The University Of Sheffield.

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Evaluating River Water Quality Modelling Uncertainties at Multiple Time and Space Scales

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To my son Rafael,

Eres el motorcito de mi vida

Abstract

Maintaining healthy river ecosystems is crucial for sustaining human needs and biodiversity. Therefore, accurately assessing the ecological status of river systems and their response to short and long-term pollution events is paramount. Water quality modelling is a useful tool for gaining a better understanding of the river system and for simulating conditions that may not be obtained by field monitoring. Environmental models can be highly unreliable due to our limited knowledge of environmental systems, the difficulty of mathematically and physically representing these systems, and limitations to the data used to develop, calibrate and run these models. The extensive range of physical, biochemical and ecological processes within river systems is represented by a wide variety of models: from simpler one-dimensional advection dispersion equation (1D ADE) models to complex eutrophication models. Gaining an understanding of uncertainties within catchment water quality models across different spatial and temporal scales for the evaluation and regulation of water compliance is still required. Thus, this thesis work 1) evaluates the impact of parameter uncertainty from the longitudinal dispersion coefficient on the one-dimensional advection-dispersion model and water quality compliance at the reach scale and sub-hourly scale, 2) evaluates the impact of input data uncertainty and the representation of ecological processes on an integrated catchment water quality model, and 3) evaluates the impact of one-dimensional model structures on water quality regulation. Findings from this thesis stress the importance of longitudinal mixing specifically in the sub daily time scales and in-between 10s of meters to 100s of meters. After the sub daily time scale, other biological and ecological processes become more important than longitudinal mixing for representing the seasonal dynamics of dissolved oxygen (DO). The thorough representation of the dominant ecological processes assists in obtaining accurate seasonal patterns even under input data variability. Furthermore, the use of incorrect model structures for water quality evaluation and regulation leads to considerable sources of uncertainty when applying duration over threshold regulation within the first 100s of meters and sub hourly time scale.

Keywords: Integrated water quality modelling, uncertainty analysis, longitudinal dispersion, water quality processes, ecological modelling

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List of symbols

μ	Viscosity (m^2 s^{-1})
A	Cross sectional area (m^2)
B	River with (m)
c	Concentration (mg l^{-1})
C_{CSO}	Concentration of combined sewer overflows runoff (mg l^{-1})
c_D	Downstream concentration (mg l^{-1})
C_{Rural}	Concentration of rural runoff (mg l^{-1})
c_u	Upstream concentration (kg m^{-3})
C_{WWTP}	Concentration of wastewater treatment plant discharge
e_m	Molecular diffusion coefficient (m^2 s^{-1})
ETp	Potential Evapotranspiration (mm hr^{-1})
Fr	Froude number (-)
H	River depth (m)
Jx	Mass flux in x direction (kg s^{-1})
kx	Longitudinal mixing coefficient (m^2 s^{-1})
ky	Transverse mixing coefficient (m^2 s^{-1})
kz	Vertical mixing coefficient (m^2 s^{-1})
L	Length (m)
M	Mass of tracer (kg)
P	Precipitation (mm hr^{-1})
Pr	Predictive ratios (-)
Q	Discharge (m^3 s^{-1})
Q_{CSO}	Runoff from combined sewer overflows (m^3 s^{-1})
Q_{river}	River discharge (m^3 s^{-1})
Q_{Rural}	Rural runoff (m^3 s^{-1})
Q_{WWTP}	Runoff from wastewater plant (m^3 s^{-1})
R^2	Coefficient of determination (-)
Re	Reynolds number (-)
Rh	Hydraulic Radius (m)
Sn	Sinuosity (-)

S_o	Slope (-)
t	Time (s)
$\bar{t}$	Mean travel time (s)
T	Travel time (s)
Tr	Time delay (s)
$u*$	Shear velocity (m s^{-1})
u_x	longitudinal velocity (m s^{-1})
u_y	transverse velocity (m s^{-1})
u_z	vertical velocity (m s^{-1})
v	Longitudinal mean velocity (m s^{-1})
V	Volume (m^3)
x	longitudinal direction (m)
y	transverse direction (m)
z	vertical direction (m)
ρ	Density (kg m^{-3})
τ	Initial travel time (s)

List of abbreviations

1D ADE	One-dimensional Advection Dispersion Model
2D ADE	Two-dimensional Advection Dispersion Model
3D ADE	Three-dimensional Advection Dispersion Model
ADE	Advection Dispersion Equation
ADZ	Aggregated Dead Zone
BMA	Bayesian Model Averaging
BOD	Biological Oxygen Demand
CSOs	Combined Sewer Overflows
Det	Detritus in water
DO	Dissolved Oxygen
DOT	Duration Over Threshold
DRM	Dam Regulation Module
ECFD	Empirical Cumulative Distribution Function
EU	European Union
FIS	Fundamental Intermittent Standards
ICM	Integrate Catchment Model
IM	Inorganic Matter
KNMI	Dutch meteorological agency
MCMC	Markov Chain Monte Carlo
NDet	Nitrogen in detritus
NH_4	Ammonium
Nkj	Kjeldahl nitrogen
NO_3	Nitrate
NPhyt	Nitrogen in phytoplankton
NSC	Nash Sutcliffe Coefficient
OM	Organic Matter
PAIM	Adsorbed phosphorus in inorganic matter
PBIAS	Percent Bias
PDet	Phosphorus in detritus
Phyt	Phytoplankton

PO_4	Phosphate
PPhyt	Phosphorus in phytoplankton
Ptot	Total phosphorus
QUICS	Quantifying Uncertainty in Integrated Catchment Studies
RMSE	Root Mean Square Error
RSR	RMSE - observations standard deviation radio
RWQM1	River Water Quality Model No. 1
SWAT	Soil and Water Assessment Tool
TN	Total Nitrogen
TP	Total Phosphorus
TS	Transient Storage
TSM	Transient Storage Model
TSS	Total Suspended Solids
UPM	Urban Pollution Management
WALRUS	Wageningen Lowland Runoff Simulator
WASP	Water quality Analysis Simulation Program
WFD	Water Framework Directive
WWTP	Wastewater Treatment Plant

1. Introduction

1.1 Background and motivation

The healthy functioning of river systems is crucial for sustaining human needs and biodiversity. Moreover, improving and maintaining good water quality conditions in surface waters for the different uses (drinking, recreation, ecological habitat, etc.) is a challenging task due to the complex nature of the physical, biogeochemical and hydrochemical processes of surface waters and anthropogenic and climate change impacts.

Water policies such as the Water Framework Directive (WFD) (2000/60/EC) in Europe have been implemented to ensure that waters are protected and have a 'good ecological status' (European Commission, 2000). For surface waters, the ecological status depends on biological, hydro-morphological and physico-chemical elements. The WFD uses a combined approach to evaluate the river basins' ecological functioning having taken into consideration the various protection objectives (European Commission, 2000) . In addition to the WFD, the Foundation for Water Research (2012) in the United Kingdom suggests following the Urban Pollution Management (UPM) Manual to address the impacts of urban wet weather discharges (e.g. Combined Sewer Overflows, Wastewater Treatment Plants). Several standards under the UPM have been researched and implemented; for instance, the Fundamental Intermittent Standards (FIS) address wet weather impacts on dissolved oxygen and un-ionised ammonia using a duration-concentration-frequency threshold analysis based on the ecosystem's suitability for salmonid fishery, cyprinid fishery and marginal cyprinid fishery (Foundation for Water Research, 2012). For a detailed description of how regulation for intermittent discharges is implemented, for example in England, see Environmental Agency (2018). Understanding and predicting the functioning of surface water systems in response to dry and wet weather pollution events are key for the adequate management of the water bodies and compliance with water regulation.

Water quality modelling assists in the assessment and improvement of water systems by simulating and predicting water quantity and quality conditions. The complexity of water quality models spans from zeroth dimensional models, representing water volumes and concentrations without dispersion to biochemical models which include reaction terms to describe the biochemical processes in river systems (Shanahan et al., 2001). However, environmental modelling can be highly unreliable (Rode et al., 2010) and uncertainties should be considered since the early stages of the model development process (Refsgaard et al., 2007). Quantifying and communicating these uncertainties in model predictions is crucial to the decision-making process and the proper management of water resources (Refsgaard et al., 2006; Tscheikner-Gratl et al., 2018; van Griensven & Meixner, 2006)

Many different definitions of sources of uncertainty in models exist, however, this thesis will focus on the definitions described in Freni and Mannina (2010) as they are quantifiable sources of uncertainty in environmental models. These uncertainties are: 1) structural uncertainty, which are inherited from the physical, mathematical and biochemical representation of the pollutant transport, mixing and transformations processes, 2) parameter uncertainty, due to the quantification, selection and calibration of parameters, and 3) input data uncertainty attributed to inaccuracies in the input data and boundary conditions.

Although several studies have investigated these uncertainties in isolation, there is a need to evaluate and compare uncertainties across multiple time and space scales to provide guidance on how to reduce uncertainties in water quality modelling. For instance, studies focusing on rainfall input data uncertainty have shown that rainfall variability is a main source of uncertainty when predicting the catchment hydrological response in small (< 15 km^2) urban catchments (Cristiano et al., 2016; Niemczynowicz, 1988; Rico-Ramirez et al., 2015; Schellart et al., 2012). On the other hand, Moreno-Rodenas et al. (2017) found that the effect of tested rainfall time-accumulation level did not influence the predicted seasonal dynamics of dissolved oxygen for the Dommel River (with a catchment area of approximately 913 km^2). Another important source of uncertainty has been attributed to the interlink between sub-models of varying space and time scales within Integrated Catchment Models (ICM) (Tscheikner-Gratl et al., 2018). By coupling a data-intensive sewer model to a coarse river water quality model, the detailed information from the sewer model is lost potentially leading to large uncertainties in water quality concentrations (Schellart et al., 2010; Tscheikner-Gratl et al., 2018). However, an understanding on the importance of the different types of water quality modelling uncertainties and their dominance across the time and space scales is still pending.

This PhD work studies the structural, parameter and input uncertainties from river water quality models evaluating the time and space domains where each uncertainty type influences water regulation. The work is limited to models compatible with concentration-duration-frequency regulation, such as the FIS regulation specified in the UPM standards (Foundation for Water Research, 2012). This require the model to retrieve results that allow for the temporal dynamics evaluation at the catchment scale. Thus, the work is limited to one-dimensional models capable of simulating the flow and water quality temporal and spatial dynamics (zeroth models are not currently capable of representing the temporal dynamics. 2D and 3D models are data intensive and not feasible to use in large catchments). Further emphasis is made on understanding the structural and parameter uncertainties inherited from the pollutant mixing processes and their implications on concentration-duration-frequency type water quality regulation.

1.2 Contributions and thesis structure

A literature review presenting the background and the definitions used throughout this PhD thesis, and knowledge gaps within modelling of water quality uncertainties is provided in Chapter 2. The overall aim, hypothesis and specific objectives of this PhD thesis are presented in Chapter 3.

Chapter 4 presents the propagation of parameter uncertainty in the longitudinal dispersion coefficient, first for a case study for which detailed tracer data is available (Chillan river in Chile), followed by four rivers of varying geometry evaluating the effect on water quality regulation. This chapter is based on:

- Camacho Suarez, V. V., Schellart, A. N. A., Brevis, W., & Shucksmith, J. D. (2019). Quantifying the Impact of Uncertainty within the Longitudinal Dispersion Coefficient on Concentration Dynamics and Regulatory Compliance in Rivers. *Water Resources Research, 55*(5), 4393-4409. doi:10.1029/2018WR023417

The modelling capabilities and input sensitivity of a complex hydrodynamic-ecological long-term catchment model are evaluated in Chapter 5. This analysis simulates dissolved oxygen concentrations in the River Dommel, Netherlands. This chapter is based on:

- Camacho Suarez, V. V., Brederveld, R. J., Fennema, M., Moreno-Rodenas, A., Langeveld, J., Korving, H., . Shucksmith, J. D. (2019). Evaluation of a coupled hydrodynamic-closed ecological cycle approach for modelling dissolved oxygen in surface waters. *Environmental Modelling & Software, 119*, 242-257. doi:https://doi.org/10.1016/j.envsoft.2019.06.003

Chapter 6 evaluates the potential impact of uncertainty in longitudinal dispersion in models of different complexity and varying spatial and temporal scales. First, the uncertainty from modelling the dispersion processes in the Dommel River case is studied, followed by evaluating the impact of dispersion uncertainty in pollutant model structures, which are implemented within commercial models.

The overall conclusions (and recommendations??) of this thesis are presented in Chapter 7.

2. Literature review

The aim of this literature review is to provide a synthesis of the state of the art literature relevant to water quality modelling and uncertainty evaluation. River water quality modelling is important for both, point and non-point source pollution management. Point source pollution sources (e.g. combined sewer overflows, industrial, domestic or wastewater discharges) may have adverse effects on river health. Similarly, non-point source pollutants from agricultural or urban runoff (for which quantification may be more difficult due to their diffuse nature) can alter the natural ecosystems in rivers leading to oxygen depletion and poor water quality conditions (Zheng et al., 2014). This section also highlights where the knowledge gaps are within understanding and assessing the sources of uncertainty associated with water quality modelling for the various temporal and spatial scales.

2.1 River water quality processes

River water quality processes can be subdivided into their physical and bio-chemical processes (Runkel & Bencala, 1995). These processes are often non-linear and non-independent making rivers complex systems to describe. Rivers interact with the landscape and are greatly affected by the catchment characteristics. Within river hydraulics, river width, depth, velocity, and energy slope are the most common relationships used in studying discharge and channel characteristics. On the other hand, the geomorphology is influenced by sediment supply and transport which consequently influence the flow, turbulence and bed forms (Robert & Robert, 2003).

2.1.1 Physical Processes

Key physical processes in rivers that pollutants undergo are advection, molecular and turbulent diffusion and dispersion. These processes are often termed ‘transport and mixing’. Then, further key processes are related to sediment movement.

2.1.1.1 Advection

Advection is the process by which the tracer cloud moves bodily in the flowing stream under the action of an imposed current (Rutherford, 1994; Sharma & Ahmad, 2014). In rivers, advection is defined by a balance between the hydraulic forces (gravity and hydrostatic pressure). These are influenced by the channel slope and flow resistance. Advection does not change the concentration of a solute but transports the pollutant cloud through the river system. Advection is an important process because it dictates the time of passage and arrival of a pollutant.

2.1.1.2 Molecular diffusion

Molecular diffusion refers to the spreading of the pollutant due to random motion of molecules (Sharma & Ahmad, 2014). Fick's law is used to describe the spreading of a tracer from a region of high concentration to a region of low concentration (Rutherford, 1994). This flux is proportional to the concentration gradient, and is dependent on the energy states (temperature) and mass of the relative molecules. This concentration gradient causes the pollutant to mix moving from areas of higher concentration to lower concentration.

2.1.1.3 Turbulent diffusion

In most open channels, flows are turbulent. The chaotic nature of turbulent flow acts to increase local concentration gradients and rapidly increases mixing. In a landmark paper, Taylor (1954) demonstrated that turbulent diffusion can still be described in terms of Fickian processes provided the Lagrangian timescale had been reached. The Lagrangian coordinate system travels at the mean velocity (Rutherford, 1994). The rate of mixing is a function of the turbulence within the flow, and is hence difficult to characterise fully.

2.1.1.4 Dispersion

Dispersion is the process by which the tracer cloud spreads due to the non-uniform vertical and transversal velocity profiles (in rivers, the maximum velocities occur at the centre and top surface of the stream and minimum velocities occur at the river edges and bed) and turbulent diffusion (Figure 1). The velocity profile distribution causes that at the centre surface of the river, the concentration of the pollutant will travel faster than at the edges and at the bottom of the stream. The differences in concentration profiles due the differences in advective flow then enhance lateral and vertical diffusion (Figure 1). This gradient causes the tracer to mix in the perpendicular direction enhancing lateral mixing (Deng et al., 2002; Fischer, 1967; Rutherford, 1994; Sharma & Ahmad, 2014; Taylor, 1954). The combination of the differences in velocity shear and lateral diffusion are referred as dispersion.

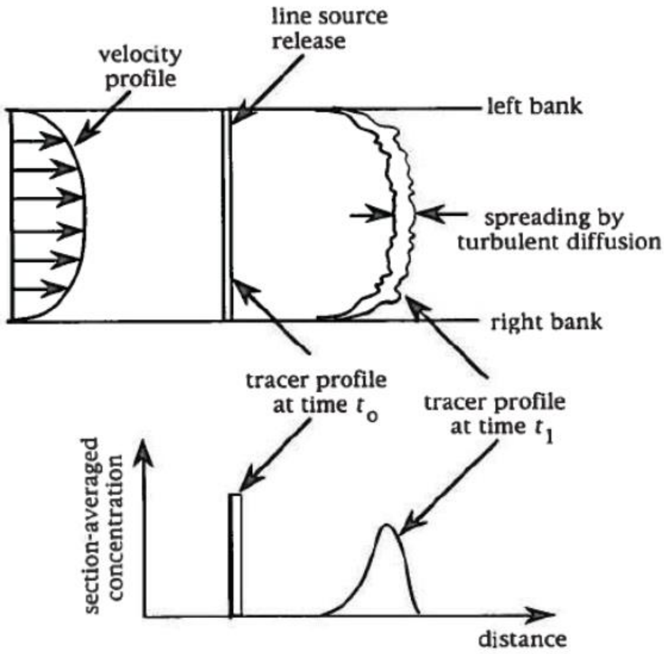
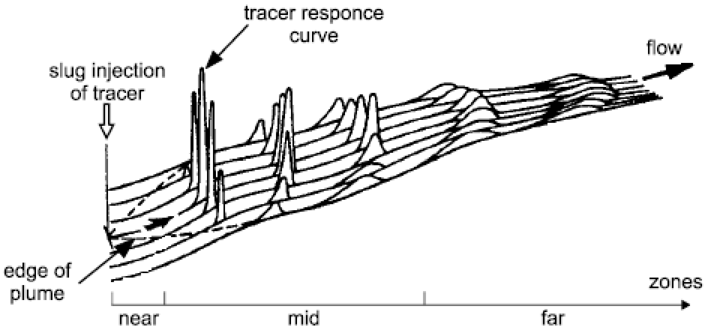


Figure 1. Diagram showing the combined effects of transverse velocity shear and transverse turbulent diffusion on longitudinal spreading (Rutherford, 1994)

2.1.1.5 Dimensions of mixing

Mixing occurs in the three dimensions. Vertical mixing refers to mixing over the depth of the river. Transverse mixing indicates mixing over the river cross section (river width), and longitudinal mixing denotes mixing in the direction of the river flow. Generally, rivers have a greater length and width than depth. This causes the tracer to mix fully in the vertical direction in a relatively short time. Then, the tracer mixes transversally before it mixes in the longitudinal direction.



zone	dominant mixing
near field	vertical
mid field	transverse
far field	longitudinal

Figure 2. Representation of river mixing showing advection dispersion in the near, mid and far field (Kilpatrick & Wilson, 1989)

Rutherford’s terminology (Rutherford, 1994) can be used for defining the spatial domain as longitudinal (far field), transverse (mid field) and vertical (near field). The longitudinal domain is the river length in the direction of the river flow as depicted in Figure 2. The transverse domain is defined by the river cross section (river width) and the vertical domain is defined by the river depth.

2.1.1.6 Transient storage and hyporheic zones

Transient storage characterises the areas where the flow has been significantly reduced in comparison to the main flow (Bencala & Walters, 1983; Briggs et al., 2009), and hyporheic zone is the area where the river flow interacts with the river bed exchanging mass and momentum (Bottacin-Busolin & Marion, 2010). Several studies have evaluated the effects of transient storage and hyporheic zones on dispersion. For instance, Bottacin-Busolin and Marion (2010) illustrated the complex temporal and spatial dynamics of advective flow and dispersion on bed-induced hyporheic exchange. Their results found that both competitive processes, advective pumping and dispersion, were required for the adequate estimation of solute transfer mass.

2.1.1.7 Sediments

Sediments are generally classified as silt or clay (<0.07 mm), sand (0.07-2 mm) and gravel (2-20 mm). Depending on their size and density, sediments undergo the processes of suspension, settling, rolling, sliding, saltation, precipitation and sorption (Robert & Robert, 2003). Sediments play a crucial rule in the flow regime and the geomorphology of streams. Sediments can clog up riverbeds disrupting e.g. fish spawning, and sediments can be a vector for pollutants, as various pollutants such as heavy metals can be attached to sediments.

2.1.2 Biochemical reactions

An extensive range of biochemical processes occur in streams. Depending on the problem that is examined, the variables of interest and the associated relevant river processes are identified. In this literature review, the variables covered are dissolved oxygen, temperature, nitrogen and phosphorus, sediments, phytoplankton and macrophytes since these are often included within water quality models (Fu et al., 2018; Kannel et al., 2011; Koelmans et al., 2001).

2.1.2.1 Dissolved Oxygen (DO)

Oxygen is one of the most important variables in water quality, as it is needed for sustaining life within aquatic ecosystems. The main sources of dissolved oxygen are from the atmosphere (re-aeration), oxygen production from photosynthetic plants, and denitrification (Loucks et al., 2005). In unpolluted river systems, oxygen levels are approximately at saturation levels, but when pollution is introduced, for instance untreated wastewater, the quantity of organic matter rises increasing the oxygen demand for mineralization and nitrification processes. (Janse, 2005). This increased quantity of decomposer organisms reduces the available oxygen in the water (Chapra, 1997).

