Emerging contaminants have raised increasing concerns on river-water quality (Liu et al., 2019; Sim et al., 2010; Zhao et al., 2010). Among these contaminants, pharmaceuticals are widely detected (Kunkel & Radke, 2012; Sim et al., 2010; Zhao et al., 2010). Their concentrations are typically in the range of nanograms to micrograms per liter (Açuña et al., 2015; Li et al., 2016). Pharmaceuticals have negative impacts on aquatic organisms (Gelsleichter & Szabo, 2013; Grabicova et al., 2017), but their environmental fate and ecotoxicological effects are not well understood, especially under field conditions (Aristi et al., 2016; Hughes et al., 2012; Pal et al., 2010). Wastewater treatment plants (WWTP) have been reported to be the main source of pharmaceuticals in streams (Launay et al., 2016; Musolff et al., 2009; Phillips et al., 2012). WWTP effluents and stormwater overflow emit incompletely removed pharmaceuticals into rivers. The fraction of WWTP effluent to the total river discharge and the absence of quaternary sewage treatment essentially determine the magnitude of pharmaceutical concentrations downstream of the WWTP inlet and, consequently, their environmental impacts. During dry seasons, the WWTP effluent can contribute over 70% to the total discharge in rivers with low base flow, such as the Steinlach River, a tributary to the Neckar River in southwestern Germany, considered in this study (Guillet et al., 2019). The overall discharge (a mixture of WWTP effluent and water from the catchment) controls the hydrodynamics of a river and thus the transport, distribution, and degradation of contaminants within the river (Cranwick et al., 2014; Lewandowski et al., 2011). Flow and pollutant transport may behave differently under low-flow conditions than under high-flow conditions (Mortensen et al., 2016). The attenuation mechanisms of pharmaceuticals in streams include photodegradation and biodegradation, whereas reversible sorption to bed sediments, which may be estimated by solid/water distribution coefficients, retards the transport of hydrophobic pollutants (Barber et al., 2013;
Photodegradation undergoes a diurnal pattern due to the fluctuations of solar radiation (Hanamoto et al., 2013). While biodegradation can occur in the water column, the density of microbial biomass, catalyzing the degradation, is considerably higher in the riverbed and on its surface than in open water. Thus, some authors attribute biodegradation mainly to the hyporheic zone, which is the top bed layer where river water infiltrates and exfiltrates back into the river. In addition, stagnant water pools may show larger microbial activity than zones of flowing water. Compared to the main channel, these immobile zones comprise the transient-storage zones where water resides over longer time periods and microorganisms have enough specific surface area to grow on (Burke et al., 2014; Kunkel & Radke, 2008). Acuña et al. (2015) fitted a joint first-order rate law to reflect the total pharmaceutical attenuation in a river. Riml et al. (2013) calibrated a model considering transient-storage zones and in the main channel to concentration measurements of six pharmaceuticals in a Swedish river. Guillet et al. (2019) quantified photo-dependent and photo-independent degradation processes of pharmaceuticals by applying a conservative-tracer based transfer function to combined conservative-tracer experiments, a time series of pharmaceutical concentrations at the upstream end of a river stretch, and grab samples at the downstream end at different times of the day. The latter authors could not explicitly account for transient-storage mechanisms. Also, in other studies, the quantification of different attenuation processes of emergent pollutants in different compartments has rarely been reported.

Substantial research in the past years has concentrated on quantifying and characterizing transient-storage processes, often under the premise that the transient-storage zone is hyporheic (Runkel, 1998) even though the earliest works on “dead zones” in rivers attributed the immobile water to features of the surface-water body (e.g., Nordin & Troutman, 1980). A recent study of Kelleher et al. (2019) highlighted the difficulties of fitting models with two or more transient-storage zones to tracer data. The latter authors relied on the resazurin-resorufin reactive-tracer system to differentiate between metabolically active and passive transient-storage zones (for a review of the latter, see Knapp et al., 2018). A key problem is that the most successful studies on hyporheic exchange and the reactivity of the hyporheic zone were performed in small, comparably steep, low-order streams whereas waste-water treatment plants are typically located at somewhat larger, less steep, higher-order rivers with little hyporheic exchange. Also, the transferability of resazurin reactivity to aerobic metabolism is limited (Knapp & Cirpka, 2018). Finally, there is no experience and reasonable way to relate or transfer any such rates to the turnover rate of emerging pollutants. Hence, in typically less steep rivers affected by WWTP effluents, the dead surface zone may comprise a notable fraction of transient storage such that it is not clear to which extent transient storage occurs in the hyporheic zone and where the turnover of pharmaceuticals or other emerging pollutants takes place. Typically, advection-dispersion equations with first-order reactions are used to quantify the effective pollutant removal and degradation processes from measured data. However, these processes are not well associated to the different river domains (such as the attribution of biodegradation to the transient-storage zone and the channel mobile water). This, in turn, violates the transfer of fitted degradation rate coefficients to other river systems and under different flow conditions than during the sampling time. In this study, we used the data of Guillet et al. (2019) who synchronously performed tracer experiments and sampled pollutants at both day and night time; they analyzed the conservative-tracer data by nonparametric deconvolution and determined apparent first-order rate coefficients of photodegradation and biodegradation by fitting models with modified transfer functions to the concentration data of the pharmaceuticals. By construction, the latter model could not distinguish between transport and reaction in the main channel and transient-storage zones. We used the same field data of a small number of representative pharmaceuticals and calibrated two variants of a one-dimensional reactive transport model with transient-storage under different assumptions on the localization of biodegradation in the mobile and immobile zones. We had also access to another conservative-tracer test results but not to concentrations of pharmaceuticals, under different flow conditions, so that we could fit coefficients of advective-dispersive transport and mobile-immobile mass exchange for the other flow conditions. Altogether, we aimed at (i) estimating surface and subsurface transient storage parameters and quantifying the influence of flow conditions on transient-storage related parameters; (ii) exploring the equipollutant of pollutant-removal concepts with different attributions of degradation processes to different river compartments and quantifying the contributions of these processes to the pollutant removal under these assumptions; and (iii) simulating the influence of flow rates on the removal of the studied pharmaceuticals.
2. Materials and Methods

2.1. Study Site

Figure 1 shows the studied reach of River Steinlach, located in Tübingen in southwestern Germany. River Steinlach is a fourth-order tributary of the Neckar River within the Rhine Basin. It receives water from the WWTP in Dußlingen and drains a 140-km² hilly catchment, including the karstic Jurrassic Swabian-Alb escarpment, with a mean discharge of 1.84 m³ s⁻¹ (http://www.hvz.badenwuerttemberg.de). The WWTP (red pentagon in Figure 1) treats an inhabitant equivalent of 99,000 including domestic and industrial wastewater, which releases the effluent with a mean discharge of 0.26 m³ s⁻¹ to the river. River Steinlach is very dynamic; the flood of 2-year return period reaches 38.4 m³ s⁻¹, whereas the low-flow discharge can drop to 0.1–0.2 m³ s⁻¹. This strongly influences the pollutant concentration and the removal of organic compounds in the river under different flow conditions. In particular, the WWTP effluent dominates river discharge and water quality under low-flow conditions. The average bed slope of the river is 7‰, and the bed material is mainly composed of medium sized gravel to larger cobbles (Schwientek et al., 2016). The river reach that passes through the southern city districts of Tübingen has been straightened in 1861. The general double-trapezoidal profile consists of a main channel and overbanks on both sides. In the 1970s, the bed was stabilized with concrete armoring and regular concrete step pools with armored receiving basins. In 2009, the armoring and steps were removed and replaced by boulder cascades and other macroroughness elements within the main channel. The revitalization has not led to a reconnection to the original floodplain. The frequent occurrence of macroroughness elements, shown in Figure 2, increases the contribution of transient-storage zones in the hyporheic zone and in stagnant pools when flow rates are small. River Steinlach is a common urban river with respect to its morphology. Practically, all rivers that receive effluents of a WWTP in Central Europe have been engineered and do not remain their natural course and morphology. This may result in limited hyporheic exchange, especially under high flows.
2.1.1. Tracer Tests and Measurements of Pharmaceuticals

In 2015, Guillet et al. (2019) conducted tracer tests in River Steinlach. Figure 1 indicates the injection site and four downstream measuring stations (MS1–MS4). The distance between the tracer injection site and the first measuring station (MS1) was sufficient to ensure complete mixing of the tracer over the cross-section when reaching MS1. The distances between the measuring stations, that is, MS1–MS2, MS2–MS3, and MS3–MS4, were 410, 475, and 425 m, respectively. Sodium-fluorescein was used as tracer, which is conservative at night but undergoes photodegradation during daytime (Gutowski et al., 2015). Two conservative-tracer campaigns were performed, in which tracer concentrations were recorded every 10 s at the four measuring stations. The first campaign, reported by Guillet et al. (2019), took place on 7–8 August 2015 with daytime and nighttime samplings. The very low flow rates of 0.18 m$^3$/s and 0.16 m$^3$/s during the daytime and nighttime hardly differed. In addition, a conservative-tracer experiment was performed on 21 September 2016 with nighttime measurements only; here the flow rate was higher than in the 2015 campaign, namely, 0.25 m$^3$/s. River contaminants were measured on 7–8 August 2015 during both the daytime and nighttime campaigns. At MS1, six 1-hr composite samples were taken by autosamplers and analyzed for various micropollutants. Triplicate grab samples were taken at a single time at MS2. Single grab samples were taken at MS3 and MS4. Details about the sample collection, storage, and analysis are reported by Guillet et al. (2019).

In this study, we selected four representative pharmaceuticals of the mentioned campaign to investigate the effects of different processes on their environmental fate. They are as follows: the anticonvulsant carbamazepine, the antibiotic sulfamethoxazole, the beta-blocker metoprolol, and the antidepressant venlafaxine.

2.2. Model Description

2.2.1. Governing Equations

We adopted the concept of the one-dimensional transport with inflow and storage model (Runkel, 1998) and extended it to separate different degradation processes (Figure 3). The model consists of three compartments, the main channel and two transient-storage zones. Water in the main channel is mobile, thus facilitating advection and dispersion. By contrast, the transient-storage zones are considered immobile and assumed to be composed of the hyporheic zone and of stagnant surface-water pools, respectively.
exchange between the main channel and the transient-storage zones is approximated by a linear driving-force expression. The following assumptions are made.

1. Solutes in the main channel are well-mixed in the transverse direction; therefore, only longitudinal dispersion is considered;
2. The model is used for shallow water depth such that the vertical attenuation of sunlight is negligible, and similar effective photodegradation rates apply in the main channel and the surface transient storage zone.
3. The distribution of times spent in the transient-storage zones is exponential.

For compounds undergoing first-order photodegradation and biodegradation potentially in the main channel (mobile) and the surface and subsurface transient-storage zones (immobile), the advection-dispersion-reaction equation with transient storage reads as follows:

\[
\frac{\partial c_{MC}}{\partial t} = -v \frac{\partial c_{MC}}{\partial x} + D \frac{\partial^2 c_{MC}}{\partial x^2} - f_{TS,sub} k_{ex} (c_{MC} - c_{TS,sub}) - f_{TS,sur} k_{ex} (c_{MC} - c_{TS,sur}) - (k_{pho,MC} + f_{MC,biol} k_{biol}) c_{MC},
\]

\[
\frac{\partial c_{TS,sub}}{\partial t} = k_{ex} (c_{MC} - c_{TS,sub}) - k_{biol} c_{TS,sub},
\]

\[
\frac{\partial c_{TS,sur}}{\partial t} = k_{ex} (c_{MC} - c_{TS,sur}) - (k_{pho,TS,sur} + k_{biol}) c_{TS,sur},
\]