2.1.2.2 Temperature

Temperature affects almost every water quality process such as the capacity of water to hold DO as well as microbial activity. The main sources of heat are solar radiation, heat conduction from atmosphere and direct inputs (e.g. wastewater, groundwater) while the sinks of heat from rivers are mainly evaporation and conduction of heat from water to atmosphere (Loucks et al., 2005).

2.1.2.3 Nitrogen and Phosphorus

Nitrogen affects oxygen in the water cycle through nitrification, de-nitrification, nutrient uptake, and eutrophication processes among others. Denitrification comprises the transformation of nitrate into volatile nitrogen compounds such as nitrogen gas. This process usually occurs in the water column and sediment layer when an electron is accepted for the mineralization of organic matter. Thus, it requires nitrate and organic carbon under an anaerobic process (Gold et al., 2019). Nitrification refers to the process of transforming ammonia to nitrate by microbial organisms under aerobic conditions (Janse, 2005). Nitrification is influenced by various parameters including pH, dissolved oxygen, water temperature, organic matter, and nitrifying bacteria (Chen et al., 2006; Le et al., 2019). A wide range of the minimum dissolved oxygen concentration required for nitrification to occur have been found in the literature (Bellucci et al., 2011; Park & Noguera, 2004; Stenstrom & Poduska, 1980). These range from 0.3 mg l^{-1} to 4.0 mg l^{-1} of DO.

Phosphorus in river systems can be found in organic or inorganic forms. Inorganic phosphorus is readily available for uptake usually in the form of PO_4 while organic phosphorus may be in the form of sugars or various decomposing microbial or plant tissues (Records et al., 2016).

Both, phosphorus and nitrogen can be limiting elements in macrophytes growth. The underlying problem of nitrogen and phosphorus are the excess nutrients that leads to oxygen and light depletion and therefore eutrophication (Janse et al., 2008).

2.1.2.4 Phytoplankton

Phytoplankton are photosynthetic organisms. They are primary producers in aquatic ecosystems (Litchman, 2007). Phytoplankton are a diverse group, thus they are usually divided into functional groups covering organisms such as cyanobacteria and algae (Raven & Maberly, 2009) . They are often used as indicators of water quality regime of pristine versus turbid states (Reynolds et al., 2002).

2.1.2.5 Macrophytes

Macrophytes are vascular plants which transport water and minerals from the true roots through specialized cells (Hauer et al., 2007). They are traditionally classified under emergent plants (usually erect over water), floating-leaved plants (permanently submerged and produce floating leaves), submerged plants (permanently submerged), and free-floating plants (not attached to the substrate) (Hauer et al., 2007). Macrophytes are sensitive to human intervention. Increased runoff velocities, may be responsible for the decrease in macrophytes population. (White & Hendricks, 2000)

2.2 River Water Quality Modelling

River water quality modelling assists in the management of water resources by providing information in situations were monitoring data may be incomplete or non-existent or where the analysis of future scenarios are required (Loucks et al., 2005). Moreover, river water quality models provide a tool to evaluate water ecosystems in response to environmental management actions and/or pollution impacts (Arhonditsis et al., 2006). River water quality modelling is mainly based on mathematical relationships based on theoretical understanding of the physical, biogeochemical and ecological processes.

2.2.1 Space and time scales in water quality modelling

When deciding an appropriate model for the successful simulation of water quality processes, Shanahan et al. (2001) suggested a six-step decision process for the model selection. The first step involves the definition of the temporal representation. This highlights the importance of using the correct time scales when modelling. The time constant denotes the temporal domain expressed as the inverse relationship between the length scale and the mean velocity of the water body.

Blöschl and Sivapalan (1995) define the term scale as the characteristic time or length of the studied process. The 'process scale' should be in accordance with the 'observed scale' and 'modelling scale'. Smaller space scales tend to be associated with smaller time scales. Cristiano et al. (2016) highlight the wide ranges of time and space variability as shown in Figure 3 where the various hydrological processes span over several orders of magnitude.

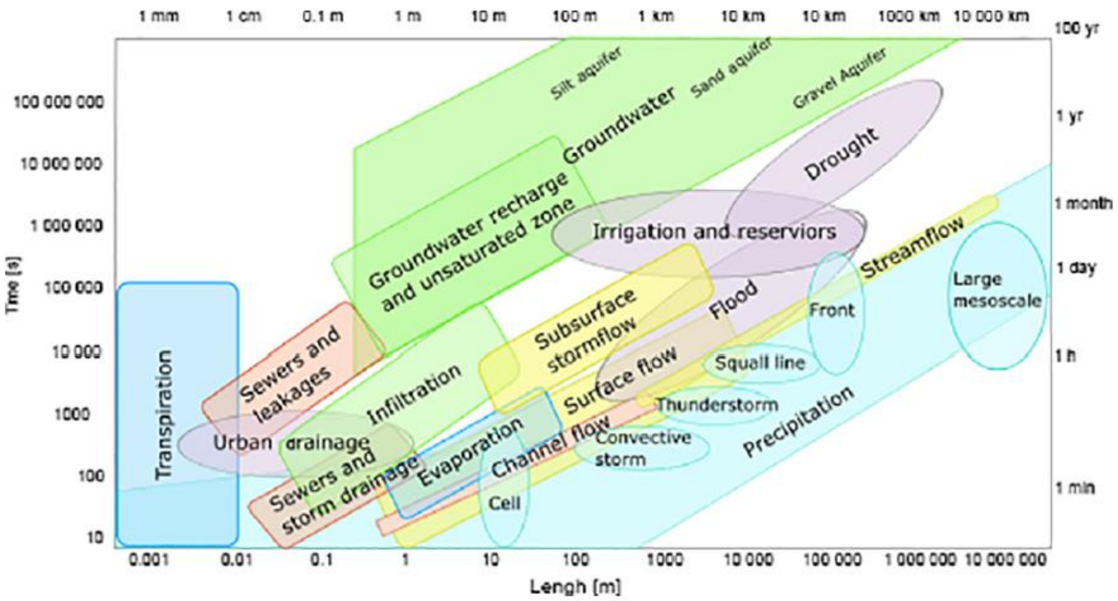


Figure 3. Spatial and temporal variability of hydrological processes in Cristiano et al. (2016) (modified from Berndtsson & Niemczynowicz, 1988; Blöschl & Sivapalan, 1995; Salvadore et al., 2015)

2.2.2 Physical pollutant behaviour

The advective process can be mathematically described by the open channel flow equations, the Saint-Venant equations describing the mass and momentum conservation in its one-dimensional form as shown in:

Equation 1

$$\frac{\partial A_W}{\partial t} + \frac{\partial Q}{\partial x} = \ q_t$$

Equation 2

$$\frac{\partial Q}{\partial t} + \frac{\partial (Qu)}{\partial x} + gA_W \frac{\partial \varsigma}{\partial x} + g\frac{Q|Q|}{C_z^2\ RA_W}$$

Where A_W is the wetted area (m^2), Q is the flow (m^3s^{-1}), q_t is the lateral flow per unit length ($m^3\ s^{-1}\ m^{-1}$), u is the fluid average velocity in the x direction ($m\ s^{-1}$), ς is the water level (m), C_z is the Chezy coefficient in ($m^{1/2}s^{-1}$), R is the hydraulic radius (m) , g is the gravity constant (m^2s^{-1}) (Chow, 1959; Xu et al., 2012).

2.2.2.1 Fick's law of diffusion

Fick’s law of diffusion, developed in 1855 by Adolf Eugen Fick (Fick, 1855), originated from the analogy that salt diffuses in a water as heat diffuses in a metal rod. This lead to the creation of Fick’s law (shown in Equation 3) indicating that the net flux of tracer concentration is proportional to the concentration gradient:

Equation 3

$$J_x = -e_m \frac{\partial c}{\partial x}$$

Where J_x is the mass flux in ($M\ T^{-1}$), $-e_m$ is the molecular diffusion coefficient ($L^2\ T^{-1}$) and c is the tracer concentration in ($M\ L^{-3}$).

Turbulent diffusion relates to the short-term fluctuations of the fluid velocities. It is characterised by the dominance of inertial forces over viscous forces. In turbulent flows, particles released from the same point follow irregular and different paths. However, the particles and flow velocities are correlated. These correlations decrease with distance. The study of the circular currents and the correlations between flow velocities has led to the understanding and development of eddy viscosity theory (Rutherford, 1994).

In 1921, Taylor demonstrated that the tracer cloud can be modelled using Fickian diffusion given that enough time has occurred and the equilibrium zone has been reached (Taylor, 1921).

Taylor (1954) showed that in pipe flow, there is a point downstream (after the pollutant has been released) where the velocity shear and turbulent diffusion reach equilibrium as discussed in the dispersion Section 2.1.1.4. At this point, the variance of the concentration profile increases linearly, the skewness reduces and the concentrations tend towards a Gaussian distribution and hence can be described as a Fickian process. Figure 4 shows the advective and equilibrium zones of a concentration profile. The advective zone is the region closest to the source where the velocity distribution plays a crucial role in mixing of the solute. The equilibrium zone is referred as the zone where the variance of the concentration profile becomes linear, the skewness reduces (Rutherford, 1994) and the pollutant cloud can be theoretically modelled as a Fickian process.

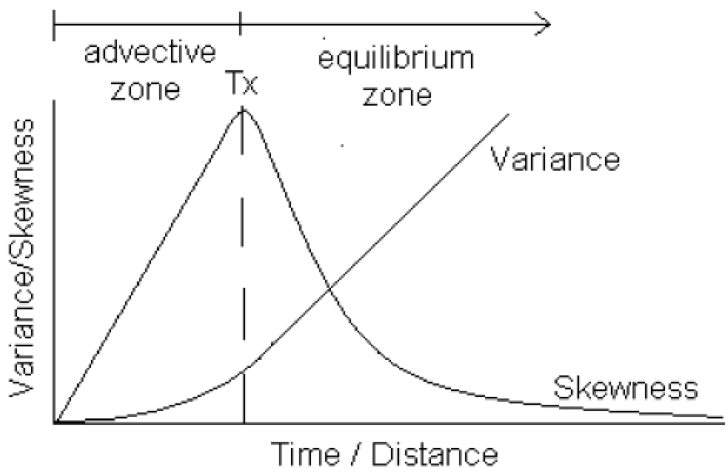


Figure 4. Variance and skewness versus distance of a change of concentration profile according to Fickian model predictions (Rutherford, 1994; Shucksmith et al., 2007)

2.2.2.2 Advection Dispersion Equation (ADE) Model

The Advection Dispersion Equation (ADE) is derived from the conservation of mass in a unit volume where the accumulation of mass equals the mass input minus the mass output. Assuming that the flow and cross section are constant, the advective influx is characterized as the river velocity times the solute concentration.

The flux out of the volume is equal to the influx plus the change in flux in the control volume. Then, Fick's law (Equation 3) is used to describe the dispersive flux where the mixing coefficient is proportional to the concentration gradient. Both, advective and dispersive fluxes are then placed in the conservation of mass equation leading to the 3D ADE equation:

Equation 4

$$\frac{\partial c}{\partial t} + u_x \frac{\partial c}{\partial x} + u_y \frac{\partial c}{\partial y} + u_z \frac{\partial c}{\partial z} = \frac{\partial}{\partial x}\left(k_x \frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(k_y \frac{\partial c}{\partial y}\right) + \frac{\partial}{\partial z}\left(k_z \frac{\partial c}{\partial z}\right) + R(c, P)$$

Where c is the solute concentration in (M L^{-3}), x y z are the longitudinal, transverse and vertical directions in (L), u_x u_y u_z are the velocities (LT^{-1}), k_x k_y k_z are the mixing coefficients in (L^2T^{-1}) . The mixing coefficient represents mixing due to both turbulence and molecular diffusion, but they are usually combined into a single coefficient.

The three dimensional form of the ADE (3D ADE) is the basis for complex mixing models and the most detailed method for estimating concentrations. The 3D ADE is difficult and impractical to solve in most natural channels and it requires information on water depths, velocities and diffusion coefficients which are expensive to collect (Rutherford, 1994). In natural rivers, the vertical dimension is usually much smaller than the longitudinal and transverse dimensions. This leads to the simplification of the 3D ADE to its two-dimensional form by depth averaging the concentrations. Similarly, once enough time has passed and the transverse concentration gradients become negligible, attention is given to the longitudinal directions and the 3D ADE can be further reduced to its one-dimensional form by focusing on the cross-sectional averaged concentrations. These simplifications are reasonable in shallow rivers or rivers of narrow width. (Runkel & Bencala, 1995).

Advection Dispersion Equation semi 2D (2D ADE) – This model neglects transverse velocities (u_x>>u_y), but includes the effect of mixing in the transverse direction. The 2D ADE is also an analytical solution of Equation 4. Concentrations are estimated using Fisher's (1979) analytical solution:

Equation 5

$$c(x, y, t) = \frac{M}{4\pi dt\sqrt{k_x k_y}} \exp\left[-\frac{(x - u_x t)^2}{4\, k_x t} - \frac{y^2}{4\, k_y t}\right]$$

Where the transverse dispersion coefficient k_y and location y are introduce in the equation. The release of pollutant with mass M occurs at x=0, y=0 (at the middle section of the stream width) and time t=0.

Advection Dispersion Equation 1D (1D ADE) – Using Fick's law of dispersion in the longitudinal dimension (Equation 3), the tracer is assumed to mix instantaneously over the cross sectional area. This equation is simplified from the three-dimensional advection dispersion equation presented in Equation 4 by assuming fully mixed conditions over the vertical and transverse planes. The Fisher (1979) analytical solution to the 1D ADE equation is shown where the pollutant concentration is:

Equation 6

$$c(x,t) = \frac{M}{A\sqrt{4\pi\, k_x t}} \exp\left[-\frac{(x-u_x t)^2}{4\, k_x t}\right]$$

Where M is the mass of the pollutant released at t=0 and x=0 and A is the cross sectional area of the channel, k_x is the longitudinal dispersion coefficient, u_x is the average velocity in the longitudinal direction, x is the spatial location and t is time. The advection dispersion equation is widely used to predict solute concentrations (Kashefipour & Falconer, 2002)

Figure 5 shows a conceptual representation of the pollutant mixing processes due to Advection-only, 1D ADE, and semi 2D ADE. As noted in Figure 5, the advection-only model transports the pollutant, but the concentration remains the same after a certain distance of the pollutant release. The 1D ADE model spreads the pollutant in the longitudinal direction, but remains constant along the cross section since it assumes that the cross section is fully mixed. The semi 2D ADE model spreads in both directions, transverse and longitudinal, having the maximum concentration in the centre of the pollutant cloud (for this case, the maximum concentration coincides with the centre of the cross section).

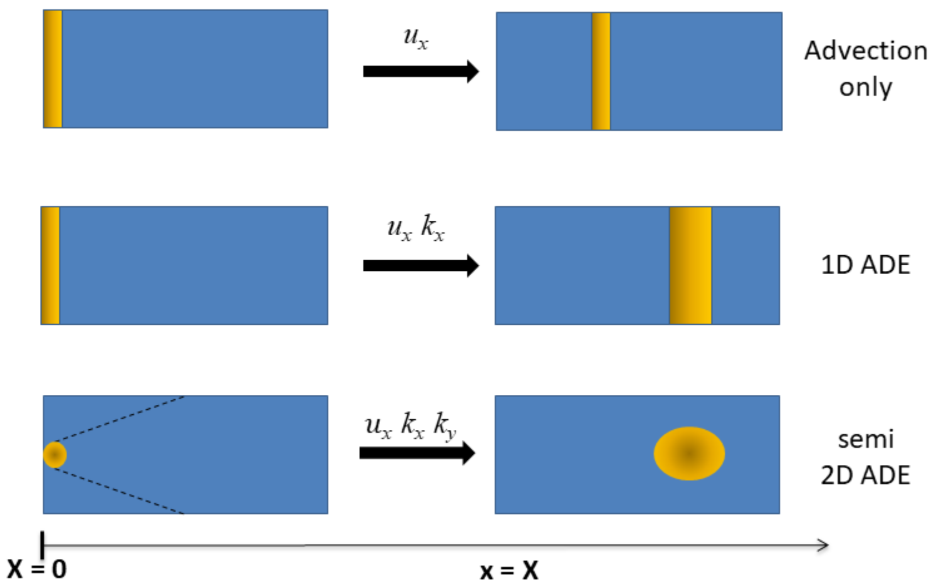


Figure 5. Conceptual diagram of pollutant transport due to advection and dispersion in the longitudinal and transverse direction. Please note that no differences in transverse velocities are considered

The 1D Advection Dispersion Equation (ADE) is the most widely used model within water quality applications representing the transport of pollutants (Cox, 2003a). Additional terms can be added to the ADE to characterise the biochemical transformations of water quality parameters (Reichert et al., 2001; Rode et al., 2010). Moreover, as the river length increases, reaching the catchment scale, the vertical and transverse directions become negligible (as the river length largely exceeds the river depth and width (Cox, 2003a). Thus at the catchment scale, the ADE can be reduced to its one-dimensional form (1D ADE). This facilitates the modelling by reducing the computational time/costs and data requirements (Launay et al., 2015). Many studies in rivers have shown that the 1D ADE is sufficiently complex to capture the main features of concern for water quality assessments (Ani et al., 2009; Marsili-Libelli & Giusti, 2008).

The successful application of the 1D models relies on the assumption that the cross section has fully mixed in the transverse direction (Rutherford, 1994). The significance of this assumption and its impact on water quality concentrations and regulation has not, however, been robustly evaluated yet. Studies have shown that to reduce the uncertainty due to transverse mixing, 2D models can be applied (Moghaddam et al., 2017). However, this solution is computationally and data intensive raising the question if increasing the model complexity is worth the reduction in uncertainty.

An alternative to reduce the uncertainty due to transverse mixing, is to apply the ADE after an equilibrium is established between the velocity shear and the turbulent diffusion (Taylor, 1954). This region, also known as the equilibrium zone, is the region where the variance of the tracer profile increases linearly with time and Fick's law of diffusion can be applied (Rutherford, 1994).

Estimating the time and space where the equilibrium zone starts is a challenging task. Experimentally, Rutherford (1994) used a database of transverse dispersion coefficients in straight, sinuous and meandering natural channels to estimate the transverse mixing length suggesting that full transversal mixing occurs in-between 100 to 300 channel widths from the point where the source has been discharged at the middle of the stream. Moreover, the time and space scales of the mixing length cannot be obtained theoretically (Rutherford, 1994), and their impact over water quality concentrations and legislation still requires evaluation.

2.2.2.3 Aggregated Dead Zone (ADZ) model

The ADZ model is an alternative to the ADE. Developed by Beer and Young (1983), the ADZ considers the river an imperfectly mixed system where advection takes place first and then dispersion occurs in a mixing zone (Lees et al., 2000).

The ADZ model assumes that dispersion occurs mainly due to dead zones. The model can be used for estimating tracer concentrations using the discretization:

Equation 7

$$c(x_2, t) = \alpha\, c(x_2\,, t-1) + \beta\, c(x, t-\delta) \text{ Where}$$

$$\alpha = -\exp\left(\frac{\Delta t}{T_R}\right)$$

$$\beta = 1 + \alpha$$

$$\delta = \tau/\Delta t \; T_R = \bar{t} - \tau$$

Where T_R is the residence time (s), τ is the time delay (s), Δt is the time step (s), and $\bar{t}$ is the mean travel time (s).

The parameters tau and mean travel time for the Aggregated Dead Zone model can be associated to the 1D ADE dispersion parameters by the method of moments of the concentration profiles as shown in Equation 8 and Equation 9 (Gonzalez-Pinzon, 2008).

Equation 8

$$\bar{t} = 2\, k_x \left(\frac{A}{Q}\right)^2 + L\left(\frac{A}{Q}\right)$$

Equation 9

$$\tau = \bar{t} - \sqrt{\frac{8{k_x}^2}{\frac{Q^4}{A}} + \frac{2Lk_x}{\frac{Q^3}{A}}}$$

Where $\bar{t}$ (s) is the average travel time, τ is the time delay in (s), k_x is the longitudinal dispersion coefficient in ($m^2\,s^{-1}$), A is the cross-sectional area (m^2), Q is the discharge ($m^3\,s^{-1}$) and L is the river reach length (m).

2.2.3 Biochemical models and ecological modelling

Water quality models have substantially evolved since the first water quality model established by Streeter and Phelps to evaluate dissolved oxygen (DO) and biological oxygen demand (BOD) in the Ohio River (Streeter et al., 1925). Since then, the understanding and advances in modelling the dynamics of physical, biochemical and ecological variables have significantly increased (Shimoda & Arhonditsis, 2016) by using differential equations, initial conditions, specific parameters and forcing functions (Chen, 1970).

Streeter and Phelps model used a differential partial equation to estimate the total oxygen deficit (D) as shown in:

Equation 10

$$\frac{dD}{dt} = k_1 L_t - k_2 D$$

Where $k_1$is the de-oxygenation rate in (d^{-1}), k_2 is the reaeration rate in (d^{-1}), and L_t is the oxygen demand at time t.