in which \(c_{MC} \, [\text{ngL}^{-1}]\), \(c_{TS,sub} \, [\text{ngL}^{-1}]\), and \(c_{TS,sur} \, [\text{ngL}^{-1}]\) denote the concentration of a dissolved compound in the main channel (MC), the subsurface (TS,sub), and surface transient-storage zone (TS,sur), respectively; \(t \, (s)\) and \(x \, (m)\) are time and the length coordinate; \(v \, (\text{m s}^{-1})\) and \(D \, (\text{m}^2 \text{s}^{-1})\) are the flow velocity and the longitudinal dispersion coefficient; \(f_{TS,sub} \, [\text{\%}]\) and \(f_{TS,sur} \, [\text{\%}]\) represent the ratio of the cross-sectional area in the subsurface \((A_{im,sub} \, [\text{m}^2])\) and surface transient storage \((A_{im,sur} \, [\text{m}^2])\) over that of the main channel \((A_m \, [\text{m}^2])\); \(f_{MC,biol} \, [\text{\%}]\) represents a scaling factor of biodegradation in the main channel in comparison to the...
transient-storage zones, which is assumed identical for all pharmaceuticals. \( k_{\text{ex}} (s^{-1}) \) is the first-order exchange rate constant between the main channel and the transient-storage zones, which is considered identical for the surface and subsurface transient-storage zones for simplification. \( k_{\text{pho},i} (s^{-1}) \) and \( k_{\text{bio}} (s^{-1}) \) represent first-order rate constants of photodegradation and biodegradation, respectively, with \( i \) referring to the MC and the surface transient-storage zone (TS,sur). Photodegradation is assumed to be proportional to solar radiation \( R(t) \) (Wm\(^{-2}\)):

\[
k_{\text{pho},i} = \frac{R(t)}{R_0} k_{\text{pho},0,i}.
\]

in which \( k_{\text{pho},0} (s^{-1}) \) denotes the reference photodegradation rate constant in both the main channel and the surface transient-storage zone for a reference solar radiation \( R_0 \) of 500 Wm\(^{-2}\).

Note that in the following implementation of the model all coefficients that could be deduced from the fluorescein-tracer experiment (velocity, dispersion coefficient, and transient-storage related coefficients) are defined for each river section, whereas the reactive parameters of the pharmaceuticals are set uniform over the entire river reach investigated. Also, since the water depths in the main channel and the surface transient storage zone are both shallow under the low-flow condition in our study, we use the same photodegradation rate coefficient for the two zones, that is, \( k_{\text{pho},\text{TS,sur}} = k_{\text{pho,MC}} \). These simplifications are mainly the result of having only few measurements of the pharmaceuticals that restrict the number of reactive parameters that can reliably be estimated from the data, whereas the fluorescein data are full concentration time series allowing the distinction of the different reaches.

### 2.2.2. Model Setup

In the reactive solute transport simulations, we assume steady-state flow. We use finite volume discretization in space and finite differences in time (applying explicit Runge-Kutta (4,5) integration). The time step size is set to the temporal resolution of the tracer test. The simulated domain starts at MS1. Thus, the measured time series of tracer concentrations at MS1 is used as Dirichlet boundary condition in the conservative-tracer simulations. We calibrated the coefficients of advection, dispersion, and transient storage using the measured time series of fluorescein at MS2, MS3, and MS4.

In the simulation of pollutant transport, we also used pollutant measurements at MS1 as Dirichlet boundary condition, but we needed to reconstruct a continuous time series of concentrations from the six measurements averaged over 1 hr each. We did this by minimizing the integral of the squared time derivatives while meeting the values of the time-averaged concentrations and ensuring nonnegativity of the reconstructed time series (Guillet et al., 2019):

\[
c_{\text{rec}}(t) = \arg\min_{c(t)\geq 0} \int_0^T \left( \frac{dc(t)}{dt} \right)^2 dt.
\]

subject to

\[
\frac{1}{\Delta t} \int_{(i-1)\Delta t}^{i\Delta t} c_{\text{rec}}(t) dt = c_{i,\text{meas}},
\]

in which, \( c_{\text{rec}}(t) \) (ng L\(^{-1}\)) is the reconstructed concentration at time \( t \) (s). \( c_{i,\text{meas}} \) (ng L\(^{-1}\)) is the \( i \)th hourly average concentration. \( \Delta t \) is the averaging duration (1 hr in this study).

### 2.2.3. Model Scenarios

Biodegradation is widely believed to occur in transient-storage zones, but it can also take place in the mobile water, mainly due to the activity of biofilms on the riverbed surface. Photodegradation depends on the light penetration into the water column and can only take place in the surface-water body, which includes the main channel and potentially surface-water pools (surface transient-storage zone).

To quantify the surface and subsurface transient-storage parameters, we fitted the first-order photodegradation of fluorescein at daytime compared to the nighttime conservative transport. Because biodegradation cannot explicitly be attributed to the main channel and/or transient-storage zones, we have tested two scenarios (see Table 1) with different attributions of biodegradation to the river compartments to investigate the range of rate coefficients under the different assumptions and the
corresponding performance of the different conceptual models regarding the attenuation processes. If different conceptual models show practically identical model performance, we face a conceptual equifinality problem. In order to avoid overparameterizing we assume that certain coefficients are identical for different compartments, such as the two rate coefficients of mass transfer between the transient-storage zones and the main channel, and the biodegradation coefficients in the two transient-storage zones. We also assume that the effective rate coefficient of biodegradation in the main channel scales with that in the transient storage zone by a fixed factor that does not depend on the compounds. This parameter essentially represents the ratio of grain-surface-area to water volume in the main river scaled by the same ratio in the transient-storage zones.

2.3. Parameter Estimation

We used the differential evolution adaptive metropolis (DREAM (ZS)) algorithm to estimate the hydraulic parameters based on the tracer tests and degradation rate constants of pharmaceuticals. DREAM (ZS) is a Markov Chain Monte Carlo sampling algorithm, which efficiently estimates the posterior probability density function of model parameters (Vrugt, 2016; Vrugt et al., 2008, 2009). For the evaluation of the model performance, we only consider the maximum a posteriori parameter set rather than the posterior distribution (which is given in the supporting information). We used the Nash-Sutcliffe efficiency (NSE) to evaluate the model fit of the conservative-tracer time series. Since we have only one measurement value for each pollutant at each downstream measurement station (MS2-MS4, at MS2 the mean value of the three replicates is used), we calculated the root-mean-square error (RMSE) and the relative mean absolute difference (RMD) to denote the model performance in the fit of the concentrations of pharmaceuticals. The used metrics are defined as follows:

\[
\text{NSE} = 1 - \frac{\sum_{i=1}^{n}(O_i - M_i)^2}{\sum_{i=1}^{n}(O_i - \overline{O})^2},
\]

\[
\text{RMSE} = \sqrt{\frac{1}{n} \sum_{i=1}^{n}(O_i - M_i)^2},
\]

\[
\text{RMD} = \frac{1}{n} \sum_{i=1}^{n}\frac{|O_i - M_i|}{\overline{O}},
\]

in which \(O_i\) and \(M_i\) are the \(i\)th observed and modeled values, \(\overline{O}\) is the mean of all measurements. An NSE value approaching unity indicates good agreement between model and data, whereas an NSE value smaller than zero implies that the model performs worse than taking the mean of all observations. RMSE and RMD are nonnegative. The smaller the RMSE and RMD values, the better the fit.