Based on Streeter and Phelps model (Equation 10), the complexity of models has increased to integrate additional processes. Dobbins (1964) modified the Streeter and Phelps model to include the effects of: 1) longitudinal dispersion, 2) removal of BOD by sedimentation, 3) addition of BOD along the path of flow, 4) removal of oxygen by plant respiration and by the oxygen demand of benthic deposits, and 5) the addition of oxygen by photosynthesis. Their findings showed that the effect of longitudinal dispersion was negligible while the micro-scale turbulence energy was responsible for replenishing the interfacial liquid film (the layer between air and water interface) upon which aeration depends.

From the 1970s, the inclusion of state variables in water quality models increased, and non-linear models were developed to account for nitrogen and phosphorus nutrient cycling and phytoplankton, zooplankton and plankton growth as a function of nutrients, sunlight and temperature available (Wang et al., 2013; Yih & Davidson, 1975).

Reichert et al. (2001) illustrate the variety of biochemical process equations implemented within the River Water Quality Model No. 1 (RWQM1) to simulate water quality processes under aerobic conditions. Sub-models with case-specific processes can be derived using the Peterson matrix, a stoichiometric 23×24 matrix (relating to the coefficients of the reaction equations), which includes aerobic and anoxic growth, respiration of heterotrophs, algae and nitrifiers, growth of algae and nitrifiers, death of algae, hydrolysis, and aerobic and anoxic degradation of organic material, as developed by Vanrolleghem et al. (2001).

Moreover, water quality and ecological modelling is not only complex due to the large quantity of modelled variables and processes, but also, it is a challenging task due to the lack of understanding of the plankton and macrophytes processes, lack of data, aggregation of diverse species into functional groups, and their sensitivity to external factors (Anderson, 2005). Shimoda and Arhonditsis (2016) presented an extensive review of 124 studies regarding the modelling of plankton functional groups. Their study found that ecological understanding was key for the adequate spatiotemporal parametrization of plankton functional groups

2.2.4 Water quality modelling software

To date, tens of water quality software models are available in the literature for water quality modelling. Fu et al. (2018) reviewed 42 catchment scale water quality models determining that Soil and Water Assessment Tool (SWAT), Simulation Program - Fortran (HSPF), Integrated Catchment Model (INCA) and SPAtially Referenced Regressions on Watershed attributes (SPARROW) were among the most studied models. Although each modelling study has a specific purpose, these water quality models have the following capabilities:

- Representation of transport and mixing processes.
- Modelling of sediments, nitrogen and phosphorus. More commonly, nitrogen variables are represented by nitrate, nitrite, ammonia and total nitrogen, and phosphorus is commonly represented by dissolved and/or particulate forms of organic and/or inorganic phosphorus
- Spatiotemporal distribution of water quality variables

Due to the external influences and interactions between land practices and in-stream nutrient processes, integrated water quality models have been developed and implemented for catchment evaluation. These integrated models may link several sub-models such as rainfall-runoff, urban drainage, rural runoff routing, river and wastewater treatment plant models (Tscheikner-Gratl et al., 2018). Moreover, eutrophication and contaminant fate models have generally been studied separately. Thus there is a need to link these models to assess the capacity of surface waters to attenuate pollution and purify themselves in response to changes in nutrient loadings (Koelmans et al., 2001).

A review of water quality modelling software pointing out the variables that are modelled, the governing equations implemented and the uncertainty analysis options is available in Appendix A.

2.2.4.1 Commercial water quality models used for water quality evaluation and compliance

Several commercial models are used for evaluating compliance of water regulation, and/or determining water quality improvement options. For instance, in Verghetta and Taylor (2019), three small urban catchments of approximately 60km in river length were selected to evaluate the impact of bacteria and E.coli originating from urban discharges on bathing waters. Several models were used (MIKE11, Infoworks ICM, compliance assessment tool, and a bathing water prediction system) to integrate the interactions between the sewer network, river, estuary and coastal waters. However, significant simplifications such as setting head losses to zero had to be implemented to minimise modelling instabilities and improve run times. Despite such simplifications and the use of one-dimensional models (e.g. Mike11 and Infoworks ICM), a good match between the model predictions and observations of the concentration of E.coli were obtained, as well as the match between the predicted and observed distribution of impacts on the water body. Southern Water in the UK is currently using this framework for specific investigations on measures to improve their services (Verghetta & Taylor, 2019).

Scottish Water carried out a pilot study using a MIKE11 hydrodynamic model on the Almond River in Scotland (Jones et al., 2019). The main contributor of flow during dry weather to the Almond River is inflow from eight wastewater treatment plants (WWTP). The river also receives discharges from combined sewer overflows, septic tanks, industrial states and agricultural runoff. Scottish water studied four cases that would improve the concentrations of reactive phosphorus (SRP), ammonia, and biochemical oxygen demand (BOD) in the river for bathing purposes. The cases included the optimization of the WWTP processes, inclusion of best available technologies to the WWTP, improvement of diatoms and compliance through changes in the effluent of the WWTP and CSOs. Results showed that the four options could be practically implemented by Scottish Water in order to improve the water quality in the Almond River.

Schellart et al. (2010) showed a UK pilot case study to demonstrate the impact of model uncertainties on predicted water quality failures under the Fundamental Intermittent Standards (Foundation for Water Research, 2012) in an existing study for a UK Water Utility where industry standard software was used. The integrated water quality model included the rainfall-runoff MIKE NAM model, the sewer network and wastewater treatment plant (modelled in Infoworks CS), and the river water quality model (RIOT) for the prediction of river flow, DO and ammonia. RIOT is an in-house software package developed by a UK consultant and used in studies for UK Water utilities. It assumes instantaneous mixing of pollutants across the river reach studied (Priestley and Barker, 2006).The area of coverage by the sewer system was approximately 294 ha serving approximately 11,000 inhabitants. Their findings revealed that the predicted number of water quality failures could vary by approximately 45% for dissolved oxygen and approximately 32% for ammonia (Schellart et al., 2010).

2.3 Water Quality Regulation

The European Union (EU) Water Framework Directive (WFD) since 2001 has been implemented to ensure clean rivers, lakes, groundwater and bathing waters for citizens of the European Union (European Commission, 2000). The WFD requires that a holistic approach is taken to obtain a “good ecological status” for surface water and groundwater. This good ecological status is classified according to the biological, chemical and hydrological characteristics of the water body. Specific implementations of the WFD fall into each member of the European Union. For instance in the Netherlands, key ecological factors indicate the ecological status which then is matched with the human pressures on the water body. These pressures range from diffuse pollution to intervention measures such as channelization or vegetation maintenance (STOWA, 2015).

In the United Kingdom, the Foundation for Water Research developed the Urban Pollution Manual (UPM) which establishes specific standards for the implementation of the WFD (Foundation for Water Research, 2012). Furthermore, the UPM manual specifies a range of wet weather discharges criteria to protect receiving waters and aquatic life. Environmental Quality Objectives are defined to indicate the desired used of the water body, and accordingly, Environmental Quality Standards are set to accomplish these objectives. Regulators may use intermittent standards that directly affect the ecosystem during or after an event, or high percentile standards (99 percentiles) based on the extrapolation of 90/95 percentile thresholds used to protect the water body. (Foundation for Water Research, 2012). The Fundamental Intermittent Standards (FIS) are the former method. FIS are applied to dissolved oxygen (DO) and un-ionised ammonia establishing duration thresholds for a range of return periods (1 month, 3 months, and 1 year) for individual pollution events (Foundation for Research, 2012) Three levels of protection are defined within FIS to provide protection to aquatic life during their various stages of development.

Currently, there is a lack of research on the interactions between water quality model development, model uncertainty and water quality regulations (Sriwastava et al., 2018; Tscheikner-Gratl et al., 2018). An example of this was studied by Yorkshire Water, where historical sampling data were used to determine compliance. However, no modelling methods were implemented to determine current or future water quality failures (Priestley & Barker, 2006).

2.4 Sources of Uncertainty

As stated in the introduction, this thesis will focus on the definitions described in Freni and Mannina (2010) as they are quantifiable sources of uncertainty in environmental models. These include: i) input data uncertainty, corresponding to the data used for the initial and boundary conditions, ii) parameter uncertainty, due to the quantification, selection and calibration of parameters, and iii) model structure uncertainties due to the equations and algorithms used in the representation of the real processes and/or coupling these processes (Freni & Mannina, 2010). It is important to note that these uncertainties may fall under other categories of uncertainty classification. Moreover, other sources of uncertainty such as 'ignorance' as described by Wynne (1992) will not be the focus of this literature review. In addition, the scope of this thesis is limited to catchment scale studies and up to the seasonal time scale for the evaluation of the impact of uncertainties when applying the Fundamental Intermittent Standards (FIS).

2.4.1 Structural uncertainty

Model structure uncertainty is usually referred to the uncertainty associated with the deficiencies in matching the model to the real processes of interest (Refsgaard et al., 2006). Frequently, in order to simplify complex processes, key components are not considered or undergo scaling problems (Blumensaat et al., 2014). Model structure uncertainty is also associated with the mathematical expressions chosen to represent reality. Although widely accepted as a major source of uncertainty, structural uncertainty has received less attention in the literature than parameter and input uncertainty (Freni & Mannina, 2010; Lindenschmidt et al., 2007; Refsgaard et al., 2006).

Several sources of structural uncertainty are identified within the pollutant transport and mixing models. For instance, within pollutant transport modelling, representing the skewness in observed pollutant concentration profiles from field data has been challenging. Although skewness is considerably higher within the advective zone, skewness has also been noted over extended distances (Rutherford, 1994). Explanations for this skewness have been attributed to the effects of trapping areas (frequently called dead zones), shear velocities (e.g. data collected in the advective zone), and the hyporheic zone. Dead and hyporheic zones release the stored water slowly attenuating the peak concentrations resulting in longer concentration profiles (Bencala & Walters, 1983; Nordin & Troutman, 1980). To address the skewness issue, models have been developed incorporating the effect of transient and storage zones. The transient storage model (TSM) is a conceptual model to simulate pollutant transport using the 1D ADE and the transverse exchange with the storage zones using a mass transfer term (Runkel, 1998). Moreover, Ge and Boufadel (2006) found that the TSM model could not fit the observed profiles estimated after a large pool formation in the river section. They attributed the poor fit to the poor mixing of the river cross section. Due to the effect of transverse velocities, the solute did not mix completely along the cross section causing a 2D problem with higher velocities at the centre of the pool and lower velocities at the edges. This example illustrates how the assumption of full cross sectional mixing may lead to inaccuracies in the predictions.

Among studies of structural uncertainty, Van Der Perk (1997) studied model complexity associated with modelling phosphorus concentrations in rivers by comparing eight 1D models. The accuracy of predictions increased when increasing the model complexity by adding more processes (e.g. first-order removal, adsorption, first-order uptake, etc.). Radwan and Willems (2007) studied structural uncertainty by comparing two water quality models, QUAL2E and Mike11. They found that structural uncertainty accounted for between 2% and 13% of total uncertainty depending on the studied variable. On the other hand, Lindenschmidt et al. (2007) used WASP5 package to analyze structural uncertainty in modelling dissolved oxygen, phytoplankton dynamics, sediment and micropollutants. They found that for organic soluble pollutants, uncertainties due to the structure of coupling models was more significant than parameter uncertainty. Blumensaat et al. (2014) compared three models of dissolved oxygen to study structural sensitivity (model flexibility). Their study suggests that more complex models result in higher structural sensitivity which leads to less model error as long as adequate data is available. Although strucural uncertainty has been identified as a major source of uncertainty, only a few studies have quantified it. Quantifiying structural uncertainty is a challenging task due limitations in representing real physical and biochemical processes and often overparametrization of these processes (Radwan & Willems, 2004).

Another aspect of structural uncertainty is the reduction from the three-dimensional space to one-dimensional space. Most solute transport studies involving uncertainty analysis have been carried out in one dimension as observed in G. Mannina and G. Viviani (2010a), Choi and Han (2014) and Ani et al. (2009). However, the question of the level of uncertainty from dimensionality reduction remains. It is important to note that the inclusion of a second or third dimension involves the inclusion of other parameters, which will add parameter uncertainty to the overall uncertainty analysis (Ani et al., 2009).

2.4.2 Parameter uncertainty

Parameter uncertainty is associated with the process of selection of the parameters used in the model (Freni et al., 2011). Although model structural uncertainty and parameter uncertainty are not independent of each other (as model complexity increases so does the number of parameters), this review refers to parameter uncertainty as the uncertainty from the data and/or methods used for estimating the parameters. There are several parameters that require attention in the water modelling process. For instance, roughness coefficients can be an important source of uncertainty (Lindenschmidt, 2006). Moreover, this review focuses on parameter uncertainties within water quality models rather than the hydrodynamic model.

***ADE Dispersion Coefficients* –** Mixing processes and therefore dispersion coefficients are highly variable over the time and space scales. Riverine features such as irregular bed-forms, channel meandering, vegetation, pools and riffles can largely influence hydraulic and geometric conditions which contribute to the dispersion processes (Guymer, 1998; Noss & Lorke, 2016; Shucksmith et al., 2010).

The concept of longitudinal dispersion was first introduced by Taylor (1954) in a circular pipe. Then, Elder (1959) derived a more theoretical dispersion equation for an infinite width channel. Elder's equation has been scrutinized for underestimating the natural dispersion in rivers (Fischer, 1979). Since then, more methodologies for estimating or calibrating the dispersion coefficients have been developed given their importance in predicting solute concentrations. These include: regression analyses methods based on bulk river hydraulic and geomorphological properties (Kashefipour & Falconer, 2002; Liu, 1977; Magazine et al., 1988; McQuivey & Keefer, 1974; Seo & Cheong, 1998); theoretical formulations (Fischer, 1967; Seo & Baek, 2004); genetic algorithms (Etemad-Shahidi & Taghipour, 2012; Sahay & Dutta, 2009), and geostatistical methods (Altunkaynak, 2016). However, most theoretical and regression methods developed do not incorporate the heterogeneity and non-linearity of catchments (Altunkaynak, 2016).

Through tracer experiments, dispersion coefficients may also be estimated. These experiments are more site-specific and may give better parameter estimations. However, they are also associated with field collection errors.

ADZ time delay and residence time –The time delay and residence time are obtained from the pollutant cloud travelling times. The time delay is the advective time it takes for the cloud to move only due to advection of the bulk flow while the residence time is a lumped parameter that describes the travel time associated with dispersion (González-Pinzõn et al., 2013). These parameters can also be obtained from experimental studies. Relationships between the ADZ parameters and hydraulic conditions have been studied for instance by Holguin-Gonzalez et al. (2013)

Model calibration parameters – Calibration or estimation of model parameters is generally implemented by minimizing the discrepancy between model outputs and predicted data by adjusting the model parameters. This practice assumes that the model provides an accurate representation of reality (Arhonditsis et al., 2008). Calibration is subject to both, structural uncertainty (due to the assumption that the mathematical model is a fair representation of reality), and input data uncertainties (potentially due to the lack of data).

Parameter uncertainty in complex models **-** For more complex models, such as eutrophication models, the number of parameters required to have a realistic description of the ecological system dynamics increases. Reichert and Omlin (1997) argue that a set of global optimum parameters which describe the real system is not achievable. To address this issue, the use of distributions instead of point estimates for describing parameters has been suggested (Arhonditsis et al., 2008; Hornberger & Spear, 1981). Another alternative to assist with the identification of parameter uncertainty and to gain a better understanding of the natural system is the implementation of sensitivity analysis (Jia et al., 2018).

2.4.1 Input Data Uncertainty

Input data uncertainty is usually case dependent. Often, uncertainties arise from the data temporal and spatial resolution. Input data uncertainties may arise from the model forcing data (precipitation), digital elevation model representation, soil or sewer network maps (Moreno-Rodenas et al., 2019) among other sources. Several techniques have been used to reduce the input uncertainty. Han and Zheng (2018) coupled a Markov Chain Monte Carlo (MCMC) and Bayesian Model Averaging (BMA) techniques to investigate the input and parameter uncertainty associated with modelling synthetic nitrate pollution for the Newport Bay Watershed, California finding that if input uncertainty was not explicitly accounted for, it lead to large sources of uncertainty which were compensated by parametric uncertainty. Sohrabi et al. (2002) used a statistical sensitivity analysis to determine uncertain input parameters in a flow transport model, finding that input uncertainty resulted in 20% higher mean flow rates and three times the estimated atrazine leaching rates.

Studies regarding the dominance of structural, parameter and input uncertainties in water quality modelling have revealed contradictory findings regarding the importance of these uncertainties. For instance, Radwan and Willems (2007) quantified the contribution to total uncertainty from a small catchment (57.44 Km^2) west of Brussels. They analysed the uncertainties arising from input, parameter and structural uncertainties. They evaluated the water quality models MIKE11 and Qual2E models concluding that the largest uncertainty arose from input uncertainty accounting up to 61% of total uncertainty for DO, followed by parameter uncertainty (37% for DO). Structural uncertainty resulted in the smallest uncertainty (2% of total uncertainty for DO). On the other hand, Lindenschmidt et al. (2007) analysed the uncertainties from modelling the largest tributary of the Elbe River (23770 km^2). In their study, they quantified the parameter and structural uncertainties in an integrated model composed of three sub models: DYNHYD (hydrodynamic), EUTRO (dissolved oxygen and phytoplankton dynamics), and TOXI (transport and transformation of sediments and micro pollutants). Using a regression error term to quantify the structural uncertainty from the TOXI and EUTRO models, they found that the structural uncertainty was more significant that the parameter and input uncertainty. Zhang and Shao (2018) studied the Shaying River catchment (3,651 km^2) from 2003 to 2005. Their integrated catchment model was composed of a hydrological cycle module, soil erosion module, overland water quality module, water quality module in water bodies, crop growth module, soil biochemical module and dam regulation module (DRM). Zhang and Shao (2018) evaluated structural and parameter uncertainties in the runoff and water quality models and their propagation. Their study found that the 95% uncertainty intervals due to structural uncertainty were wider than those due to the parameter uncertainty when modelling daily observations of NH_4.

2.5 Concluding Remarks

There is a plethora of water quality models available for the prediction of water quality variables and the assessment of water quality compliance. However, there is still a need to evaluate the impact of parameter, input data and structural uncertainties on predicted water quality concentrations and water quality regulation (e.g. Fundamental Intermittent Discharges) at different time and space scales.

Several attempts have been made to develop improved equations of longitudinal dispersion as pointed out in Section 2.4.2 for the estimation of pollutant concentrations using one-dimensional models. However, the effect of the propagated uncertainty from the use of empirical parameter formulations of the longitudinal dispersion coefficient on simulating concentration-duration-threshold type water quality standards was not studied despite the wide ranges of longitudinal dispersion coefficients found in the literature. Etemad-Shahidi and Taghipour (2012) showed that longitudinal dispersion coefficients ranged from 0.2 to 1487 $m^2 s^{-1}$ in the database they collated. Alizadeh, Ahmadyar, et al. (2017) used statistical analysis such as the Root Mean Square Error and the percent accuracy to estimate the uncertainty from the dispersion coefficient. However, this study and previous studies have estimated the uncertainty from the coefficient itself (Alizadeh, Ahmadyar, et al., 2017; El Kadi Abderrezzak et al., 2015; Lanzoni et al., 2018; Wang & Huai, 2016; Zeng & Huai, 2014), but few studies have propagated these uncertainties within transport predictions (Kashefipour & Falconer, 2002) and to the author's knowledge, no methodology for evaluating the impact of the longitudinal parameter uncertainty on simulations used for testing compliance with water quality regulation has been proposed.

As the spatial and temporal scales increase from the reach scale to the catchment scale and from the sub-hourly time scale to the seasonal scale, the complexity of river models also increases in order to accommodate biological, chemical and ecological processes (Blumensaat et al., 2014; Rode et al., 2010). A thorough description of the biochemical processes that are added to the Advection Dispersion Equation within the River Water Quality No. 1 (RWQM1), shown by Reichert et al. (2001), illustrates the wide variety of components and processes required for the simulation of oxygen, nutrients, vegetation, algae and sediments cycling and interactions. At these longer time and space scales, the following questions remain unanswered: 1) which are the dominant processes and uncertainties at the catchment scale, and 2) what is the impact of uncertainty of the longitudinal dispersion coefficient estimation over predicted pollutant concentrations. As the river water quality model complexity increases, the potential structural uncertainty decreases. However, the parameter and inputs required by the model also increase augmenting the problem of equifinality and parameter identification (Arhonditsis et al., 2006; Beven & Freer, 2001; Rode et al., 2010). Ge and Boufadel (2006) highlight the problem of identifiability of the dispersion parameters suggesting that as the distance between the pollutant release increases, the identification of parameters becomes poorer.