First, we estimated the transport parameters (shown in Table 2) from the daytime and nighttime conservative-tracer time series: the average velocities (\(v_1-v_3\)) and longitudinal dispersion coefficients (\(D_1-D_3\)) between all measuring stations. By fitting the photodegradation of fluorescein concentrations, we estimated the fractions of surface (\(f_{TS,sur1}-f_{TS,sur3}\)) and subsurface transient-storage zone (\(f_{TS,sub1}-f_{TS,sub3}\)) and the exchange rate constant (\(k_{ex1}-k_{ex3}\)) between the mobile and immobile zones. Subsequently, keeping the hydraulic parameters determined from the nighttime conservative-tracer data constant, we estimated the biodegradation rate coefficients (\(k_{bio}\)) of the target pharmaceuticals. To estimate the scaling factor of biodegradation in the main channel (\(f_{MC,bio}\)), we used normalized
concentrations of the four representative pharmaceuticals and combined those to one observed data set for calibration. Finally, we estimated the reference photodegradation rate coefficients \( k_{\text{pho}}(0) \) for the investigated pharmaceuticals keeping the parameters of the daytime conservative-tracer data and the biodegradation rate coefficients constant.

### 2.4. Calculation of Pollutant Removal

We calculated the average pollutant removal during a specific period \( T \) as the ratio of removed pollutant mass over the total pollutant mass:

\[
R_{\text{removal}} = \frac{\int_0^T Q(t)c_0(t)\,dt - \int_0^T Q(t)c_r(t)\,dt}{\int_0^T Q(t)c_0(t)\,dt},
\]

in which \( R_{\text{removal}} \) is the average pollutant removal during time period \( T \) (s). \( Q(t) \) (m\(^3\) s\(^{-1}\)) represents the flow rate at time \( t \). \( c_0(t) \) (ng L\(^{-1}\)) and \( c_r(t) \) (ng L\(^{-1}\)) stand for pollutant concentrations without and with removal processes at time \( t \), respectively.

Both photodegradation and biodegradation contribute to the overall pollutant removal:

\[
R_{\text{removal}} = R_{\text{removal}}^{\text{photo}} + R_{\text{removal}}^{\text{bio}},
\]

in which \( R_{\text{removal}}^{\text{photo}} \) and \( R_{\text{removal}}^{\text{bio}} \) denote pollutant removals by photodegradation and biodegradation, respectively. To separate the two contributions, measurements at daytime and nighttime are needed. We further assume that the rate coefficients of biodegradation determined at nighttime also hold at daytime. Then, the remaining degradation can be attributed to photodegradation.

To calculate the pollutant removal in the 24-hr average, we reconstructed the concentrations of pharmaceuticals that were set as the boundary condition (see section 2.2.2). To investigate the influence of the flow rate on pollutant removal, we took the hydraulic parameters from the tracer tests in 2015 and 2016 and assumed the input of pollutant mass flux (same pollutant concentrations and effluent discharge) from the WWTP to be the same in both scenarios. Furthermore, the photodegradation and biodegradation rate coefficients are assumed to remain at the calibrated values determined from the pollutant measurements in 2015, while the scaling factor of biodegradation in the main channel was corrected by the increased hydraulic radius (ratio of cross-sectional area over wetted perimeter) under the conditions of larger discharge.

| Parameter | Unit | Definition | Year 2015 | Year 2016 |
|-----------|------|------------|-----------|-----------|
| \( v_1 \) | ms\(^{-1}\) | MS1-MS2 velocity | 0.097 | 0.128 |
| \( v_2 \) | ms\(^{-1}\) | MS2-MS3 velocity | 0.149 | 0.226 |
| \( v_3 \) | ms\(^{-1}\) | MS3-MS4 velocity | 0.139 | 0.175 |
| \( D_1 \) | m\(^2\) s\(^{-1}\) | MS1-MS2 dispersion coefficient | 1.5 | 2.4 |
| \( D_2 \) | m\(^2\) s\(^{-1}\) | MS2-MS3 dispersion coefficient | 0.1 | 0.3 |
| \( D_3 \) | m\(^2\) s\(^{-1}\) | MS3-MS4 dispersion coefficient | 0.6 | 2.4 |
| \( k_{\text{ex}1} \) | s\(^{-1}\) | MS1-MS2 exchange rate coefficient | \(4.3 \times 10^{-4}\) | \(1.9 \times 10^{-4}\) |
| \( k_{\text{ex}2} \) | s\(^{-1}\) | MS2-MS3 exchange rate coefficient | \(1.2 \times 10^{-3}\) | \(1.3 \times 10^{-3}\) |
| \( k_{\text{ex}3} \) | s\(^{-1}\) | MS3-MS4 exchange rate coefficient | \(6.5 \times 10^{-4}\) | \(2.0 \times 10^{-4}\) |
| \( f_{\text{TS}1} \) | - | MS1-MS2 total transient storage fraction | 0.177 | 0.153 |
| \( f_{\text{TS}2} \) | - | MS2-MS3 total transient storage fraction | 0.162 | 0.110 |
| \( f_{\text{TS}3} \) | - | MS3-MS4 total transient storage fraction | 0.325 | 0.265 |
| \( A_{\text{TS}} \) | m\(^2\) | average transient storage area | 0.22 | 0.18 |
| \( Q \) | m\(^3\) s\(^{-1}\) | flow rate | 0.16 | 0.25 |
| \( T \) | H | mean residence time | 5.4 | 3.4 |
3. Results and Discussion

3.1. Conservative-Tracer Transport and Effects of Flow Rates on Transient Storage

Figure 4 depicts the measured and simulated BTCs of the conservative tracer in the two nighttime experiments on 7 August 2015 (Figure 4a) and 21 September 2016 (Figure 4b). Both measured BTCs are reproduced very well by the model. In particular, the first arrival times, peak concentrations, and the tailings are captured. We also tried to fit the advection-dispersion model without transient storage to the tracer data but could not reproduce the main features of the BTCs, especially the long tailing. This indicates that a transient-storage mechanism is necessary to simulate solute transport in the River Steinlach under low-flow conditions, and a first-order exchange law is sufficient to describe the conservative-tracer data.