Commonly used commercial water quality models contain model simplifications, which may propagate uncertainty into water quality predictions and therefore into river management strategies designed to satisfy water quality regulation. For instance, the models SIMulation of CATchments (SIMCAT) and SIMPOL ICM developed by the Water Research Centre (WRc) predict variables such as Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Dissolved Oxygen (DO) and ammonia. SIMCAT and SIMPOL represent the river as Continually Stirred Tank Reactors in Series (CSTRS) assuming perfect mixing within each tank (Cox, 2003a). Both models have been used in evaluating water quality compliance by the United Kingdom Environmental Agency. Crabtree et al. (2009) illustrates how SIMCAT was used for a pilot study for the River Ribble in the Northwest of England to assess 80 catchment scenarios, and to developed a range of Programmes of Measures (PoM) to achieve a 'good status' under the Water Framework Directive. These PoM included alternatives to reduce diffuse pollution and options for the water industry to assess management scenarios. SIMPOL ICM is currently used to address the interactions between water company assets and the natural environment (e.g. how wastewater and businesses affect each other for a range of scenarios) (Water Resources Centre, 2012). More complex models that use the 1D ADE such as MIKE 11 (DHI Water and Environment, 2009) and Inforworks ICM (Innovyze, 2017) are also used by the water industry for the evaluation of water resources, evaluation of water quality failures and design of PoMs. (Jones et al., 2019; Schellart et al., 2010; Verghetta & Taylor, 2019). There is a need to examine the scale and magnitude of the uncertainties resulting from the structural error of such model simplifications.

3. Thesis Aim and Objectives

The overall aim of the work presented in this PhD thesis is to evaluate and quantify the dominant sources of uncertainty in river water quality modelling at multiple time and space scales for varying degrees of model complexity. The work is limited to models ranging from the reach scale to the catchment scale and from the sub-hourly time scale to the seasonal scale thus allowing the evaluation of water quality models used for water regulation under the Fundamental Intermittent Standards (FIS). Further emphasis is made on evaluating the time and space scales where mixing processes are key in estimating pollutant concentrations and duration over threshold type standards, from the Urban Drainage Pollution Manual (Foundation for Water Research, 2012).

3.1 Specific Objectives

The following specific objectives have been set to evaluate individually the dominant uncertainties at the different time and space scales:

1. To quantity the propagated uncertainty of the longitudinal dispersion coefficient on water quality concentrations and water quality regulation using the 1D ADE (Chapter 4).
2. To evaluate the performance of an integrated transport and ecological model and quantify input data uncertainty (Chapter 5).
3. To evaluate the implications of using simple and complex model structures and their uncertainty on water quality regulation (Chapter 6).

4. Quantifying the Impact of Uncertainty within the Longitudinal Dispersion Coefficient on Concentration Dynamics and Regulatory Compliance in Rivers

This chapter addresses the thesis objective associated with evaluating and quantifying the propagated uncertainty of the longitudinal dispersion coefficient on water quality estimations and water quality regulation (Objective 1). This chapter is based on the publication:

V.V. Camacho Suarez, A. N. A. Schellart., W. Brevis and J. D. Shucksmith. (2019). Quantifying the Impact of Uncertainty within the Longitudinal Dispersion Coefficient on Concentration Dynamics and Regulatory Compliance in Rivers. *Water Resources Research*, 10.1029/2018wr023417

4.1 Introduction

Maintaining good surface river water quality standards for different uses (drinking, recreation, ecological habitat, etc.) is a challenging task due to the extensive list of complex and variable natural and anthropogenic factors affecting water quality conditions. Rivers are subject to variable physical, chemical and biological processes that may affect their vulnerability to pollution loads (Chapman, 1996). River water quality models provide a tool for simulating such processes to assist in the assessment and improvement of water quality conditions that may not be otherwise obtained from field monitoring. However, lack of knowledge of water quality processes and the river system of interest can limit the reliability of the model predictions. Modelling uncertainties can thus lead to sub-optimal water or infrastructure management decisions (Sriwastava et al., 2018). Thus, quantifying and communicating the accuracy of water quality predictions is a key component for improving water quality conditions and managing better water resources (Refsgaard et al., 2006; van Griensven & Meixner, 2006).

Whilst uncertainties have been studied within other areas of catchment modelling, such as rainfall-runoff, groundwater, wastewater treatment and urban drainage models (Arnbjerg-Nielsen & Harremoës, 1996; Beven & Binley, 1992; Dotto et al., 2012; Freni & Mannina, 2010; Giorgio Mannina & Gaspare Viviani, 2010; Refsgaard et al., 2007; Schellart et al., 2010; Willems, 2008), relatively few studies have focused on the uncertainties within surface water quality modelling, of these most relate to biochemical processes of specific substances. For instance Van Der Perk (1997) explored the model uncertainty and accuracy using eight phosphate concentration models for the Biebrza River, Poland. Although they found that when increasing model complexity, the accuracy of the model also increased, the parameter identifiability decreased and the parameters became increasingly correlated. Abbaspour et al. (2007) evaluated the capabilities of SWAT (Soil and Water Assessment Tool) when modelling the Thur River basin in Switzerland. Using the 95% confidence intervals and the ratio of the mean distance in-between the 95% confidence intervals and standard deviation, they found excellent predictions for flow and nitrate and good predictions for sediment and total phosphorus. Lindenschmidt et al. (2007) examined the structural uncertainty in modelling dissolved oxygen nutrients, phytoplankton dynamics, sediment and micro pollutants using the WASP5 package (Water quality Analysis Simulation Program) which coupled three models: 1) a hydrodynamic model 2) a dissolved oxygen, nutrient and phytoplankton model and 3) a sediments model. Vandenberghe et al. (2007) utilised a Monte Carlo based uncertainty propagation approach to examine predictive uncertainties in the ESWAT model due to a selection of water quality parameters and model inputs. Despite its importance in modelling time varying/dynamic river and pollution impacts (Boxall & Guymer, 2003; G. Mannina & G. Viviani, 2010a), studies investigating the impacts of uncertainties associated with mixing processes on water quality modelling and decision making are limited (Benke et al., 2008; Tscheikner-Gratl et al., 2018). Existing studies have mostly focused on either comparing the accuracy of calibrated models of varying complexity (Moghaddam et al., 2017), or on the uncertainty in estimating dispersion (or other) parameters in themselves using different methods, without propagating the effect of these parameter uncertainties within water quality modelling predictions (Alizadeh, Shahheydari, et al., 2017; Noori et al., 2016; Piotrowski et al., 2010; Sattar & Gharabaghi, 2015).

When simulating large (catchment scale) systems, the modelling of the physical transport of pollutants in rivers is commonly implemented within water quality models using the one dimensional advection dispersion equation 1D ADE (Rutherford, 1994).

Equation 11

$$\frac{\partial C}{\partial t} = -v\frac{\partial C}{\partial x} + k_x\frac{\partial^2 C}{\partial x^2}$$

Where C is the concentration in (mg l^{-1}), t is the time (s), v is the river mean velocity (m s^{-1}), x is the distance downstream (m) and k_x is the longitudinal dispersion coefficient ($m^2\,s^{-1}$). The 1D ADE describes the change in cross sectional averaged concentration of a solute with respect to time as a result of the advection and dispersion processes in turbulent flows (Fischer, 1979; Rutherford, 1994), dispersion being a product of differential advection (velocity shear) and turbulent diffusion processes. The 1D ADE is applicable in conditions where an equilibrium becomes established between the velocity shear and diffusion processes (Shucksmith et al., 2007). An appropriate solution to Equation 11 is dependent on the boundary conditions.

Mixing processes and hence dispersion coefficients are known to be highly variable between rivers and over different hydraulic regimes. The presence of various common riverine features such as irregular bed-forms, channel meandering, vegetation, pools and riffles can largely influence such hydraulic and geometric conditions leading to significant variations in dispersion and mixing processes (Guymer, 1998; Noss & Lorke, 2016; Shucksmith et al., 2010). Despite its widespread use within modelling tools, several sources of uncertainty have been identified within the 1D ADE when applied to river systems. Primarily, the 1D ADE does not represent the asymmetry typically observed in tracer concentration profiles observed in field studies (van Mazijk & Veling, 2005).The persistent skewness in observed concentration profiles has been attributed to a number of processes, including transient storage effects and hyporheic exchange processes (Bottacin-Busolin & Marion, 2010; Briggs et al., 2009; Fernald et al., 2001; Nordin & Troutman, 1980; Zaramella et al., 2003), prolonged lack of equilibrium between diffusion and dispersion effects (Schmalle & Rehmann, 2014), and use of frozen cloud type approximations within field measurements (Rutherford, 1994). A number of modelling tools have been developed to account for profile asymmetries, which generally include additional or replacement terms and parameters to account for storage type effects in river systems (Runkel, 1998). However, this can lead to increased difficulties in parameter estimation due to issues associated with equifinality (Beven & Binley, 1992; González-Pinzõn et al., 2013), and generally requires more complex and well-designed measuring campaigns for calibration (Reichert & Vanrolleghem, 2001). Despite its limitations, the 1D ADE is still the most commonly used type of model for water quality assessments. In addition, most water quality assessments are relatively insensitive to the accurate prediction of distribution tails, instead being based on concentration exceedance frequencies, and durations over given thresholds (Foundation for Research, 2012). A number of studies have shown that the calibrated 1D ADE is able to reproduce field observations of mixing processes with accuracy sufficient for such catchment scale water quality modelling applications, without the inclusion of transient storage/increased skewness effects (Ani et al., 2009; Launay et al., 2015; Marsili-Libelli & Giusti, 2008).

A common aspect of transport and mixing models is the identification of parameters via calibration/fitting of the model to observed data (Fischer, 1979). However, field measurements needed to calibrate mixing models over a range of flow conditions at a study site are often costly and time-consuming. Several attempts have therefore been made to empirically and physically quantify the 1D ADE dispersion coefficient in terms of the underlying hydraulic processes and/or general river characteristics. Elder (1959) first derived an equation for this dispersion coefficient based on an analysis of an infinitely wide channel. This method has been generally recognized (Rutherford, 1994; Seo & Cheong, 1998) to underestimate natural dispersion in rivers due to the neglect of transverse shear dispersion processes. Fischer (1979) derived an equation for the dispersion coefficient that included a triple integral to account for the local transverse mixing. However, difficulties in accounting for the transverse mixing coefficient have been encountered mainly due to the absence of information regarding the transverse velocity and depth (Deng et al., 2001). More recently, numerous empirical equations to estimate dispersion coefficient based on geometrical river characteristics have been developed based on regression analyses of published datasets of tracer studies and the resulting fitted 1D ADE parameters (Kashefipour & Falconer, 2002; Liu, 1977; Magazine et al., 1988; Seo & Cheong, 1998; Zeng & Huai, 2014). These equations are commonly based on dimensional analysis of key hydraulic and geometric parameters known to influence dispersion and turbulent diffusion processes including the width, depth, mean velocity and mean shear velocity. Such empirically based formulations of dispersion coefficient as a function of bulk river properties are often implemented within water quality models to determine longitudinal dispersion coefficient default parameters. For instance, the default longitudinal dispersion coefficient in the Qual2K water quality model is calculated using a regression equation from Fischer (1975). The default value within the D-Water Quality module used within the software packages Delft3D and SOBEK is calculated using a function based on the mean velocity, width, Chezy coefficient and the total depth (Deltares, 2018). InfoWorks ICM uses a default equation based on bulk river characteristics (shear velocity, channel width, mean flow velocity) to determine the dispersion coefficient (Innovyze, 2017). This, however, raises important questions regarding the sensitivity of water quality assessments (and associated decision making) to inaccuracies in the estimates of such parameters. Understanding the uncertainties introduced via the use of these methodologies for quantifying the dispersion coefficient based on bulk river characteristics is therefore of importance when considering the accuracy of water quality modelling studies. Little research on error propagation through existing calibrated models for water quality in rivers has been conducted to date (Benke et al., 2008) and work to understand the implications of the longitudinal dispersion coefficient uncertainty within water quality predictions is rare. Whilst some studies have determined the accuracy of some parameter estimation techniques at specific case study sites (El Kadi Abderrezzak et al., 2015; Launay et al., 2015), or investigated the uncertainties resulting from the use of the 1D ADE (as well as an alternate stochastic transfer function based approach) at a site at different flow rates (Romanowicz et al., 2013), to the authors knowledge, there is a lack of studies that robustly estimated and propagated parametric uncertainties associated with the determination of the dispersion coefficient. The nature, scale or significance of this uncertainty, its relationship to model structure uncertainty, or the associated implications for commonly deployed water quality assessments is therefore not currently well understood.

The aim of this chapter is to quantify the impact of uncertainty introduced to river water quality modelling as a result of utilising current state of the art regression equations to determine longitudinal dispersion coefficients. The assessment is based on the 1D ADE due both to its ongoing widespread application, as well as the availability of a significant number of historical published datasets over a range of field sites with which to robustly characterise parameter uncertainty. This paper first independently evaluates six longitudinal dispersion regression equations by quantifying their statistical accuracy against published datasets of tracer studies. Then, a Monte Carlo analysis is carried out to propagate uncertainty inherent in the empirical formulations of dispersion coefficient, to time-concentration profiles for an independent river solute tracing case study. Finally, the paper estimates and discusses potential impact of this uncertainty on water quality legislation compliance based on a concentration-duration-frequency analysis using rivers of different hydraulic and geometric characteristics.

4.2 Evaluation of methodologies to estimate dispersion coefficient in rivers

This study identified and reviewed a range of methodologies and equations for predicting longitudinal dispersion coefficients in rivers. It was found that most regression analyses have been based on the same underlying dataset which has grown over time as more studies have been added. The datasets consist of published values of bulk river characteristics and 'measured' dispersion coefficients. Typically, these values are based on averaged values of cross sectional river surveys as well as the results of tracer study tests in which some form of parameter identification techniques (e.g. method of moments) have been performed to identify mixing parameters. However, given the size of the database and the unavailability of the raw data, it is not possible to robustly evaluate the accuracy of the underlying datasets. There is considerable overlap in the empirical basis for most published regression based methods found in the literature. However, a number of statistical and regression analysis methods have been deployed in order to produce numerous formulations to determine dispersion coefficients. In this study, we focus on six published equations (shown in Table 1) for a more rigorous evaluation and uncertainty analysis. These studies were selected because they contain large and clearly identifiable published datasets which are comparable, thus making a fair comparison of their potential predictive accuracy. In addition, as analysis techniques have progressed, the predictive power and accuracy of the regression equations has tended to grow over time. Therefore, by utilising relatively recent methodologies we aim to evaluate the best case in terms of uncertainty levels within water quality predictions. The identified equations are commonly based on regression analysis of key identified parameters such as the ratio between river mean velocity and shear velocity $\left(\frac{v}{u^*}\right)$ and river aspect ratio$\left(\frac{B}{H}\right)$. These parameters have been determined to be influential on calculating the dispersion coefficient by several studies via dimensional analysis and observed correlations (Kashefipour & Falconer, 2002; Zeng & Huai, 2014). The six equations selected for analysis are described in Table 3.

Table 1. Evaluated Longitudinal Dispersion Equations and number of datasets used in their development. $\boldsymbol{k_x}$ is the longitudinal dispersion coefficient (m^2 s^{-1}), $\boldsymbol{B}$ is the river width (m), $\boldsymbol{H}$ is the river depth (m), $\boldsymbol{v}$ is the river mean velocity (m s^{-1}), $\boldsymbol{u}^*$ is the river mean shear velocity (m s^{-1}), and $\boldsymbol{Fr}$ is the Froude number

Name	Equation	Number of training/calibration datasets
Deng et al. (2001)	$k_x = \frac{0.15}{8\,E_t}\left(\frac{v}{u^*}\right)^2\left(\frac{B}{H}\right)^{1.67} Hu^*, where$ $E_t = 0.145 + \left(\frac{1}{3520}\right)\left(\frac{v}{u^*}\right)\left(\frac{B}{H}\right)^{1.38}$	73
Etemad-Shahidi and Taghipour (2012)	$if\,\frac{B}{H} \leq 30.6, k_x = 15.49\left(\frac{B}{H}\right)^{0.78}\left(\frac{v}{u^*}\right)^{0.11} H\,u*$ $if\,\frac{B}{H} > 30.6, k_x = 14.12\left(\frac{B}{H}\right)^{0.61}\left(\frac{v}{u^*}\right)^{0.85} H\,u*$	149
Zeng and Huai (2014)	$k_x = 5.4\left(\frac{B}{H}\right)^{0.7}\left(\frac{v}{u^*}\right)^{0.13} H\,v$	116
Disley et al. (2015)	$k_x = 3.563\,Fr^{-0.4117}\left(\frac{B}{H}\right)^{0.6776}\left(\frac{v}{u^*}\right)^{1.0132} H\,u*$	56
Wang and Huai (2016)	$k_x = 17.648\left(\frac{B}{H}\right)^{0.3619}\left(\frac{v}{u^*}\right)^{1.16} H\,u*$	116
Wang et al. (2017)	$k_x = \left(0.718 + 47.9\frac{H}{B}\right) v\,B$	116

The equation presented in Deng et al. (2001) is based on Fischer's (1975) triple integral for longitudinal dispersion coefficient. By deriving an expression for the transverse velocity profile in alluvial rivers, they considered the local velocity deviation from the cross-sectional average velocity and solved the triple integral to derive an analytical equation for the longitudinal dispersion coefficient. A regression dataset was used to test the proposed equation to determine the suitability of the coefficients in the equation. Etemad-Shahidi and Taghipour (2012) developed a model tree method to produce an alternate equation to derive the longitudinal dispersion coefficient. The method consists of a recursive algorithm that performs the regression analysis on the underlying datasets by reducing a standard deviation factor. Zeng and Huai (2014) used a non-dimensional analysis to determine that most previous equations underestimate the longitudinal dispersion coefficient for rivers with aspect ratios between 20 and 100. They suggested that a more accurate formula for longitudinal dispersion can be found via implementing an additional factor based on the mean velocity. Disley et al. (2015) performed dye tracing experiments on a small stream in Ontario. Using the collected data and a selection of rivers from previous studies, they developed a new regression equation of longitudinal dispersion. Disley et al. (2015) incorporated the Froude number to capture the effect of the slope on dispersion processes. Wang and Huai (2016) based a new equation on an analysis of dispersion in a rectangular flume and applied this understanding to natural rivers. To obtain the longitudinal dispersion coefficient from a rectangular flume, they transformed the non-integral form of the velocity distribution into a Fourier series to solve the triple integral for longitudinal dispersion. Consequently, they used 80% of their selected dataset to train the algorithm developed for predicting the dispersion equation. Finally, Wang et al. (2017) suggested a concise form of the dispersion coefficient equation for various flow conditions. The study developed a general dispersion equation for pipe flows and calibrated it for natural rivers using a genetic algorithm model.

To initially evaluate the predictive accuracy of each of the regression equations presented in Table 1, a statistical analysis was conducted using the original regression datasets employed in the construction of each formulation (Table 2). The corresponding datasets were selected for the analysis to provide a fair evaluation of each model, so that each equation is only compared against its own regression dataset. The statistical criteria used to evaluate the equations include: i) percent accuracy, ii) the RMSE-observations standard deviation ratio (RSR), iii) percent bias (PBIAS), iv) coefficient of determination (R^2), and v) Nash-Sutcliff Coefficient (NSC). A definition of these criteria can be found in Table 2. The optimal value of the RMSE-observations standard deviation ratio (RSR) is 0.0. RSR standardizes the Root Mean Square Error (RMSE) using the observations and describes the residual variance (Moriasi et al., 2007). The percentage bias (PBIAS), is used to measure the tendency of the formulations to overestimate or underestimate the observed value. The optimal value of the PBIAS is 0.0. Therefore, the best performing equation is the one with the smallest absolute value of PBIAS (Gupta et al., 1999). Negative PBIAS value indicates that the equation is over-predicting the value of the longitudinal dispersion coefficient, while positive values indicate under-prediction. The accuracy is the percentage of Predictive ratios (Pr) between 0.5 and 2 or its equivalent logarithmic range between -0.3 and 0.3 (Seo & Cheong, 1998; White, 1973). The R^2 describes the degree of collinearity between the predicted and observed data. It also indicates the proportion of the observed data that is explained by the variance. Higher values indicate less error variance. However, R^2 does not detect systematic over or under-predictions (Krause et al., 2005). The NSC is a normalized indicator of the performance of the equation. The weakness of the NSC is that, because it is squared, it is sensitive for high values in the dataset, but not for lower values (Krause et al., 2005). These statistical measures were selected because they are commonly used to evaluate, train or optimise the dispersion equations (Disley et al., 2015; Etemad-Shahidi & Taghipour, 2012; Sattar & Gharabaghi, 2015; Seo & Cheong, 1998).

Table 2 presents the statistical results of the evaluation of the dispersion equations. According to the statistical model evaluation techniques described above, Disley et al. (2015) equation has the highest accuracy, lowest RSR, least absolute PBIAS, highest R^2, and highest NSC. The Etemad-Shahidi and Taghipour (2012) equation has the second lowest RSR, and second highest R^2 and NSC. Deng et al. (2001) equation has the second highest accuracy. From the negative PBIAS (Table 2), it is noted that the Disley et al. (2015), Zeng and Huai (2014) and Deng et al. (2001) equations tend to over-predict the dispersion coefficient.