The NSE values calculated with the best-fit parameter set for the nighttime tracer experiments in 2015 and 2016 are 0.996 and 0.999, respectively, suggesting a very good model fit at nighttime when fluorescein is conservative. Table 2 lists the best-fit parameters of the simulation. Our model can also reproduce the BTC of the daytime tracer experiment on 7 August 2015 and capture the diurnal pattern of photodegradation of fluorescein by using the time series of solar radiation (Figure A1). The NSE value of the model fit is 0.985 with the best-fit parameter set. By considering the photodegradation in the surface transient-storage zone, we can estimate the surface and subsurface fractions of the total transient storage (Table A1). Our fitted photodegradation rate coefficient of fluorescein is $9.4 \times 10^{-5} \text{ s}^{-1}$ under the reference solar radiation of 500 Wm$^{-2}$. Wang et al. (2008) reported $11.2 \times 10^{-5} \text{ s}^{-1}$ (recalculated based on our solar radiation reference, 500 Wm$^{-2}$) for this rate coefficient from the lab experiment. Our result shows a good agreement with this lab experiment. Leibundgut et al. (2011) provide a half-life time of fluorescein (11 hr) which is equivalent to a first-order decay coefficient of $1.8 \times 10^{-5} \text{ s}^{-1}$. They also discussed that this value can be larger in natural conditions.

Figure 4. BTC fitting for the conservative tracer (fluorescein) campaigns at nighttime in 2015 and 2016 at three measuring stations MS2 to MS4 (cp. Figure 1).
Table 3

Estimated Biodegradation and Photodegradation Rate Coefficients of Four Representative Pharmaceuticals for the Cases of Attributing Biodegradation and Photodegradation to the Main Channel (MC) and the Transient-Storage Zone (TS, Where Surface Transient Storage is TS,sur) (see Table 1)

| Time  | Pharmaceuticals       | $k_{bio,MC}^{a}$ (×10^{-4} s^{-1}) | $k_{bio,TS}^{b}$ (×10^{-4} s^{-1}) | $k_{pho,MC}^{c}$ (×10^{-5} s^{-1}) | $k_{pho,TS,sur}^{d}$ (×10^{-5} s^{-1}) | RMSE$^{e}$ (ng L$^{-1}$) | RMD$^{f}$ (%) |
|-------|-----------------------|----------------------------------|-----------------------------------|-----------------------------------|-------------------------------------|--------------------------|--------------|
| Night | Carbamazepine         | Case 1: 0.0074                    | 0                                 | 0                                 | 0                                   | 6.3                      | 1.1           |
|       |                       | Case 2: 0.057                     | 0.057                             | 0                                 | 0                                   | 9.2                      | 1.1           |
|       | Metoprol              | Case 1: 0                         | 0                                 | 1.233                             | 0                                   | 10.1                     | 1.0           |
|       |                       | Case 2: 0.836                     | 0.836                             | 0                                 | 0                                   | 12.9                     | 1.7           |
|       | Sulfamethoxazole      | Case 1: 0                         | 0.802                             | 0                                 | 0                                   | 10.2                     | 1.3           |
|       |                       | Case 2: 0.562                     | 0.562                             | 0                                 | 0                                   | 0.7                      | 0.2           |
|       | Venlafaxine           | Case 1: 0                         | 0.991                             | 0                                 | 0                                   | 1.7                      | 0.5           |
|       |                       | Case 2: 0.705                     | 0.705                             | 0                                 | 0                                   | 1.7                      | 0.5           |
| Day   | Carbamazepine         | Case 1: 0.074                     | 0.074                             | <0.001                            | <0.001                              | 9.5                      | 1.9           |
|       |                       | Case 2: 0.057                     | 0.057                             | <0.001                            | <0.001                              | 9.7                      | 1.9           |
|       | Metoprol              | Case 1: 0.0074                    | 0                                 | 1.233                             | 2.206                               | 36.3                     | 5.1           |
|       |                       | Case 2: 0.836                     | 0.836                             | 2.206                             | 2.206                               | 38.8                     | 5.6           |
|       | Sulfamethoxazole      | Case 1: 0                         | 0.802                             | <0.001                            | <0.001                              | 65.7                     | 7.8           |
|       |                       | Case 2: 0.562                     | 0.562                             | <0.001                            | <0.001                              | 65.6                     | 7.9           |
|       | Venlafaxine           | Case 1: 0                         | 0.991                             | 1.687                             | 1.687                               | 8.2                      | 3.4           |
|       |                       | Case 2: 0.705                     | 0.705                             | 1.655                             | 1.655                               | 8.6                      | 3.6           |

Note. Rate coefficients of biodegradation are obtained from the nighttime measurements and photodegradation coefficients from the daytime measurements. In the scenarios where biodegradation takes place in the transient-storage zones and in the main channel, we used a scaling factor of the biodegradation rate coefficient in the main channel of 0.069, which is the best-fit value for this parameter obtained by DREAM (zs) shown in Figure S4. Cases 1 and 2 are described in Table 1. $^{a}$ $k_{bio,MC}$: rate coefficient for biodegradation occurring in the main channel. $^{b}$ $k_{bio,TS}$: rate coefficient for biodegradation occurring in the surface and subsurface transient-storage zone. $^{c}$ $k_{pho,MC}$: reference rate coefficient for photodegradation occurring in the main channel. $^{d}$ $k_{pho,TS,sur}$: reference rate coefficient for photodegradation occurring in the surface transient-storage zone. $^{e}$ RMSE: root-mean-square error. $^{f}$ RMD: relative mean absolute difference.

3.2. Influence of Process Attributions on Degradation Rate Coefficients

Table 3 contains the calibrated first-order biodegradation and photodegradation rate coefficients of four representative pharmaceuticals (carbamazepine, metoprolol, sulfamethoxazole, and venlafaxine) for the two scenarios attributing biodegradation to only the transient storage zones or also to the main channel, as listed in Table 1. By fitting our model to the nighttime measurements, we obtained biodegradation rate coefficients for the studied pharmaceuticals, which were then kept constant when fitting our model to the daytime measurements to deduce the photodegradation rate coefficients. Like Guillet et al. (2019), we
could separate the effects of overall biodegradation and photodegradation by having access to both daytime and nighttime measurements. Furthermore, with the estimate of the surface transient storage area, we could constrain the contributions of the main channel and surface transient-storage zone to photodegradation and obtain almost identical rate coefficients of photodegradation. By contrast, attributing biodegradation to the different river compartments is affected by the assumption whether biodegradation is allowed to take place at the river bed surface attributed to the main channel or not. If we allow biodegradation in the main channel, we can obtain a best-fit value of 0.069 with a range of 0−0.3 for the scaling factor \( f_{MC, bio} \) of the biodegradation rate coefficient in the main channel at the discharge of 0.16 m\(^3\) s\(^{-1}\) (see Figure S4). The corresponding degradation rate coefficients were identifiable for each conceptual model tested, shown by the posterior distributions compared to the prior parameter ranges (Figures S4 and S5). For the two studied cases listed in Table 1, we obtained similar metrics of model performance, that is, values of RMSE and RMD between measurements and model simulations. This implies that the measured pollutant concentrations of the 2015 campaign cannot entirely reduce the equifinality of biodegradation of pharmaceuticals in the transient-storage zones and the main channel.

For the four studied pharmaceuticals, the fitted biodegradation rate coefficients are smaller in the scenarios assuming biodegradation in both mobile and immobile water than in those restricting biodegradations to the immobile water. This is a simple compensation to achieve the same overall nighttime attenuation in the different conceptual models.

Because the model performances of the two scenarios are similar, we take case 1 as an example to show the model fit of the simulated to the measured pharmaceutical concentrations. Figure 5 shows that our model reproduces the trends of the pharmaceutical-concentration measurements well both for the nighttime and daytime campaigns. The model fits of cases 2 look similarly good. The fits are comparable to those of Guillet et al. (2019) who used a non-parametric transfer-function approach to model physical transport and could not differentiate between the main channel and transient-storage zones in their reactive-transport simulations.
Table 3 shows that the four pharmaceuticals can be classified into three groups. Carbamazepine is relatively conservative with very small photodegradation and biodegradation rate coefficients. This is consistent with in situ experiments and other modeling studies (Andreozzi et al., 2003; Guillet et al., 2019; Tiehm et al., 2011). Sulfamethoxazole undergoes biodegradation, but hardly photodegradation in River Steinlach. Xu et al. (2011) and Radke et al. (2009) also reported that the elimination of sulfamethoxazole in rivers is mainly caused by biodegradation in sediments, whereas photodegradation of this compound has hardly been observed (Xu et al., 2011). In this study both photodegradation and biodegradation are found to be relevant for metoprolol and venlafaxine, which has also been reported by Fono et al. (2006) and Liu et al. (2009) in other river systems. However, photodegradation and biodegradation rate coefficients are river specific and are influenced by environmental conditions, so that the two processes may be negligible in other rivers (Aymerich et al., 2016).

3.3. Conceptual Equifinality of Pharmaceutical Degradation

Figure 6 depicts the modeled average removal of studied pharmaceuticals by photodegradation and biodegradation during a 24-hr period in the Steinlach River under the two assumptions of attributing biodegradation only to the subsurface transient-storage zone or also the main channel. The pollutant removal was calculated for the 1,310-m reach between the first (MS1) and last (MS4) measuring station with an overall travel time of 3.2–3.6 hr. For the two simulated cases, we obtained almost identical total removals for each pharmaceutical, which is expected as the two cases showed almost identical performances in the model fit. Also, the split between overall biodegradation and photodegradation, regardless of the spatial attribution, hardly differs between the two scenarios. In additional calculations (not shown), we also tested other, more extreme model variants, in which the entire transient-storage zone was considered to be hyporheic or at the surface or where the rate coefficient of biodegradation was identical in all compartments. These different model variants which led to similarly good model fits regarding the pollutants. This indicates the equifinality of attributing biodegradation to the main channel and/or to the transient-storage zones. Testing competing assumptions regarding the attribution of degradation processes to different river compartments is important to avoid premature conclusions on the fate of pharmaceuticals in rivers. For instance, we could have restricted the analysis to a model that restricts biodegradation to the transient-storage zone, resulting in a good model fit. The premature conclusion would have been that the underlying assumption on the nature of biodegradation was indeed correct, which may ultimately influence decisions on management
strategies: If biodegradation is assumed to be restricted to transient-storage zones, enhancing hyporheic exchange must be seen as the most relevant strategy to enhance natural attenuation, whereas the expected effects of such a measure would be smaller if the same data are interpreted by a model that assumes biodegradation to take place in both the main channel and the transient-storage zones.

The two cases differ in attributing the biodegradation to the mobile and immobile domains. For instance, biodegradation removal of metoprolol in the transient-storage zone in case 1 (biodegradation only in the transient-storage zone) is 1.4 times larger than that in case 2 (biodegradation in both the transient-storage zones and the main channel), which is influenced by the total transient-storage fraction and the scaling factor of biodegradation in the main channel. The overall contribution of biodegradation to pollutant removal, however, hardly differed between the two cases. When reducing the biodegradation in the main channel, the biodegradation rate coefficient would increase to compensate it. For metoprolol and venlafaxine, the removal by photodegradation in the surface and subsurface transient-storage zones is mainly influenced by the surface and subsurface fractions of the total transient storage.

Overall, if the aim is to estimate the total pollutant removal, it does not matter in our application whether the degradation processes are assumed to be restricted to one of the two domains (main channel and transient-storage zones) or not. It is more important to have access to data obtained at both daytime and nighttime. However, if the goal is to accurately attribute the pollutant removal to different degradation processes in different compartments of the river, the model assumptions are crucial and additional information is needed to verify these assumptions.