Table 2. Summary of statistical analysis based on individual datasets used in the construction of dispersion equations. Analysis includes percent accuracy, RMSE-observations standard deviation ratio (RSR), Percent bias (PBIAS), Coefficient of determination (R^2), Nash-Sutcliff coefficient (NSC)

	Wang et al. (2017)	Wang and Huai (2016)	Disley et al. (2015)	Zeng and Huai (2014)	Etemad-Shahidi and Taghipour (2012)	Deng et al. (2001)
Percent Accuracy	61.2	63.8	73.2	61.2	62.4	64.4
$\boldsymbol{RSR = \frac{\sqrt{\sum_{i=1}^{n}(kx_i^M - kx_i^P)^2}}{\sqrt{\sum_{i=1}^{n}\left(kx_i^M - \overline{kx}^M\right)^2}}}$	0.78	0.83	0.39	0.88	0.68	1.4
$\boldsymbol{PBIAS = \frac{\sum_{i=1}^{n}(kx_i^M - kx_i^P) * 100}{\sum_{i=1}^{n} kx_i^M}}$	20.8	3.49	-3.01	-7.48	31.9	-47.0
$\boldsymbol{R^2 = \left[\frac{\sum_{i=1}^{n}(kx_i^M - \overline{kx}^M)(kx_i^P - \overline{kx}^P)}{\sqrt{\sum_{i=1}^{n}(kx_i^M - kx^M)^2}\sqrt{\sum_{i=1}^{n}(kx_i^P - \overline{kx}^P)^2}}\right]^2}$	0.41	0.43	0.85	0.44	0.63	0.36
$\boldsymbol{NSC = 1 - \frac{\sum_{i=1}^{n}(kx_i^M - kx_i^P)^2}{\sum_{i=1}^{n}(kx_i^M - \overline{kx}^M)^2}}$	0.39	0.31	0.84	0.23	0.53	-0.99

Figure 6 shows the distribution of Predictive ratios (Pr = k_{Xp} / k_{xM}; where k_{Xp} and k_{xM} are the predicted and measured longitudinal dispersion coefficients), grouped into histogram bins, for each of the equations. The equations that have the highest percentages of Pr values within 0.5 and 2.0 are the most accurate equations as also shown by the "Percent Accuracy" in Table 2. Among the studied equations, it is observed that Disley et al. (2015) equation has the largest amount of Pr values between 0.5 and 2.0 (73.2%). The other equations all have similar Pr values between 0.5 and 2.0, namely 61.2% and 64.4%.

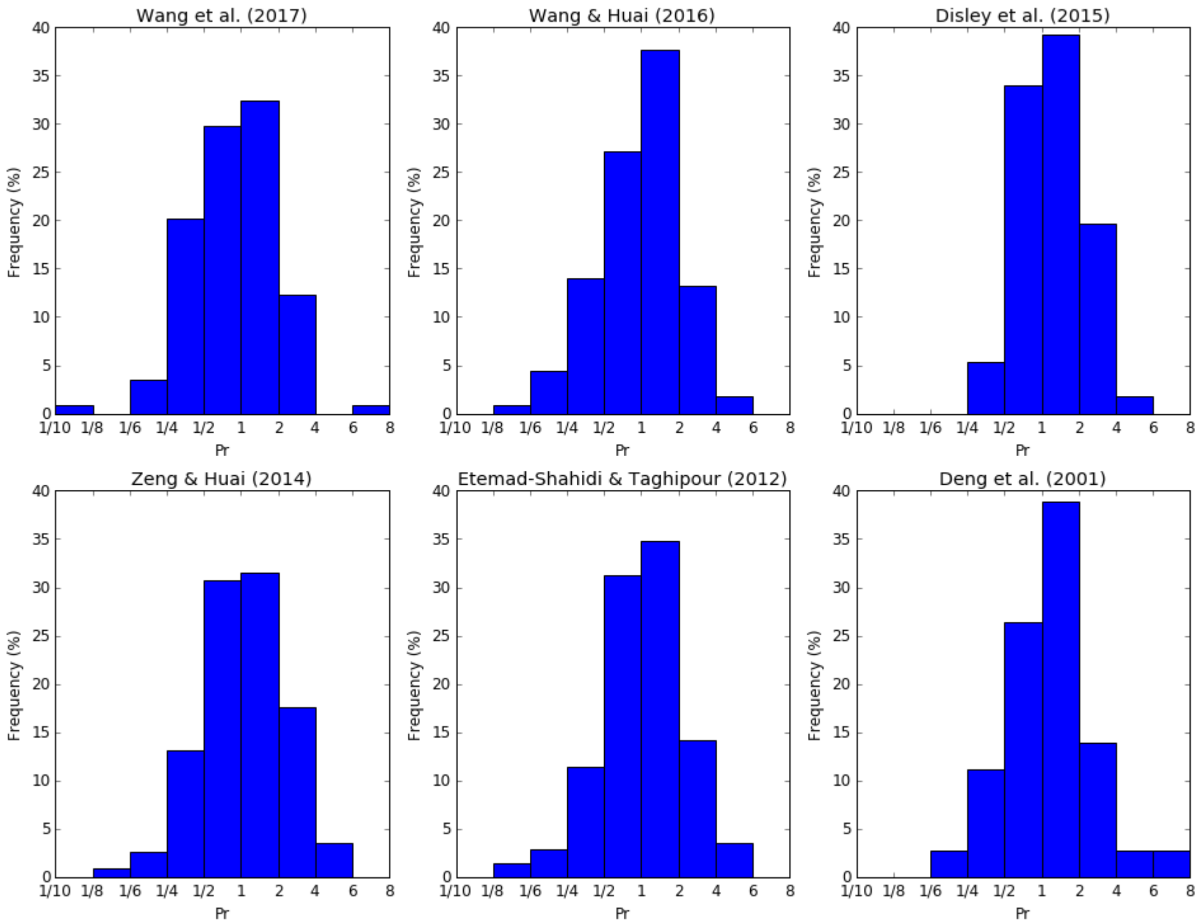


Figure 6. Probability histograms of Predictive ratios (Pr) obtained from individual regression datasets used in the construction of dispersion equations

4.3 Methodology for Uncertainty Propagation

This section presents a methodology to evaluate the uncertainty within water quality modelling due to the selection of the dispersion coefficient using the equations detailed in Table 1, utilising a dataset from an independent dye tracing experiment conducted in the Chillan River. A general background description and discussion of uncertainty propagation using Monte Carlo methods within environmental modelling can be found in e.g. Benke et al. (2018) and Helton (1993). The Chillan River field study has been selected as the data has not been included in the derivation of any of the studied dispersion coefficient equations, and because field survey and solute concentration versus time profiles are available, measured downstream of an instantaneous release of tracer. The Chillan River is located in Chile's 8th Region, approximately 400 km south of Santiago de Chile. It emerges from the Andes Mountains and flows west until it meets the Ñuble River (Brevis, 2001). In May and April of 2003, river survey information was collected alongside two tracer experiments at a site close to the city of Chillan. 60 ml of 20% Rhodamine WT tracer was released in the river following the general guidelines described in Hubbard et al. (1982). The tracer experiment carried out in May 2003 was selected because the tracer breakthrough curve was complete and the river hydraulic and geometric data were available. The data were obtained following the same methodology for concentration measurements as the one used in De Smedt et al. (2005), also taken at the Chillan river. A calibrated fluorimeter, Turner Designs Model 10, with a detection limit of 0.01 ppb was used for the concentration measurements. Samples were analysed in-situ and in the laboratory. The in-situ samples were immediately analysed using the fluorimeter. Due to time overlap between concentration curves at different sampling stations, some of the samples were stored in thermally-isolated compartments and later analysed using the same fluorimeter and the same calibration curves. The samples were periodically checked for changes in the pH of the river. Comparison of the total mass between the sampled concentrations curves confirmed that losses of Rhodamine mass between stations can be assumed negligible. The resulting river concentration versus time profiles in the study reach were obtained from samples taken at measurement points positioned 2.5 km and 3.8 km downstream of the release (after full cross-sectional mixing of the solute). A total of 28 cross-section surveys were carried out between the upstream and downstream sampling points containing hydraulic and geometric information. The study reach was divided into several consecutive sub-reaches between each pair of cross-sections. Longitudinal and transverse survey data were collected and then digitized using AUTOCAD 2000 to determine the cross-sectional area (reach mean: 10.6 m^2, std. dev: 7.5 m^2), wetted perimeter (reach mean: 17.2 m, std. dev: 5.7 m), surface width (reach mean: 16.4 m std. dev: 6.1 m), depth (reach mean: 0.7 m, std. dev: 0.5 m), sinuosity (reach mean:1.5, std. dev: 0.2) and average slope (reach mean: 0.005, std. dev: 0.002). During the selected tracer experiment, flow measurement was carried out at the injection site. A current meter (OTT Waterflow) was used to determine velocity over the cross-section, and these measurements were integrated over the cross-section to calculate mean flow rate according to standard practice described in standard ISO-748:2007(E) (ISO, 2007). The flow rate was calculated as 2.6 $m^3 s^{-1} \pm 0.05 m^3 s^{-1}$. The mean velocity at each measured cross-section was calculated using the flow rate and measured wetted area resulting in a reach mean and standard deviation of 0.45 $m s^{-1}$ and 0.34 $m s^{-1}$ respectively. Further details and results of the experiment are presented in Segura (2004).

To quantify and propagate the parameter uncertainty from the various dispersion equations, the following steps were conducted for each equation analysed:

1. Probability functions were fitted to the distributions of Predictive ratios (*Pr*, from Figure 6). The distributions were fitted using the Python package (Fitter) developed by (Cokelaer, 2014). Fitter evaluates 80 function types from the statistical distributions of the Scipy package (Oliphant, 2007). In all cases, the *Pr* distributions were best described by lognormal functions. This concurs with previous studies which evaluate predictive ratios (Kashefipour & Falconer, 2002; Seo & Cheong, 1998; Zeng & Huai, 2014). The probability distributions with their corresponding mean, sum of square errors and kurtosis are shown in Figure 7
2. A Monte Carlo analysis was carried out obtaining 2000 randomly drawn Pr values from each logarithmic probability function. These *Pr* values were used to adjust the deterministic dispersion coefficient value calculated using each dispersion coefficient equation for each river sub-reach using the measured and calculated hydraulic and geometric information (B,h, v, u* Fr) derived from the field measurements. This is similar to the method used by Schellart et al. (2010a) for studying uncertainty inherent in coefficients in existing regression equations. For example, Figure 7 shows that following Disley et al. (2015) equation, the predicted k_x could be anywhere between approximately 0 and 10 times the 'possible real k_x', so dividing the predicted k_x by each of the randomly drawn Pr values, would give 2000 'possible real k_x' values. A straightforward Monte Carlo simulation was deemed the most suitable approach, due to its conceptual simplicity as well as its ease of explanation to e.g. regulators (Benke et al., 2018; Helton, 1993; Sriwastava et al., 2018).
3. Using an analytical solution of the 1D ADE, given by Equation 12 below (Rutherford 1994), and the 'possible real k_x values' (based on the drawn *Pr* value from step 2) the downstream concentration profile located at 3.8 km was calculated. This was achieved by successively routing the observed upstream concentration profile (at 2.5 km) over each sub-reach until the concentration profile at the last sub-reach was obtained (utilising the geometric and hydraulic data). This resulted in 2000 possible predicted downstream concentration profiles.
4. The 12.5th, 50th and 87.5th percentiles of each concentration distribution were then identified and compared with the observed concentration profile and with the routed

concentration profile obtained using the deterministic dispersion coefficient. The 75% confidence intervals were selected because these can be estimated more reliably than larger confidence intervals based on the relatively limited available data.

5. To remove errors caused by the field measurements of velocity, the observed concentration profile at the last sub-reach was used to calibrate the travel time and mean velocity of each sub-reach, i.e. the total travel time was adjusted until a match was achieved between the observed and predicted concentration distribution centroids. This was required as the aim of this work is to identify the uncertainty associated with the dispersion coefficient, rather than the initial estimation of velocity caused by field measurement. Consequently, the velocities for each sub-reach were corrected proportionally based on the re-calculated travel time. Steps 2-4 were repeated with the corrected mean velocity and travel time values to produce the final predictions and confidence bands.

Equation 12

$$C(x_2,t) = \sum_{\tau=-\infty}^{\infty} \frac{C(x_1,t_i)\ v\ \Delta\tau}{\sqrt{4\pi\ k_x T}}\, exp\left(-\frac{v^2\ (T-t+t_i)^2}{4k_x\,T}\right)$$

Where $C(x_1,t_i)$ is the temporal concentration profile at x_1 (upstream of each sub reach) at time t_i, $C(x_2,t)$ is the concentration at the location x_2 (downstream of each sub reach) and time t, v is the mean velocity over the sub reach, k_x is the longitudinal dispersion coefficient, T is the travel time over the cross section, initially calculated (pre calibration) using the cross section distances and measured velocity. Equation 12 is based on Taylor's analytical solution to Equation 11, utilising the frozen cloud approximation to convert between the temporal and spatial domains. A full discussion of this solution can be found in Rutherford (1994).

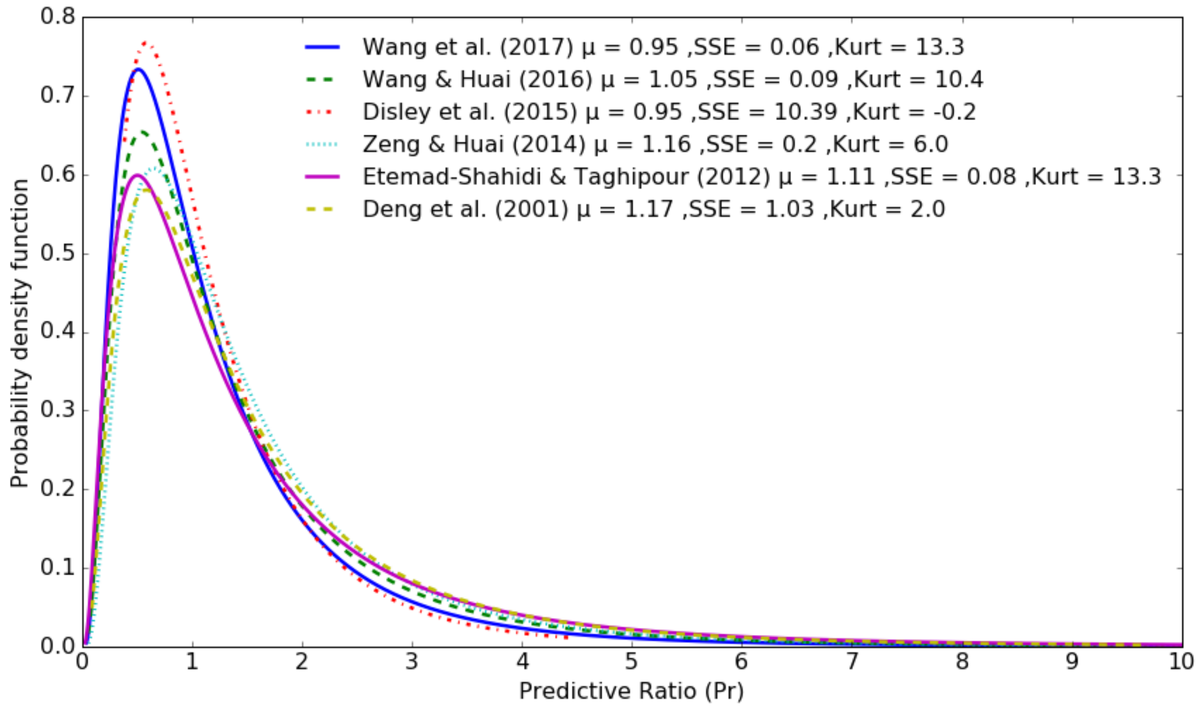


Figure 7. Fitted probability distributions for Predictive ratio (Pr) using regression datasets with their corresponding mean (μ) Sum of Square Errors (SSE), and Kurtosis (Kurt).

4.3.1 Uncertainty Quantification Results

The mean, sum of square errors and kurtosis of each fitted lognormal distribution for the corresponding dispersion equations are shown in Figure 7. The mean values of the distributions range between 0.95 and 1.17 (with 1.0 representing as the perfect agreement between predicted and measured coefficients). Wang et al. (2017), Wang and Huai (2016) and Disley et al. (2015) have the narrowest distributions and mean values closest to 1.0 as also noted by the narrower histogram in Figure 6, while the remaining dispersion equations have wider distributions and have mean values higher than 1.0 (hence an average over-prediction). Disley et al. (2015) has the largest SSE while Wang et al. (2017) has the smallest SSE indicating a better fit between distributions and predictive ratios. Wang et al. (2017), Wang and Huai (2016) and Etemad-Shahidi and Taghipour (2012) have the highest levels of kurtosis indicating longer tails. Heavier tails indicate that some predictions heavily overestimate the dispersion coefficients. However, it should be noted that distribution tails are very sensitive to small numbers of outlying data. Disley et al. (2015) equation results in the highest probability density in Figure 7 which is in agreement with having the highest accuracy in Figure 6.

Figure 8 presents the results of the uncertainty propagation methodology when applied to the field dataset from the River Chillan. Figure 8 displays the observed concentration profiles at the upstream and downstream measurement stations, and the predicted concentration profiles based on the dispersion coefficients calculated using each of the deterministic equations in Table 1 and the analysis presented above. The predicted concentration profiles include the deterministic prediction, the 50th percentile (median), and the 12.5th and 87.5th percentiles (75% confidence interval) resulting from the Monte Carlo analysis. To show the influence of the changes of the river characteristics (e.g. river depth and width) on the deterministic dispersion coefficients, the reach mean and standard deviation values of the river reaches deterministic dispersion coefficients are shown in Figure 8. It is noted that the standard deviation of predicted dispersion coefficient over the sub reaches varies significantly between the equations, indicating that some equations are more sensitive to longitudinal variations in the river characteristics. The largest mean deterministic longitudinal dispersion coefficient leads to flatter concentration profiles as observed in Figure 8 for Etemad-Shahidi and Taghipour (2012) with lower peak concentration values. The opposite is true for a low dispersion coefficient when using Deng et al. (2001) equation. This results in a taller and narrower concentration versus time profile. It is noted that a significant proportion of observed concentration values fall outside the 75% confidence intervals when using Etemad-Shahidi and Taghipour (2012) and Disley et al. (2015) equations. The concentration versus time profiles obtained using Wang et al. (2017), Wang and Huai (2016) and Zeng and Huai (2014) dispersion equations have similar 75% confidence intervals, median and deterministic concentrations. The deterministic predictions from these dispersion equations still underestimate the observed concentrations, but the observed concentrations are within the 75% confidence intervals. The simulated concentrations using the deterministic dispersion coefficient predicted by the Deng et al (2012) equation visually resemble the observed concentrations more accurately than the other equations, with the observed concentrations well within the 75% confidence interval. It is noted that almost all predicted profiles within the 75% confidence interval fail to reproduce the early leading edge of the observed concentration profiles. Overall, the methodology has been shown to provide additional information in regard to concentration predictions over and above the use of the deterministic models, with uncertainty bands encompassing the observed concentration values. Five out of the six studied deterministic equations underestimate observed peak concentration levels (by an average of 29%). Etemad-Shahidi and Taghipour (2012) equation results in the largest underestimation among the studied equations by approximately 64%. Such under-predictions indicate that mixing processes are generally lower in the River Chillan than is predicted by the studied regression equations. Confidence intervals are of considerable size, but are approximately equivalent between the equations, indicating the inherent uncertainty associated with the evaluation of dispersion coefficients by using regression equations derived from data from other rivers. The simulated 12.5th percentile concentration profiles resulted in simulated peaks between 26% and 81% of the measured value.

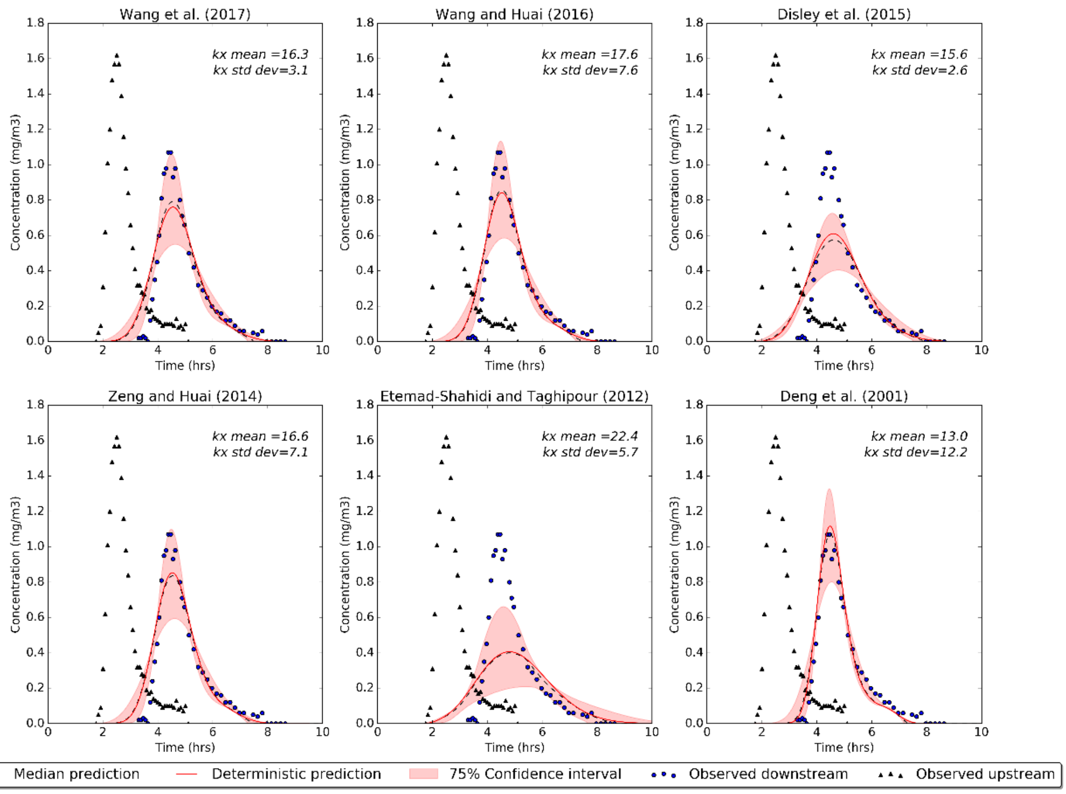


Figure 8. Concentration versus time profiles retrieved when using six different dispersion equations and their corresponding datasets for sampling stations of the river Chillan. Shaded bands represent the 75% confidence interval. k_x mean and k_x std dev are the results of the mean and standard deviation of the dispersion coefficients for the 28 river cross-sections.