The total removal of carbamazepine by photodegradation and biodegradation in the investigated total reach is very limited, <1.6%. This is consistent with the very small degradation rate coefficients and reflects the relatively conservative character of carbamazepine. For sulfamethoxazole, biodegradation contributes to almost the total removal since photodegradation was found to be negligible in River Steinlach. The total removal of sulfamethoxazole over the reach is approximately 14.4%, which is higher than in studies performed in three Swedish rivers (Li et al., 2016). The enhanced biodegradation of sulfamethoxazole in River Steinlach may be explained by (i) the measurements being conducted in August with optimal water temperatures (20 to 25 °C) for microbial metabolism and (ii) the WWTP effluents contributing over 70% of the total river discharge during the measurement campaign. The effluent could have provided adequate substrates for bacterial growth: Also, (iii) the flow rate at the time of the campaign was low (0.16–0.18 m³ s⁻¹) compared to the mean discharge of 1.84 m³ s⁻¹. This increased both the transient storage fraction (see above) and the residence time in the entire river stretch.

Preceding studies have already reported the elimination of metoprolol (Liu et al., 2009; Nödl er et al., 2014) and venlafaxine (Rúa-Gómez & Püttmann, 2013) in rivers by both photodegradation and biodegradation. Our study confirms that biodegradation and photodegradation both contribute to the total removal of 24.4%–29.4% in the 1,310-m reach of River Steinlach (Guillet et al., 2019) with biodegradation removal of 16.5%–19.2%. In addition, metoprolol and venlafaxine undergo obvious removal by photodegradation (7.9%–10.2%). The physical conditions for photodegradation during the campaign were favoring because (i) the water depth was very shallow, (ii) the shading of the studied reach can be neglected, and (iii) solar radiation in August is intensive and the sunshine duration of approximately 15 hr is long. In addition, during the campaign the sky was mostly clear. On the contrary, Aymerich et al. (2016) reported an insignificant load reduction of venlafaxine in a Spanish river and Li et al. (2016) reported a wide range (from >5% to nearly 60%) of metoprolol depletion in four Swedish rivers. It can be seen that the degradation of pharmaceuticals that may be photodegradable and biodegradable are substantially influenced by the local environment (such as temperature, solar radiation, and fraction of WWTP effluents).

### 3.4. Flow Rates Affect the Simulated Removal of Pharmaceuticals

Figure 7 shows simulated removals of the four pharmaceuticals for the two cases studied above under the two flow conditions of the 2015 and 2016 campaigns with river-discharge values of 0.18 m³ s⁻¹ (first percentile) and 0.25 m³ s⁻¹ (fourth percentile), respectively. In these calculations, we chose identical biodegradation and photodegradation rate coefficients for both discharges and the same surface and subsurface fractions of the total transient storage, whereas the scaling factor of biodegradation in the main channel was reduced by the increased hydraulic radius and the coefficients for conservative transport (velocities,
dispersion coefficients, transient-storage fractions, and rate coefficients of mobile-immobile mass exchange) differed according to the fits to the conservative-tracer measurements.

Increasing the discharge decreases the removal of all pharmaceuticals in both scenarios. This is expected as the overall residence time in the river stretch decreases with increasing flow rates. Apparently, the decrease of the pharmaceutical removal is almost the same for both cases attributing biodegradation to only transient-storage zones and also to the river bed surface of the main channel. Attributions of photodegradation and biodegradation to different river compartments result in a small variation of pollutant removal at both discharges, such as the removal of venlafaxine is 22.1%–22.3% at $Q = 0.18 \text{ m}^3 \text{s}^{-1}$, while 14.7%–14.9% at $Q = 0.25 \text{ m}^3 \text{s}^{-1}$.

In order to understand why changing discharge and the corresponding coefficients of conservative transport have similar effect on the overall removal regardless of restricting biodegradation to the transient-storage zone or to both domains, we may consider the simplified case of steady-state transport with constant coefficients. As derived in Appendix B, we can express the overall degradation by an apparent first-order decay coefficient $\lambda_{\text{app}} (s^{-1})$ in the mobile zone (Botter et al., 2010; González-Pinzón & Haggerty, 2013):

$$\lambda_{\text{app}} = f_{TS} k_{ex} \frac{k_{\text{tot,TS}}}{k_{ex} + k_{\text{tot,TS}}} + k_{\text{tot,MC}} A$$

in which $k_{\text{tot,MC}} (s^{-1})$ and $k_{\text{tot,TS}} (s^{-1})$ are the rate coefficients of total first-order decay in the mobile and immobile domain, respectively. $k_{\text{tot,MC}}$ is affected by scaling factor of biodegradation in the main channel ($f_{\text{MC, bio}} [-]$) and the degradation rate coefficients.

The contribution of degradation in the transient-storage zone to $\lambda_{\text{app}}$ depends positively on both the exchange rate coefficient $k_{ex}$ and the total transient-storage fraction ($f_{TS}$). As listed in Table 2, both coefficients decrease with increasing discharge, implying that the contribution of degradation in the transient-storage zone to $\lambda_{\text{app}}$ decreases. However, the contribution of degradation in the main channel to $\lambda_{\text{app}}$ also decreases because the scaling factor of biodegradation in the main channel ($f_{\text{MC, bio}}$) decreases with increasing hydraulic radius. Also, with an estimated value of 0.069, $f_{\text{MC, bio}}$ is small to begin with.

Figure 7. Comparison of the 24-hr average removals of representative pharmaceuticals at the two flow conditions of the 2015 and 2016 conservative-tracer campaigns.
It may be worth noting that the predictions of total pollutant removals shown in Figure 7 are based on a series of assumptions on the discharge dependence of several parameters, which can all be questioned. With larger water depth and hydraulic radius at larger discharge, both the effective biodegradation rate coefficient and the photodegradation rate should decrease, but already purely geometric coefficients are difficult to assess in a river with as many macroroughness elements as the studied reach of River Steinlach. When significantly higher flow rates, the turbidity of the river would increase and the increased bottom shear stress may lead to detachment of biofilms.