4.4 Impact of dispersion coefficient uncertainty on concentration-duration threshold based standards

Section 4.3 presented a propagation methodology to estimate uncertainty within surface water quality predictions associated with the dispersion coefficient derived using the regression equations based on river characteristics. To understand the potential implications of this uncertainty, this section evaluates the propagated uncertainty from the dispersion coefficient taking into consideration water quality standards and regulatory guidance in a site specific context. Such guidelines and water quality standards have been developed and improved over the years to protect aquatic life from situations that may cause stress in river environments (Milne I, 1992). One methodology widely used in the UK to regulate rainfall driven time varying releases (e.g. from urban drainage systems) into receiving waters is the intermittent standards approach. This consists of defined concentration-duration-frequency thresholds for specific substances (UPM, 2012). With this approach, dissolved oxygen and un-ionised ammonia concentrations must not exceed given thresholds for longer than specified durations, with values based on the return period of the storm event.

To evaluate the uncertainty due to the empirical dispersion equations with regard to concentration-duration-frequency water quality regulation, an analysis of four rivers of different geometrical and hydraulics properties (Table 3) obtained from the dataset in Wang and Huai (2016) is conducted. This dataset was selected because it was the most extensive dataset with the most overlapping data among the evaluated studies. The measured, deterministic (from each equation in Table 1), and the upper, median and lower quantiles of the dispersion coefficients for the four rivers as calculated using the method described in Section 4.3 are also shown in Table 3. John Day River represents a deep (2.5 m) river with one of the lowest aspect ratios $\left(\frac{B}{H}\right)$ of 13.8 in the dataset. The measured dispersion coefficient of 65 $m^2\,s^{-1}$ was the largest among the studied rivers. The Monocacy River is a shallow river with one of the largest aspect ratios (130.8) and largest widths (92.9 m). Its measured dispersion coefficient was 41 $m^2\,s^{-1}$. The Copper Creek and New River show the contrast between a low versus a high mean to shear velocity ratio $\left(\frac{v}{u^*}\right)$. Copper Creek has a mean shear velocity of 0.116 $m\,s^{-1}$ thus a low mean to shear velocity ratio (1.2) and a measured dispersion coefficient of 10 $m^2\,s^{-1}$. The New River has a lower shear velocity (0.008 $m\,s^{-1}$), high mean to shear velocity ratio (21.3), and a measured dispersion coefficient of 22 $m^2\,s^{-1}$. In each river, we utilise a pseudo concentration distribution of ammonia and route it downstream, utilising the same methodology as presented in Section 4.3 to estimate confidence intervals. A constant cross section and flow were applied to the simulated rivers. At discrete positions (every 200m) downstream of the release, the duration over a specified threshold is determined and evaluated in light of UK concentration-duration water quality standards for ammonia (Foundation for Research, 2012). The analysis illustrates how uncertainty in the use of dispersion coefficient regression equations has the potential to influence the degree of compliance with water quality regulation within modelling studies.

Table 3. Measured and deterministic dispersion coefficient values together with median and 75% percentile values obtained from Monte Carlo analysis for the four selected rivers

	John Day River			**Monocacy River**			**Copper Creek**			**New River**		
Width (m)	34.1			92.9			18.6			102		
Depth (m)	2.5			0.71			0.39			4.4		
Mean Velocity (m s^{-1})	0.82			0.16			0.14			0.17		
Shear Velocity (m s^{-1})	0.18			0.046			0.12			0.0080		
Aspect ratio $\frac{B}{H}$ (-)	13.8			130.8			47.7			23.2		
Mean to shear velocity ratio $\frac{v}{u*}$ (-)	4.6			3.5			1.2			21.3		
Measured k_x (m^2 s^{-1})	65.0			41.4			9.9			22.4		
k_x Equation (m^2 s^{-1})	**Deterministic k_x**	**$k_{x\ 50}$**	**$k_{x\ 12.5}$, $k_{x\ 87.5}$**	**Deterministic k_x**	**$k_{x\ 50}$**	**$k_{x\ 12.5}$, $k_{x\ 87.5}$**	**Deterministic k_x**	**$k_{x\ 50}$**	**$k_{x\ 12.5}$, $k_{x\ 87.5}$**	**Deterministic k_x**	**$k_{x\ 50}$**	**$k_{x\ 12.5}$, $k_{x\ 87.5}$**
Wang et al. (2017)	117.1	119.6	19.4, 420.2	16.1	14.2	6.1, 34.0	4.5	3.9	1.5, 10.6	48.3	42.6	16.4, 110.1
Wang and Huai (2016)	117.9	127.0	20.5, 500.5	14.3	15.0	5.9, 33.7	4.0	4.1	1.5, 10.2	67.1	65.9	25.1, 177.7
Disley et al. (2015)	91.3	107.4	42.2, 297.7	35.5	41.3	24.2, 76.0	7.9	9.0	5.0, 17.9	105.1	122.7	67.6, 249.0
Zeng and Huai (2014)	83.7	91.2	15.8, 344.0	21.9	24.6	10.5, 54.0	4.5	5.1	1.9, 12.3	54.3	58.8	21.7, 147.4
Etemad-Shahidi and Taghipour (2012)	63.1	67.5	8.4, 329.4	26.0	27.6	10.0, 70.0	7.9	8.4	2.5, 23.9	8.9	9.5	2.9, 26.4
Deng et al. (2001)	71.2	81.2	15.0, 344.4	25.8	29.7	12.8, 67.6	3.6	3.9	1.5, 10.7	92.5	100.3	39.8, 267.6

The initial concentration distribution (upstream boundary condition) is based on an integrated modelling study presented by Norris et al. (2014) where an integrated catchment in the UK was modelled using Infoworks ICM. The peak of the simulated initial concentration profile was 0.61 mg Nl^{-1} and its duration was 15 hours. The distribution is considered only as an indicative description of a potential concentration, and is used in the analysis to determine the confidence intervals of predictions using 1D ADE modelling. The water quality threshold was obtained from the Urban Pollution Drainage Manual (UPM, 2012) for Salmonid Fishery Standards for 1-hour/1-year event, specified as 0.105 mg Nl^{-1} unionised ammonia. It is noted that to model ammonia concentrations, it may require to incorporate other processes such as Biological Oxygen Demand (BOD) decay, nitrification, uptake by plants and bacteria and heterotrophic respiration as applied in other studies (Lopes et al., 2005; Radwan et al., 2001). However, as more parameters are added to the transport model, the parameter uncertainty is less identifiable. This study aims to analyse the uncertainty from the dispersion coefficient only, thus the ammonia concentration is assumed conservative within the river reach.

4.4.1 Duration over Threshold Analysis Results

Figure 9 presents the resulting simulated durations that the ammonia concentrations exceed the water quality threshold (0.105 mg Nl^{-1}) as a function of distance downstream of the simulated initial distribution within the John Day river when utilising i) observed dispersion coefficient values (from the original database), ii) dispersion values predicted using each of the deterministic equations and iii) median plus 75% confidence intervals derived using the method described above.

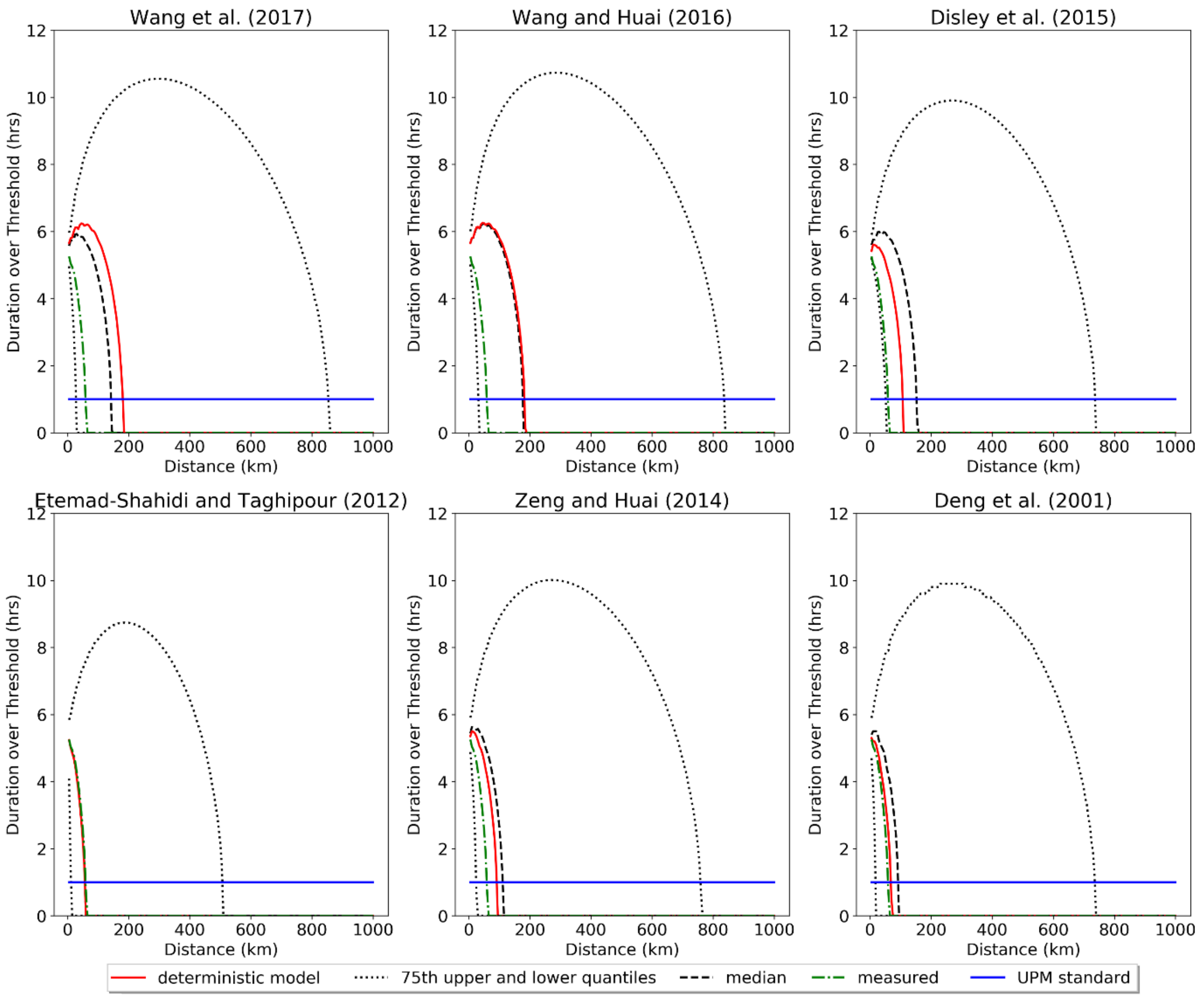


Figure 9. Duration over threshold versus distance for John Day River. Dotted lines present upper and lower 75% confidence intervals, red continuous line displays the deterministic k_x equation used, black dashed line presents the median of Monte Carlo simulation, blue continuous line presents the water quality set threshold, and green semi dotted line represents the DoT values obtained when using the measured k_x.

The horizontal line represents the specified maximum 1-hour duration of exceedance for a 1-year return period event; when the simulated duration falls below this level of compliance, the standard is achieved. Figure 9 shows that four deterministic equations overestimate the length of river stretch where the water quality threshold is exceeded compared to observed mixing parameters in the John Day River. Overall, there is considerable uncertainty regarding the length of river section that exceeds the 1-hour/1-year return period standards for ammonia when using regression equations for the determination of the dispersion coefficient. For example, when using Wang et al. (2017) equation, the duration over threshold exceeds one hour at 181 km downstream of the release when the deterministic dispersion coefficient is used.

However, this distance varies between 28 km and 854 km if the 75% confidence interval is considered. Figure 9 shows that when using the measured dispersion coefficient, the duration over threshold values fall within the 75% confidence interval bands in all cases. The Etemad-Shahidi and Taghipour (2012) equation results in the narrowest 75% confidence interval.

Figure 10 summarizes this information for all four of the rivers, showing the distance downstream of the release where the modelled pollutant has exceeded the 1-hour/1-year threshold using the deterministic dispersion coefficients from each of the regression equations, the 75% confidence intervals using the methodology outlined in Section 4.3, as well as when using the measured value of dispersion coefficient for each river. The larger measured dispersion coefficient values for the John Day River and the Monocacy River (see Table 3) mean that the pollutant disperses faster and the 1-hour/1-year standard is achieved after a shorter distance. In most cases, there are considerable differences between the measured and deterministically estimated dispersion coefficients. The closest prediction is obtained when using the Etemad-Shahidi and Taghipour (2012) equation in the John Day river (2 km difference). The largest difference between predicted and measured values is found when using the Deng et al. (2001) equation in the Copper Creek (236 km difference). Considering all four rivers, the Disley et al. (2015) equation provides the closest predictions on average (43 km difference). When considering the 75% confidence intervals, considerable differences are observed between rivers and between equations, however values using measured dispersion coefficients lie within predicted confidence intervals in almost all cases apart from the New River.

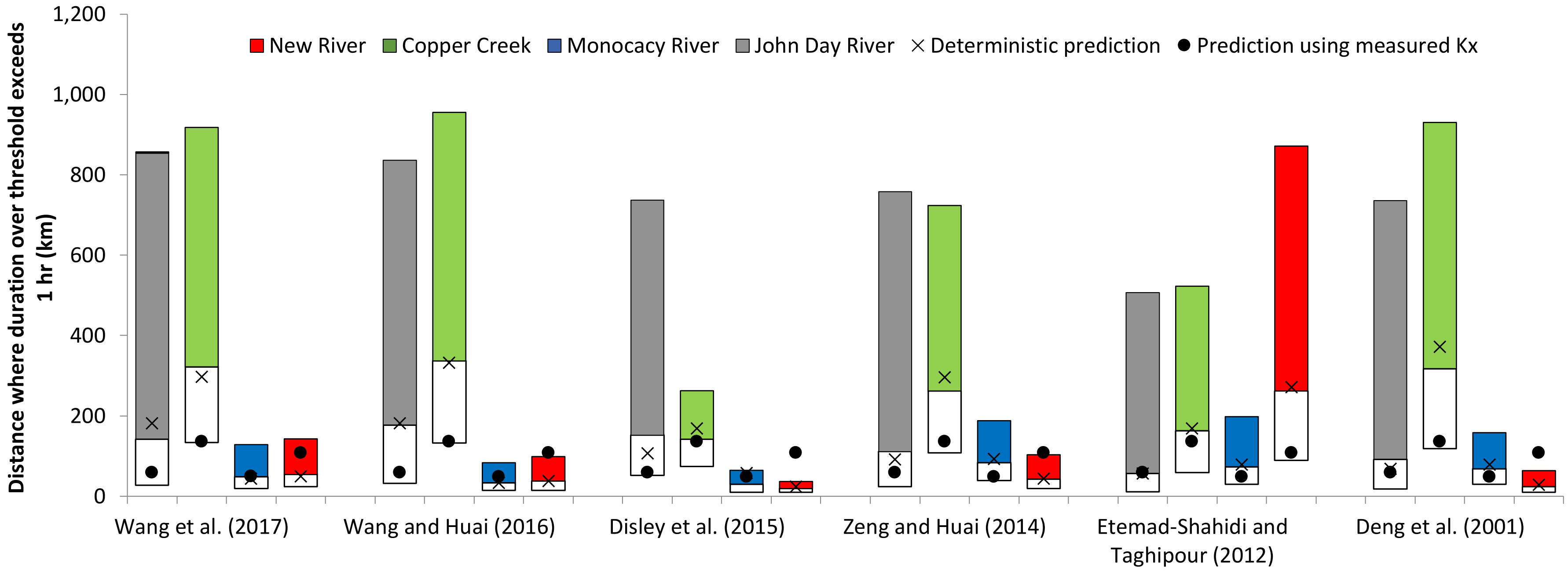


Figure 10. 75th quantile boxplots of distance where the Duration over Threshold (DoT) exceeded the allowed time as stated in the water quality regulation for the studied dispersion coefficient equations

4.5 Discussion

This study examines six published equations for estimating the longitudinal dispersion coefficient with an independent analysis of published data (Section 4.2). The study then proposes a method to propagate the uncertainty to concentration versus time profiles (Section 4.3), and assesses the implications that this propagated uncertainty may have on testing compliance with water quality regulation (Section 4.4).

The results showed that the equation by Disley et al. (2015) performed best in describing the longitudinal dispersion coefficient according to the efficiency criteria (higher percent accuracy, R^2 and NCS, least PBIAS and lowest RSR) while the equation by Deng et al. (2001) resulted in a poorer performance (second highest accuracy but most PBIAS and lowest NSC). Previous studies used similar statistical criteria to evaluate equations for predicting the longitudinal dispersion coefficient (Disley et al., 2015; Etemad-Shahidi & Taghipour, 2012; Sattar & Gharabaghi, 2015; Seo & Cheong, 1998). However, as far as the authors are aware, no studies have indicated which of these efficiency criteria would be most useful in terms of evaluating the performance of the equation when subsequently calculating concentration versus time profiles. This study presents a propagation methodology to analyse the effect of uncertainty inherent in the dispersion coefficient on the resulting concentrations when using the 1D ADE model. Section 4.3 uses this methodology to estimate confidence intervals on the concentration versus time profile of an independent tracer study measured in the Chillan River. Figure 8 shows that in the case of the river Chillan, five out of six equations tend to over-predict the dispersion coefficient. Although Deng et al. (2001) equation had a poor performance according to the efficiency criteria in Table 2, it provides the best visual resemblance to the observed concentrations. In contrast, Disley et al. (2015) is the best performing equation according to the efficiency criteria, but underestimates the observed concentrations considerably even when the confidence interval is taken into consideration (Figure 8). This demonstrates that not all the efficiency criteria (percent accuracy, RSR, PBIAS, R^2, and NSC) presented in Table 2 appear equally suitable for selecting a dispersion equation to use with the 1D ADE model. For the same reason, Nash-Sutcliffe efficiency seems particularly unsuitable for selecting the best performing dispersion equation. As described by Krause et al. (2005), the largest disadvantage of the Nash-Sutcliffe efficiency is the fact that the differences between the observed and predicted values are calculated as squared values. This means that larger values in a dataset are over emphasized whereas lower values are neglected, however, in case of the k_x coefficient both high and low values are of equal importance. If the aim of using the 1D ADE model is to check environmental standards based on concentration-duration-frequency, then looking at the PBIAS may give a better indication of how 'conservative' an equation is when checking environmental standards. A positive PBIAS value indicates that the equation is under-predicting the dispersion coefficient and hence more likely to fail a water quality standard.

The bulk river characteristics of the river Chillan would suggest that all the six longitudinal dispersion equations studied would be equally suitable for application. The performance of the equations and the scale of the uncertainty bands suggest that despite academic focus on regression equations to provide dispersion coefficients based on bulk river characteristics, considerable uncertainty remains when dispersion coefficients are utilised within modelling tools to describe concentration versus time dynamics within water quality modelling applications. Uncertainty within the estimation of dispersion coefficients is likely due to a number of reasons. These include the accuracy of the original datasets used in regression model calibration. For example, the practical difficulty in the measurement of bulk river characteristics (e.g. bed shear stress or river depth) over the same reach as the dispersion coefficient, meaning that the calibration datasets are prone to error due to the averaging of these key geometrical and hydraulic parameters over the river reach. In addition, there is lack of information regarding the original tracer experiment datasets from which the dispersion coefficients are derived. The quantification of the dispersion coefficient is prone to measurement error if data processing techniques are not conducted in a robust manner and field experiments are not conducted appropriately. It should also be noted that bulk river characteristics cannot fully describe the complexity of mixing processes in river systems, which are heavily affected by conditions such as sinuosity, presence of vegetation, pools and riffles, planform variability and hyporheic exchange amongst others. It is therefore questionable if further statistical analysis of such existing datasets can produce regression equations with the potential to describe dispersion coefficients with sufficient accuracy such that model confidence intervals could be meaningfully reduced.

The implications of the uncertainty inherent within the longitudinal dispersion coefficient equations on water quality regulation were examined by calculating the duration that a pollutant exceeded a water quality standard. This calculation was carried out for four rivers in the dataset shown in Wang and Huai (2016). It was observed that wide ranges of uncertainty are obtained for the John Day River and Copper Creek. This implies that the water quality failure can occur over a larger interval downstream of the pollutant release (over 100s of km). The opposite was found for the Monocacy River and New River. The uncertainty interval is smaller, making it more likely to obtain an accurate estimation of where the water quality failure occurs. However, the results for all four rivers indicate that even when using the most recent equations for estimating longitudinal dispersion coefficient, a considerable level of uncertainty inherent to these equations remains when determining water quality failures. To produce water quality simulations with lower uncertainties, robust calibration of a river-specific k_x, using dye tracing studies over a range of flow rates is recommended. Further options include the use of more complex 2D models in which dispersion is less important (due to the none-width averaged condition), however this option is often limited to small reaches due to computational cost. Work on alternate modelling approaches which seek to quantify and describe processes such as transient storage are of value as much due to the potential for more stable and predictable parameters (relatable to measurable physical properties, Briggs et al. 2009), as their enhanced ability to describe specific properties of the concentration distributions.

4.6 Conclusion

This paper examines uncertainty in 1D ADE model predictions of time-concentration profiles, given uncertainty inherent in using existing regression equations for estimating the longitudinal dispersion coefficient. Six recently published longitudinal dispersion equations are independently evaluated and compared. When considering dispersion coefficient prediction, this evaluation indicates that Disley et al. (2015) equation has the highest accuracy (73.2%), while the remaining equations have similar accuracies ranging between 61.2% and 64.4%. It is argued that evaluation criteria such as PBIAS may be important to include in the evaluation, due to its capability to indicate under or over-prediction of the dispersion coefficient, which are both important for estimating duration of concentration peaks over a threshold. It is also concluded that Nash-Sutcliffe is not a suitable criterion for evaluation of dispersion coefficient equations, as it neglects lower coefficient values, which for the purpose of estimating duration of concentration peaks over a threshold are equally important as high values.

Using Monte Carlo simulations, the uncertainty in the longitudinal dispersion coefficient given these six equations is propagated through the 1D-ADE to create time-concentration profiles for an independent case study. Results from a case study site suggest that when using

Deng et al. (2001) equation, the closest prediction of peak concentrations to observed values (approximately 3% difference between measured and 50th percentile predicted peak concentration) are obtained, as well as the narrowest uncertainty interval. However, resulting uncertainty intervals were considerable for all the six studied regression equations. For the Disley et al. (2015) and studied Etemad-Shahidi and Taghipour (2012) equations, the measured peak concentration values were above the simulated 87.5th percentile, for the Deng et al. (2001) equation it was close to the 50th percentile and for the other equations it was close to the 87.5th percentile. The simulated 12.5th percentile resulted in simulated peaks between 26% and 81% of the measured value.

Finally, the uncertainty methodology has been implemented into four rivers with different characteristics, and the interaction with concentration-duration-frequency type regulatory targets has been considered. It is shown that resulting model confidence intervals are likely to be significant for assessment of regulatory compliance in areas with complex prescriptive concentration based targets (e.g. the UK) as observed for the John Day River and the Copper Creek. Moreover, the effect of uncertainty is highly variable between rivers with different characteristics.

Within water quality assessments this highlights the value of using longitudinal dispersion coefficients derived specifically from field measurements for the river under study. A reduction of uncertainty in estimation of longitudinal dispersion coefficient using regression equations is likely to be dependent on further understanding and quantification of how other, more detailed river features affect mixing processes and dispersion coefficients, and an incorporation of such features within regression based models.

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5. Evaluation of a coupled hydrodynamic-closed ecological cycle approach for modelling dissolved oxygen in surface waters

This chapter aims to evaluate the performance of a complex model, which includes transport and ecological processes for longer time scales addressing the thesis Objective 2. This chapter also evaluates the sensitivity of model predictions to input data variability. This chapter is based on the publication submitted for review:

Vivian V. Camacho Suarez, R. J. Brederveld, Marieke Fennema, Antonio Moreno, Jeroen Langeveld, Hans Korving, Alma N.A. Schellart, James Shucksmith. (2019). Evaluation of a coupled hydrodynamic-closed ecological cycle approach for modelling dissolved oxygen in surface waters. Submitted to: *Environmental Modelling and Software*

5.1 Introduction

The European Union (EU) Water Framework Directive (WFD) requires that a 'good ecological status' should be achieved and maintained in all surface water and groundwater (Council of European Commission, 2000). A good ecological status is established by the biological, chemical and hydrological characteristics of the water body. Moreover, EU member states have specific interpretations of what is considered 'good ecological status'. For example in the Netherlands key ecological factors and water system analyses are used as a method to understand ecological water quality processes and to define goals and measures for water bodies. These key ecological factors cover a 'crossing' between human pressures on a water body (e.g. channelization, vegetation maintenance or diffuse pollution) and environmental factors (e.g. temperature regime, substrate variation or nutrient concentration) (STOWA, 2015). Water quality modelling can be used at different spatial and temporal scales to understand relationships between human pressures on a water body and environmental factors as well as enabling discussions amongst stakeholders of potential intervention, management or maintenance strategies. As catchments are complex systems encompassing a vast quantity of processes and components, integrated water quality modelling is currently the preferred choice (Tscheikner-Gratl et al., 2018) for determining the best management practices to address both urban and rural pressures for the improvement of the water body.

Modelling river water quality has generally been conducted using the advection dispersion-reactions approach (which may also include terms for transient storage, biota uptake, groundwater and lateral flows, sediment deposition or uptake). The advection and dispersion processes are usually described within the hydrological/hydrodynamic model and the biochemical and physical conversion processes are described within reactions equations (Rauch et al., 1998). Most surface water quality studies have focused separately on these processes and over various time scales. For instance, solute transport using advection dispersion equations with point source pollution have been widely applied in river systems (Ani et al., 2009; van Mazijk & Veling, 2005; Wallis et al., 2014) and their applications focus on modelling point source discharges over timescales of hours or days. Dissolved oxygen and biochemical models represent the dynamics of reaeration and decomposition of organic matter (Streeter et al., 1925). Important additional oxygen production and consumption processes such as the removal of Biological Oxygen Demand (Dobbins, 1964), oxygen production and uptake due to periphyton biomass (Welch et al., 1989) and the dynamics of nutrient cycling and algae have been incorporated in other water quality models such as the QUAL2 family of models (Brown, 1987) and the River Water Quality Model no. 1 (Shanahan et al., 2001). Moreover, eutrophication models in varying degrees of complexity (e.g. modelling nutrient enrichment due to various processes) can be used over longer time scales to study interactions between macrophytes, phytoplankton and nutrients in the ecosystem. However, to date eutrophication models have been primarily applied to lake systems or to study the nutrient transport to the destination ecosystems such as estuaries or oceans (Nijboer & Verdonschot, 2004).

To obtain a complete physical, chemical and ecological description of the river catchment for ecological status evaluation, integrated modelling approaches covering both urban and rural catchments, have gained popularity over the past years (Holguin-Gonzalez et al., 2013; Mouton et al., 2009). Mouton et al. (2009) used the Water Framework Directive (WFD)-Explorer Toolbox to evaluate the ecological status of the Zwalm River in Belgium. Their study integrated a hydraulic model, with a mass balance module to assess ecological pressures based on expert knowledge. However, the approach oversimplified water quality processes, and had a coarse catchment scale (Holguin-Gonzalez et al., 2013). Holguin-Gonzalez et al. (2013) developed a framework integrating a MIKE 11 hydraulic and physicochemical water quality model with two ecological models based on habitat suitability and ecological assessment with an emphasis on macroinvertebrates. However, the QUAL2E and MIKE11 models lack the ability to represent sediment processes as biological conversions. This disables their capability to model closed nutrient cycles (Trinh Anh et al., 2006) which is beneficial to account for the nutrient ratios at the various trophic levels.

A holistic ‘combined modelling approach’ incorporating the long-term intertwined dynamics of flow, nutrients and aquatic biota and physical and ecological interactions is still lacking in the literature. More specifically, the capability to model closed nutrient cycles, plant competition, organisms, water and sediment processes using an extensive ecological model coupled to a hydrologic and hydrodynamic model is still pending. Therefore, in this study, we adopt such ‘combined modelling approach’ to represent the medium to long-term hydrological processes of a catchment (precipitation, evapotranspiration and runoff), transport and mixing processes from both urban (pollution loadings of CSOs and WWTP) and rural areas, and ecological processes in a slow flowing river system. This combined approach is illustrated in Figure 11 where the three main rainfall-runoff, hydrodynamic and ecological models are shown with their corresponding data requirements. The main objectives of the chapter are: 1) to evaluate the capability of the combined modelling approach to simulate DO for medium to long-term time scales (months to years), 2) to determine the sensitivity of DO model predictions a in the river system given uncertainty in the input boundary conditions, and 3) to determine the dominant oxygen production and consumption processes and their sensitivity to the changes in input boundary conditions. The novelty of this chapter is the combination of a hydrodynamic and ecological model which include urban and rural components and their interactions within the ecological closed nutrients cycles. This can also include the effects of river management practices such as vegetation clearance and dredging. In addition, this methodology can include the effects of nutrient inputs and cycling from rural areas, Combined Sewer Overflows (CSOs) and a Wastewater Treatment Plant (WWTP) on oxygen, nutrient and biota concentrations in the river system. Inclusion of both rural and urban inputs has been recognized as the ideal modelling approach. However, to date, few studies have successfully implemented such methodology (Honti et al., 2017; Tscheikner-Gratl et al., 2018).

The nutrient and vegetation model for ditches PCDitch was used in this study. Originally developed for lakes (PCLake), PCDitch was selected because it is among the most extensive ecosystem models to date which can include the competition for nutrients, light and temperature and can model production by plants, algae, reaeration and oxygen consumption due to different water and sediment processes (Janse, 2005; Trolle et al., 2014). In addition, PCDitch is a dynamic model that describes the dominant biological components in the river using closed nutrient cycles. The closed mass balance approach is implemented through nutrient-to-dry weight ratios. This allows the stoichiometry of organisms to change with trophic level (Mooij et al., 2010). Management practices such as mowing and dredging can also be implemented in PCDitch allowing water managers to identify target measures on specific processes that assist to improve the quality of the river system. However, the capability of PCDitch to simulate ecological conditions in rivers has not been tested, neither has its capability to predict changes in dissolved oxygen (DO) concentration as a by-product of the various biochemical and ecological processes (e.g. mineralization of organic material, respiration and production of macrophytes). For this to be attempted, coupling with rainfall runoff and hydrodynamic models is required.

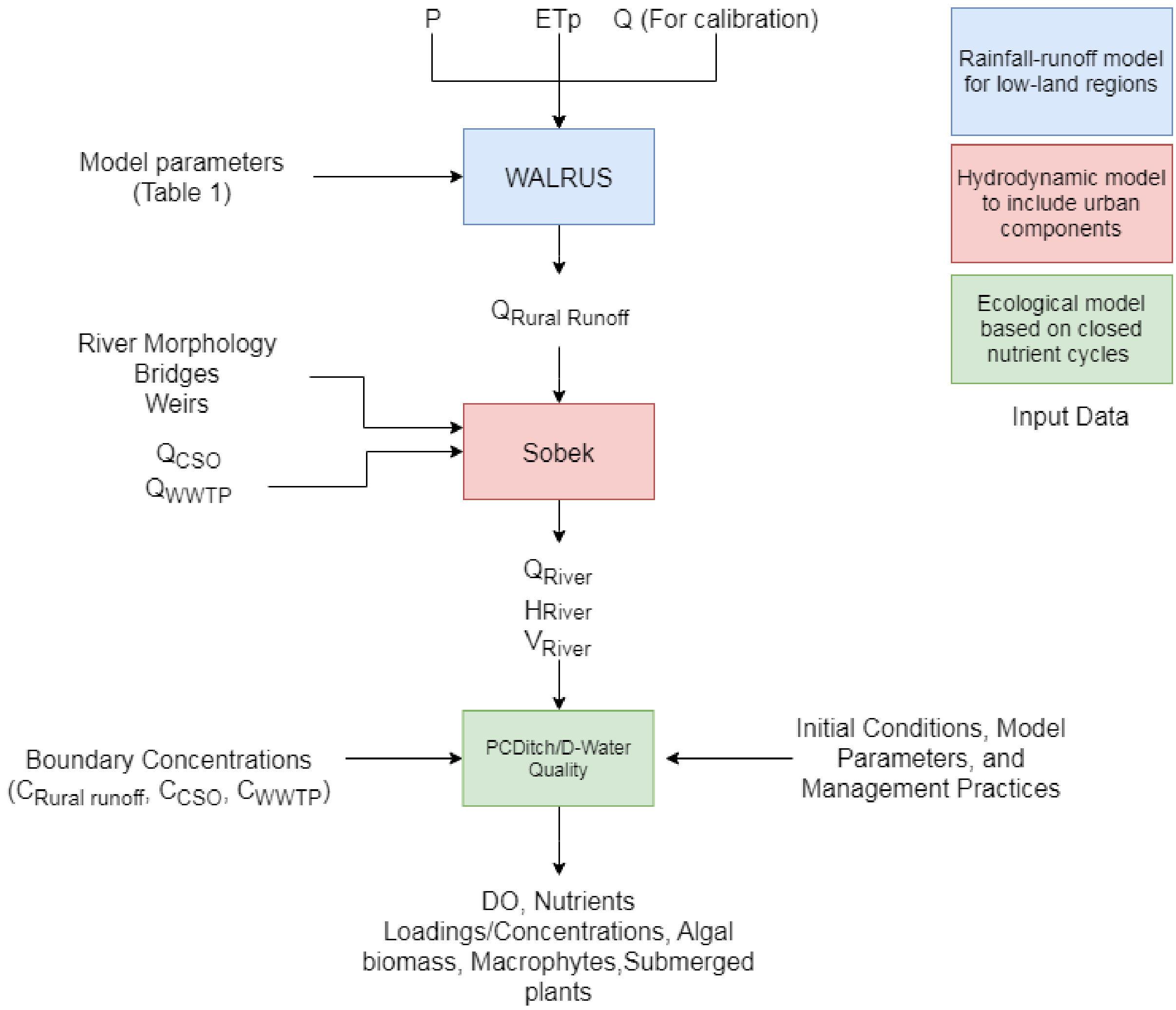

Figure 11. Combined modelling diagram. WALRUS model inputs: precipitation (P), potential evapotranspiration (ETp), river discharge (Q), and model parameters used in calculation of surface and groundwater runoff ($Q_{Rural\ Runoff}$). Sobek inputs: Combined Sewer Overflows discharge (Q_{CSO}), Wastewater Treatment Plant Discharge (Q_{WWTP}), river morphology, and river structures used in calculation of total river discharge (Q_{river}), depth (H_{river}), and velocity (V_{river}). PCDitcht/D-Water Quality inputs: Input boundary concentrations for the rural runoff ($C_{Rural\ Runoff}$), Combined Sewer Overflows (C_{CSO}), and Wastewater Treatment Plant (C_{WWTP}) to calculate DO and ecological variables.

5.2 Methodology

5.2.1 Study Area Description

The Dommel River (shown in Figure 12) flows from the northeast of Belgium to the south of the Netherlands until it joins the Meuse River. The upstream region of the catchment is heavily influenced by agriculture, mainly livestock farming, while the downstream area runs through the city of Eindhoven (Netherlands). The river receives urban discharges from approximately 750,000 P.E. (population equivalent) from the Eindhoven wastewater treatment plant (WWTP) and over 200 CSOs (Weijers et al., 2012). In the summer, the WWTP discharge on the river can account for up to 50% of the Dommel baseflow of 1.5 $m^3 s^{-1}$ (J. G. Langeveld et al., 2013). The geology is dominated by sandy deposits with small amounts of mica, feldspars and clay minerals (Petelet-Giraud et al., 2009). Pollution sources include nitrogen and phosphates leaching from agriculture (mainly manure application) and urban inputs from CSOs and WWTP discharges. Figure 12 shows the main flow contributions to the Dommel River and the locations where measured flow, dissolved oxygen, total nitrogen, and total phosphorus concentrations are available. The flow contributions include surface and groundwater runoff sources which for simplicity in this paper are referred as ‘runoff’, CSOs and the Eindhoven WWTP. These sources are described in more detail in Section 5.2.4.1.

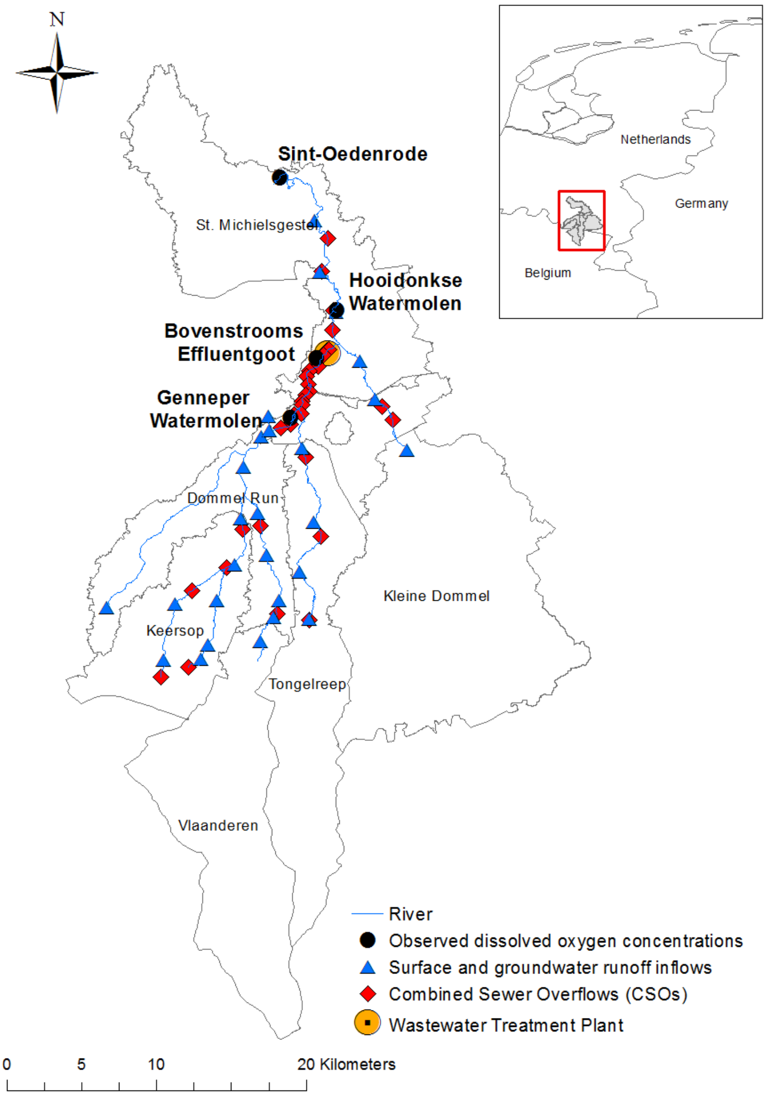

Figure 12. Model schematization and subcatchments of the Dommel River catchment

5.2.2 Rainfall-Runoff Modelling

The study area was divided into six sub catchments (Figure 12). A rainfall-runoff model was created for each sub catchment using the Wageningen Lowland Runoff Simulator (WALRUS) model. WALRUS was selected because of its ability to account for dominant low-land areas processes such as couplings between the groundwater and unsaturated zone, flow routes that depend on wetness conditions, and interactions between groundwater and surface water (Brauer et al., 2014).

The WALRUS model inputs include precipitation and evapotranspiration data. Measured discharge data was used for model calibration. Data was collected from January 1st, 2011 to December 31st, 2013. Hourly precipitation rates were obtained from merged radar and rain gauge data from the Dutch meteorological agency (KNMI) and the Dommel Water Board (Moreno-Ródenas et al., 2017). Daily Penman-Monteith evapotranspiration rates were obtained from the Foundation for Applied Water Research (Stichting Toegepast Onderzoek Waterbeheer) in the Netherlands (STOWA, 2013). Hourly discharge was available for the Keersop, Tongelreep and St. Michielsgestel sub catchments from the Dommel Water Board. The total observed runoff from the Keersop and Tongelreep catchments were separated into its rural and urban runoff components using the sub-flow separation technique suggested by Willems (2009) to account for contributing flows from combined sewer overflows (CSOs). The flow at Sint-Oedenrode (from the St. Michielsgestel sub catchment) was not subdivided into sub flows due to the large contribution of the wastewater treatment plant discharge. Therefore, this sub catchment was not used for calibration of the rainfall-runoff model. The Keersop and Tongelreep sub catchments were used to calibrate the model parameters (Table 4), which was then also applied to the other sub catchments. This calibration was carried out using the swarm optimization technique hydroPSO available in the WALRUS model. The parameters in Table 4 remained constant for the studied catchments including groundwater depths, surface water fractions, quickflow and groundwater reservoir constants and soil properties.