4. Conclusions

Transient-storage models have been applied to the transport of reactive tracers in rivers, but they are rarely used and improved for understanding the transport and fate of emerging micropollutants such as pharmaceuticals. In this study, we applied an enhanced transient-storage model that separates the surface and subsurface transient-storage zones to a stretch of the WWTP effluent-affected River Steinlach in southwest Germany. We fitted the model to data of Guillet et al. (2019) and one additional tracer experiment under a higher flow rate. Besides differentiating the overall biodegradation and photodegradation for the whole river system (without distinguishing the mobile river channel and transient-storage zones) like Guillet et al. (2019), we advanced our study by attributing the biodegradation and photodegradation to the main channel and the transient-storage zones. We further separated the surface and subsurface transient storage by fitting the photodegradation of fluorescein in the main channel and surface transient-storage zone to available data. This procedure helped us to reduce the equifinality of photodegradation of pharmaceuticals in the surface and subsurface transient-storage zones. We tested scenarios attributing biodegradation only to transient-storage zones or to both the main channel and transient-storage zones. The two scenarios could be fitted equally well to the pharmaceutical data, resulting in different rate coefficients.

The comparison of fitting tracer breakthrough curves under two different flow rates shows that the average transient-storage fraction and the exchange rate coefficient between the main channel and the transient-storage zone were smaller than under the lower-flow conditions. We took our model to predict the overall removal of the four selected pharmaceuticals at the higher flow rate. While shorter residence times at larger discharge will always decrease the overall removal, we saw almost identical removal between the cases in which biodegradation was restricted to the transient-storage zone and that where this process was assumed to occur in the main channel (or at the riverbed surface attributed to the main channel) as well. This can be explained by the similar discharge-dependence of the transient-storage coefficients and the scaling factor of biodegradation in the main channel, which is inversely proportional to the hydraulic radius.

At the current state of knowledge, reliable predictions on the fate of pharmaceuticals in rivers with dynamic discharge are problematic, the difficulties of attributing the degradation processes to the different domains of the river and identifying the nature of transient storage being only factor. We see a need of measuring pollutant removals under different flow conditions with subsequent fitting of mechanistic models to overcome ambiguities revealed in this study.

Conflicts of Interest

The authors declare no conflict of interest.

Appendix A: Daytime Fluorescein-Tracer Experiment

Here the dispersion coefficient, total transient storage fraction, and the exchange rate coefficient for fitting the daytime tracer concentrations were obtained based on the corresponding night parameters multiplied by the correction factor. The total transient storage was separated to surface and subsurface ratio (the two ratios sum up to unity). The literature photodegradation rate coefficient of fluorescein is from Guillet et al. (2019).
Appendix B: Steady-State Analysis With Constant Coefficients

In order to estimate how transport coefficients affect the removal of pharmaceuticals, we consider the simplified case of steady-state transport with constant coefficients (González-Pinzón & Haggerty, 2013):

\[
\frac{\partial c_{MC}}{\partial x} - D \frac{\partial^2 c_{MC}}{\partial x^2} + \int_{T} k_{ex}(c_{MC} - c_{TS}) + k_{tot,MC} c_{MC} = 0, \tag{B.1}
\]

\[
k_{ex}(c_{MC} = c_{TS}) - k_{tot,TS} c_{TS} = 0, \tag{B.2}
\]

in which \(k_{tot,MC} \ (s^{-1})\) and \(k_{tot,TS} \ (s^{-1})\) are the rate coefficients of total first-order decay in the mobile and immobile domain. Then the steady-state concentration in the immobile domain is as follows:

\[
c_{TS} = \frac{k_{ex}}{k_{ex} + k_{tot,TS}} c_{MC}. \tag{B.3}
\]

and substitution into the steady-state transport equation yields:

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**Table A1**

*Estimated Best-Fit (Maximum A Posteriori) Parameters by Fitting Daytime Tracer Concentrations in 2015*

| Parameter | Unit | Definition | Value |
|-----------|------|------------|-------|
| \(v_1\)  | ms\(^{-1}\) | MS1-MS2 velocity | 0.110 |
| \(v_2\)  | ms\(^{-1}\) | MS2-MS3 velocity | 0.162 |
| \(v_3\)  | ms\(^{-1}\) | MS3-MS4 velocity | 0.142 |
| \(f_{D,corr}\) | - | correction factor of dispersion coefficient | 0.999 |
| \(f_{ex,corr}\) | - | correction factor of exchange rate coefficient | 1.094 |
| \(f_{TS,corr}\) | - | correction factor of total transient storage fraction | 0.999 |
| \(r_{TS1,sub}\) | - | MS1-MS2 subsurface ratio of the total transient storage fraction | 0.999 |
| \(r_{TS2,sub}\) | - | MS2-MS3 subsurface ratio of the total transient storage fraction | 0.002 |
| \(r_{TS3,sub}\) | - | MS3-MS4 subsurface ratio of the total transient storage fraction | 0.992 |
| \(k_{pho,0}\) | s\(^{-1}\) | Photodegradation rate coefficient of fluorescein at the reference radiation | \(9.4 \times 10^{-5}\) |
| \(f_{MC,bio}\) | - | fraction of water in the main channel that can undergo biodegradation | 0.069 |
| NSE | - | Nash-Sutcliffe Efficiency for the model performance measures | 0.985 |

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**Figure A1.** Breakthrough-curve fitting of the daytime tracer experiment on 7 August 2015.
with the apparent first-order decay coefficient $\lambda_{\text{app}}$ of equation (11). The removal of the contaminant over distance $x$ then becomes

$$R_{\text{removal}}(x) = 1 - \frac{c_{\text{MC}}(x)}{c_{\text{MC}}(0)} = 1 - \exp \left( \frac{-\sqrt{\frac{\nu^2}{4D} + 4D\lambda_{\text{app}}x}}{2D} \right).$$  \tag{B.5}$$

This analysis does not directly estimate the daily mean removal for a compound undergoing photodegradation because the first-order decay coefficients change with radiation, and substituting the time average of those coefficients into the steady-state transport equations (B.1) and (B.2) does not yield the same concentration profile as the time average of the transient concentration. While the equation (B.5) calculates the pollutant removal under steady state, the equation (12) takes the radiation-dependent photodegradation and quasi-steady state (the difference of flow rate during daytime and nighttime).

**Data Statement**

Data of tracer experiments and pharmaceutical measurements used in this study are published in the database of the project “CAMPOS—Catchments as Reactors” at the University of Tübingen, available under https://fdat.esscience.uni-tuebingen.de/portal website (permanent link: http://hdl.handle.net/10900.1/e21082a0-5854-4c3d-9918-52e77035d186).

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