Table 4. WALRUS Model parameters per sub catchment

Parameter	Unit	Abbreviation	Value
Surface water parameter bankfull discharge	(mm h^{-1})	cS	4.0
Initial groundwater depth	(mm)	dG0	1200
Channel depth	(mm)	cD	2750-3250
Surface water area fraction	(-)	aS	0.0090
Soil type	(-)	st	loamy sand
Wetness index parameter	(mm)	cW	400
Vadose zone relation time	(h)	cV	4
Groundwater reservoir constant	(mm h)	cG	30,000,000
Quickflow reservoir constant	(h)	cQ	25

5.2.3 Hydrodynamic Modelling

A SOBEK-River one-dimensional (1D) model was provided by the Dommel Water Board containing the river network shown in Figure 12. SOBEK is based on the 1D Saint Venant equations and utilises the Delft numerical scheme (Deltares, 2014a). This model was used to estimate the spatially distributed hydraulic characteristics of the river network including flow velocities, volumes and discharges. The model schematization includes 1,696 cross sections, 29 runoff inflows (shown as the Surface and Groundwater Runoff inflows), 2 boundary outflows, 27 lateral flows (shown as the CSOs), 146 weirs and 211 bridges and 2018 Connection Nodes with Storage and Lateral Flow. Culverts were removed from the SOBEK model in order to accelerate the simulation and reduce instabilities, this was deemed acceptable as no flooding or culvert surcharge occurred during the simulated period.

The Surface and Groundwater Runoff inflow boundary conditions were implemented in the SOBEK hydrodynamic model from the runoff generated using the WALRUS model. The flows at the outlet of the sub catchments were divided into sub flows according to hydrological areas based on the natural drainage as observed in (J. Langeveld et al., 2013). The 27 clusters of CSOs were included in SOBEK to represent the urban inputs as lateral inflows in the river schematization, containing monitored discharge data with a frequency of every 15 minutes for the three years from Jan 1, 2011 to December 31, 2013. Similarly, hourly WWTP discharge was also included as a lateral inflow for the same period. A flow weir located between the Dommel Run and the Sint-Oedenrode subcatchments represented the flow control during summer (1.5 $m^3 s^{-1}$) and winter (0.75 $m^3 s^{-1}$).

5.2.4 Water Quality Modelling

The model PCDitch was used to simulate the biochemical and ecological components in the river such as dissolved oxygen concentrations, dry organic matter, nutrient concentrations, Secchi depth and biomass coverage. PCDitch is a plant/nutrient based competition model that includes the water column and upper sediment layer incorporating the competition for nutrients from submerged rooted and non-rooted vegetation, floating duckweed, algae, Charophytes, Nymphaeids and Helophytes. Macrophytes groups are limited by light, nutrients and temperature. A more comprehensive description of PCDitch is found in (Janse, 2005).

PCDitch is used in conjunction with the water quality and transport package D-Water Quality (Deltares, 2018). This platform uses the finite volumes method to solve the advection dispersion-reaction equation. Furthermore, the hydrodynamic information (e.g. the river mean water depths, water inflows and retention times) was still retrieved from SOBEK and processed by D-Water Quality/PCDitch. The simulation was carried out for a period of three years from Jan 1st 2011 to Dec 31st 2013. Hourly monitored temperatures were obtained from the Dommel Water Board and implemented in the model. The effects of in river mowing and dredging were included in the model. Mowing was set to twice per year removing 95% of the vegetation and dredging was set yearly with a removal of 1 cm of the bottom bed thickness.

5.2.4.1 Set-up of boundary conditions: Rural runoff, CSOs, WWTP and Connection Nodes

External water quality concentrations were defined in PCDitch for the rural runoff, CSOs, WWTP flow and connection Nodes with Storage and Lateral Flow. Table 5 presents the PCDitch inputs required for each boundary including: the dry weights of detritus (mg DW l^{-1}), inorganic matter and phytoplankton (mg DW l^{-1}), the concentrations of nitrogen in detritus, ammonium, nitrate and phytoplankton (mgN l^{-1}), the concentration of dissolved oxygen (mgO_2 l^{-1}) and the phosphorus concentrations in adsorbed inorganic matter, detritus, phosphate and phytoplankton (mgP l^{-1}). Detritus concentrations were used to describe the total amount of organic matter. Detritus was used because it is the only available parameter in PCDitch to describe organic matter loads. The detritus and inorganic matter concentrations were approximated from the percentage of organic matter (OM) and concentrations of total suspended solids in the water column (TSS). Incoming amounts of phytoplankton were assumed to be negligible from the three external sources since rural runoff, CSO and WWTP outflows usually do not contain phytoplankton, apart from some remnants of biofilm, which are accounted for in the detritus concentrations. The nitrogen and phosphorus amounts in detritus were estimated using the relationships shown in Table 5. Adsorbed phosphorus was estimated as the remainder from subtracting phosphate (PO_4) from total phosphorus (Ptot). Dissolved oxygen (O_2), ammonium (NH_4), nitrate (NO_3) and phosphate (PO_4) concentrations were obtained from collected field measurements by the Water Board. The water quality concentrations from the wastewater treatment plant discharge into the river were simulated. An explanation regarding the WWTP discharge simulation, and the description of the input concentrations for each boundary and how they were obtained is given in the following paragraphs.

Table 5. PCDitch Boundary inputs and their estimation methods. Detritus and inorganic matter are estimated from the Total Suspended Solids (TSS) and Organic Matter percentage (OM). Adsorbed phosphorus is estimated from Total Phosphorus (Ptot)

Parameter	Abbreviation	Units	Estimation method
Detritus in water	*Det*	mgDW l^{-1}	*Physical relation: TSS*OM /100*
Inorganic Matter (IM) in water	*IM*	mgDW l^{-1}	*Physical relation: TSS*(100-OM) /100*
Phytoplankton	*Phyt*	mgDW l^{-1}	*Negligible*
Nitrogen in detritus	*NDet*	mgN l^{-1}	*Standard assumption in PCDitch: Det* 0.025*
Ammonium in water	NH_4	mgN l^{-1}	*Measured, simulated for WWTP*
Nitrate in water	NO_3	mgN l^{-1}	*Measured, simulated for WWTP*
Nitrogen in phytoplankton	*NPhyt*	mgN l^{-1}	*Negligible*
Dissolved oxygen in water	O_2	mgO_2 l^{-1}	*Measured, simulated for WWTP*
Adsorbed phosphorus on IM in water	*PAIM*	mgP l^{-1}	*Physical relation: Ptot -* PO_4*- PDet*
Phosphorus in detritus	*PDet*	mgP l^{-1}	*Standard assumption in PCDitch: Det* 0.0025*
Phosphate in water	PO_4	mgP l^{-1}	*Measured, simulated for WWTP*
Phosphorus in phytoplankton	*PPhyt*	mgP l^{-1}	*Negligible*

Rural runoff water quality characterization

The rural inflows relate to surface and groundwater runoff from agricultural and natural areas. These flows were quantified using the WALRUS model. The mean concentrations in Table 6 were used for the input boundary conditions. Monthly water quality input concentrations were obtained from monitored data provided by the Dommel Water Board for the years 2011 to 2013. These include total nitrogen (TN), ammonium (NH_4), total phosphorus (TP), phosphate (PO_4), dissolved oxygen (O_2) and total suspended solids (TSS). Nitrate concentrations (NO_3) were estimated as half of the total nitrogen concentrations and Kjeldahl nitrogen (Nkj), nitrogen in organic compounds, as the other half. Nitrite was considered negligible. The organic matter content was estimated by subtracting ammonia (NH_4) from Kjeldahl nitrogen and then dividing it by the total nitrogen concentration.

CSOs water quality characterization

Over 200 CSOs discharge on the Dommel River. Probability distributions for CSO pollutant concentrations were estimated from a monitoring campaign (Moens et al., 2009). The CSO concentrations were added as lateral flows with event mean concentrations. These event mean concentrations have shown to give acceptable model results despite the difficulty in capturing the high variability of CSOs water quality parameters (Moreno-Ródenas et al., 2017).

Wastewater treatment plant water quality characterization

The Dommel receives effluent of the central WWTP in Eindhoven. The Eindhoven WWTP is composed by three biological lines (primary clarifier, activated sludge tanks and secondary clarifiers) with a capacity of 26,000 m^3h^{-1} and a bypass storm settling tank with a capacity of 9,000 m^3h^{-1}. A fully detailed ASM2d bio-kinetic model was created to simulate water quality processes in the WWTP (Benedetti et al., 2013). The influent quantity (sewer network - WWTP) was represented using observed data at the boundary connection. This was derived from three magnetic flow sensors located at three influent pressurised pipes. Influent water quality characteristics were estimated using a calibrated empirical influent generator (Langeveld et al., 2017). Effluent hourly series (Jan 01, 2011 to Dec 31, 2013) were derived from a forward uncertainty propagation scheme accounting for uncertainties in the influent water quality and quantity characteristics. This time series of WWTP water quality discharge were generated to include the dynamics of the treated wastewater quality characteristics during wet and dry weather conditions.

5.2.4.2 Scenarios for Sensitivity Analysis

To evaluate the effects of the rural runoff, CSOs and WWTP discharge and nutrient inputs on the dissolved oxygen concentrations, three nutrient levels for each of these boundaries were defined as shown in Table 6. The scenarios were selected based on the total phosphorus concentrations. Phosphorus was used as it is an indicator of eutrophication and commonly assumed to be the limiting growth factor for phytoplankton and macrophytes in oligotrophic to mesotrophic waters (Janse, 2005; Newton & Jarell, 1999). Using the observed and simulated data described in Section 5.2.4.1, the three scenarios (Table 6) were defined for each boundary as follows: 1) a ‘base’ scenario representing average nutrient inputs observed, 2) a ‘high’ scenario representing higher levels of nutrient inputs, and 3) a ‘low’ scenario representing lower levels of nutrient inputs. For the rural runoff base scenario, average observed values of total phosphorus concentrations were found with their corresponding water quality parameters (e.g. NO_3, NH_4, O_2, TSS and PO_4). Similarly, for the high and low scenarios, the maximum and minimum observed values of total phosphorus over the period of analysis (2011-2013) were selected with their corresponding datasets of water quality variables. Several datasets presented at Evers and Schipper (2015) were studied at various locations in the catchment to ensure that outliers in the data were not selected. Also, the selected input data was checked against monitored data from the Dommel River Water Board (2019) to ensure that the input concentrations selected were representative of regular water quality concentrations in the river. For the CSOs, the nature of rainfall driven sewer surcharge events results in skewed water quality distributions, with the mean value not providing a good representation of the water quality impacts on the river. Hence the modes of the water quality distributions were used for determining the water quality concentrations of the base scenario with their corresponding water quality parameters, except for the total suspended solids where monitored data was available from (Brouwer, 2012). The 2.5th and 97.5th and percentiles of the CSO frequency distributions were used for determining the high and low nutrient load scenarios. The WWTP scenarios were selected from a total of 99 samples drawn using a Latin Hypercube sampling scheme to describe the variability of the simulated WWTP output. The 2.5th and 97.5th percentiles were used to determine the low and high scenarios for the WWTP based on total phosphorus with their corresponding water quality parameters (Ptot, Kjeldahl Nitrogen, PO_4, NO_2, NH_4, TSS, and NO_3). Given the large quantity of WWTP data generated using the simulation described in Section 5.2.4.1, the WWTP low, high and base scenarios are given in Appendix B.

Table 6. High, middle and low scenarios of rural runoff and CSO Water Quality concentrations

Parameter		Rural Runoff			CSOs inflows		
		Low scenario	**Base scenario**	**High scenario**	**Low scenario**	**Base scenario**	**High scenario**
Phosphate (PO_4)	mg l^{-1}	0.04	0.05	0.08	0.5	0.8	5.7
Total phosphorus (Ptot)	mg l^{-1}	0.1	0.2	0.3	0.5	2.1	34.6
Chlorophyll-a	µg l^{-1}	30	35	40	0	0	0
Dissolved Oxygen (O_2)	mg l^{-1}	6.3	6.8	4.4	3.4	4.6	6.2
Total nitrogen (Ntot)	mg l^{-1}	2.8	3.6	4.6	4.5	8.0	16.2
Nitrite (NO_2)	mg l^{-1}	0	0	0	0	0	0
Nitrate (NO_3)	mg l^{-1}	1.4	1.8	2.3	0.7	1.2	1.7
Ammonium (NH_4)	mg l^{-1}	0.1	0.6	1.7	1.6	2.2	4.9
Kjeldahl Nitrogen (Nkj)	mg l^{-1}	1.4	1.8	2.3	3.8	4.8	14.5
Total Suspended Solids (TSS)	mg l^{-1}	1	15	50	25.0	298	397.0
Organic Matter (OM)	%	13.0	33.3	48.2	48.9	50.9	59.3

5.3 Results

The hydrological processes and runoff generation quantified using the WALRUS model for the calibrated catchments can be found in Appendix C. The results of the hydrodynamic simulation (flow versus time) can also be found in the Appendix D. The Nash Sutcliffe Coefficient (NSC) was used to determine the goodness of fit of the hydrodynamic simulation results and the observed flows. According to Moriasi et al. (2007), model performance is satisfactory when NSC is greater than 0.5. The NSC values from this study ranged from 0.5 to 0.7 for the Sint-Oedenrode and Keersop subcatchment outlets, and downstream and upstream locations at the Tongelreep catchment. In the following sections, the results of the integration of the hydrological, hydrodynamic and ecological processes is shown by presenting first the evaluation of the combined modelling approach to assess its ability to simulate DO (Section 5.3.1), followed by the sensitivity of DO to various nutrient input scenarios (Section 5.3.2) and the decomposition of the dominant oxygen consumption and production processes along with the sensitivity of these processes to changes in input boundary conditions (Section 5.3.3).

5.3.1 Evaluation of combined modelling approach

Figure 13 shows the simulated and observed DO concentrations at the four studied locations versus time. The Percent bias (PBIAS) and the Root Mean Square Error (RMSE) shown also in Figure 13 were used to give an indication of the match between observed and simulated DO concentrations. The PBIAS and RMSE equations are shown below:

Equation 13

$$PBIAS = \frac{\sum_{i=1}^{n}\left(Y_i^{Obs} - Y_i^{Sim}\right) * 100}{\sum_{i=1}^{n} Y_i^{Obs}}$$

Equation 14

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(Y_i^{Sim} - Y_i^{Obs}\right)^2}$$

Where Y_i^{Obs} and Y_i^{Sim} are the observed and simulated daily average DO concentrations respectively. The PBIAS assists in determining whether the model has a positive or negative bias. Positive values indicate underestimation, negative PBIAS indicate overestimation and zero PBIAS indicates a perfect match (Moriasi et al., 2007). Sint-Oedenrode and Hooidonkse Watermolen have negative PBIAS, showing that the model is slightly over-predicting, while

Bovenstrooms Effluentgoot and Genneper Watermolen have positive PBIAS indicating under-prediction. The RMSE compares simulated and observed data and expresses the spread in $Y_i^{Sim} - Y_i^{Obs}$. The largest RMSE was obtained at Hooidonkse Watermolen while the smallest RMSE was obtained at Genneper Watermolen.

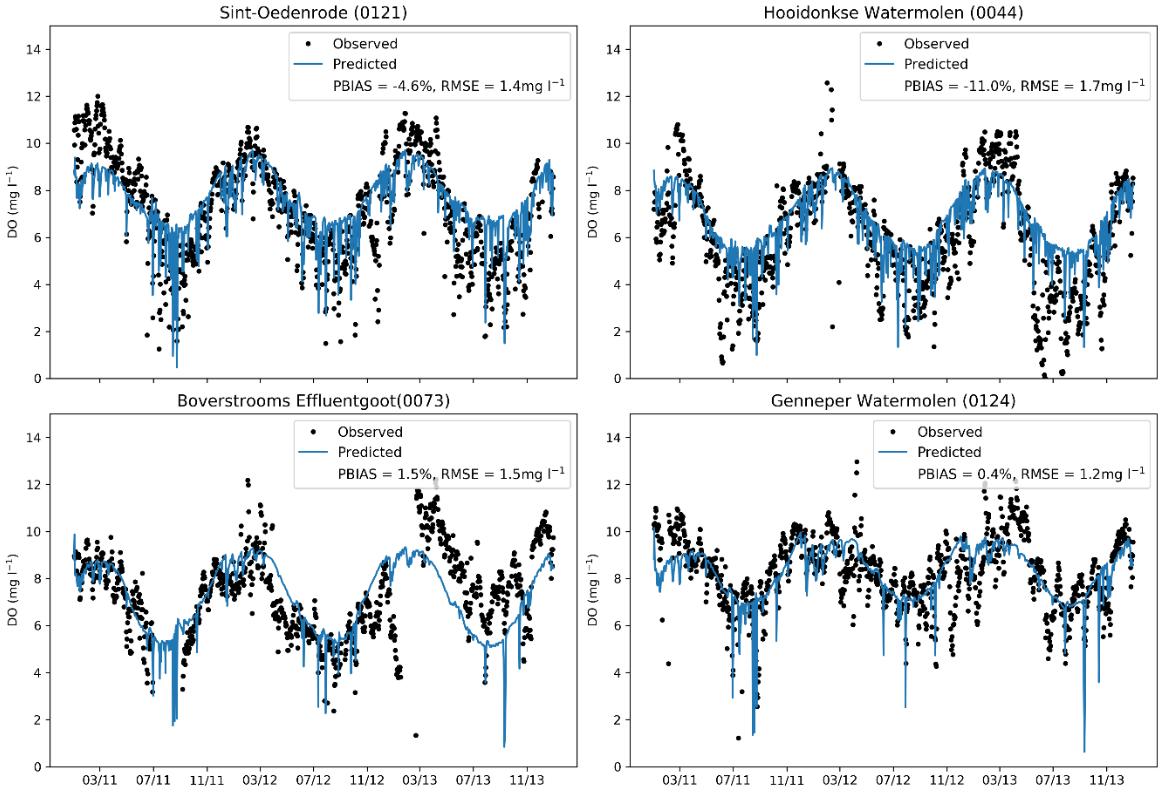

Figure 13. Simulated and observed dissolved oxygen concentrations versus time at various locations in the Dommel catchment (daily average)

Figure 14 shows the empirical cumulative distribution functions (ECFD) for the errors between the observed and predicted DO concentrations. Overall, there is a good match between simulated and observed concentrations. 83.9%, 87.9%, 71.1% and 84.2% of Sint-Oedenrode, Hooidonkse Watermolen, Bovenstrooms Effluentgoot and Genneper Watermolen predicted values were less than 1mg l^{-1} of the observed values, respectively. The largest differences between simulated and observed concentrations are observed in the recovery period following the DO falls from CSO events. This is shown by Figure 14 where EFCDs have longer tales towards the negative values. The observed DO concentrations at the Bovenstrooms Effluentgoot location after March 2013 systematically increased, potentially due to a monitoring error. These results suggest that the ‘combined modelling approach’ (referred as ‘the model’ for simplicity) can visually match the observed seasonal dynamics of dissolved oxygen. However whilst the DO falls (due to oxygen depletion from CSO events) can be observed, their recovery is not fully captured by the model.

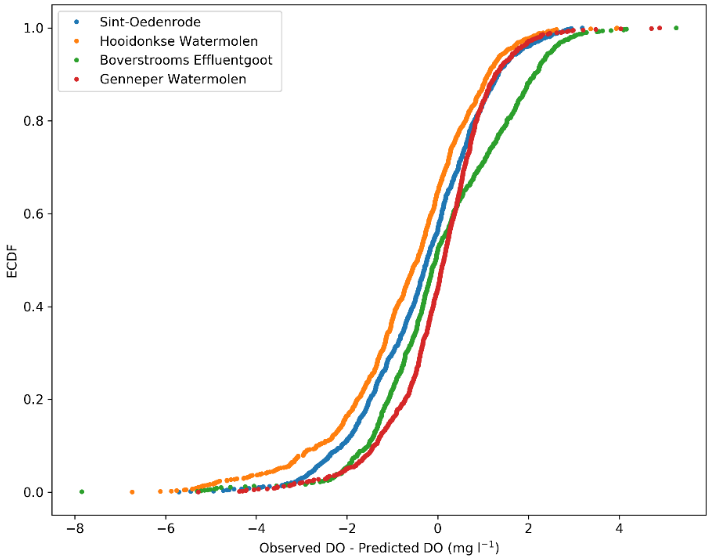

Figure 14. Empirical Cumulative Distribution Function (ECDF) of the difference between observed and predicted DO values.

5.3.2 Input Boundaries Sensitivity Analysis on Dissolved Oxygen Concentrations

The flow contributions from the boundary conditions (Rural runoff, CSOs, WWTP) are shown in Figure 15. It is important to note that Figure 15 does not show a hydrograph separation. It displays the precipitation as the average catchment precipitation, the total modelled flow at the outlet (Sint-Oedenrode), the sum of the surface and groundwater rural runoff inflows, the WWTP outflow into the Dommel upstream of the Bovenstrooms Effluentgoot sampling location, and the CSOs discharge inputs at various locations within the catchment. Figure 15 shows that the largest contribution of base flow arises from the rural inflows. These flows which are the main water inflow of the Dommel river are formed of fast surface runoff (activated during and after rainfall events) and slow groundwater baseflow. The next largest contributor of flow is the WWTP which has a constant base discharge of approximately 1.5 m^3s^{-1}. The WWTP has an overflow bypass storm settling tank which is activated during rainfall events, contributing additional flow to the river during and after rainfall events. The CSOs are significant contributors during precipitation events.

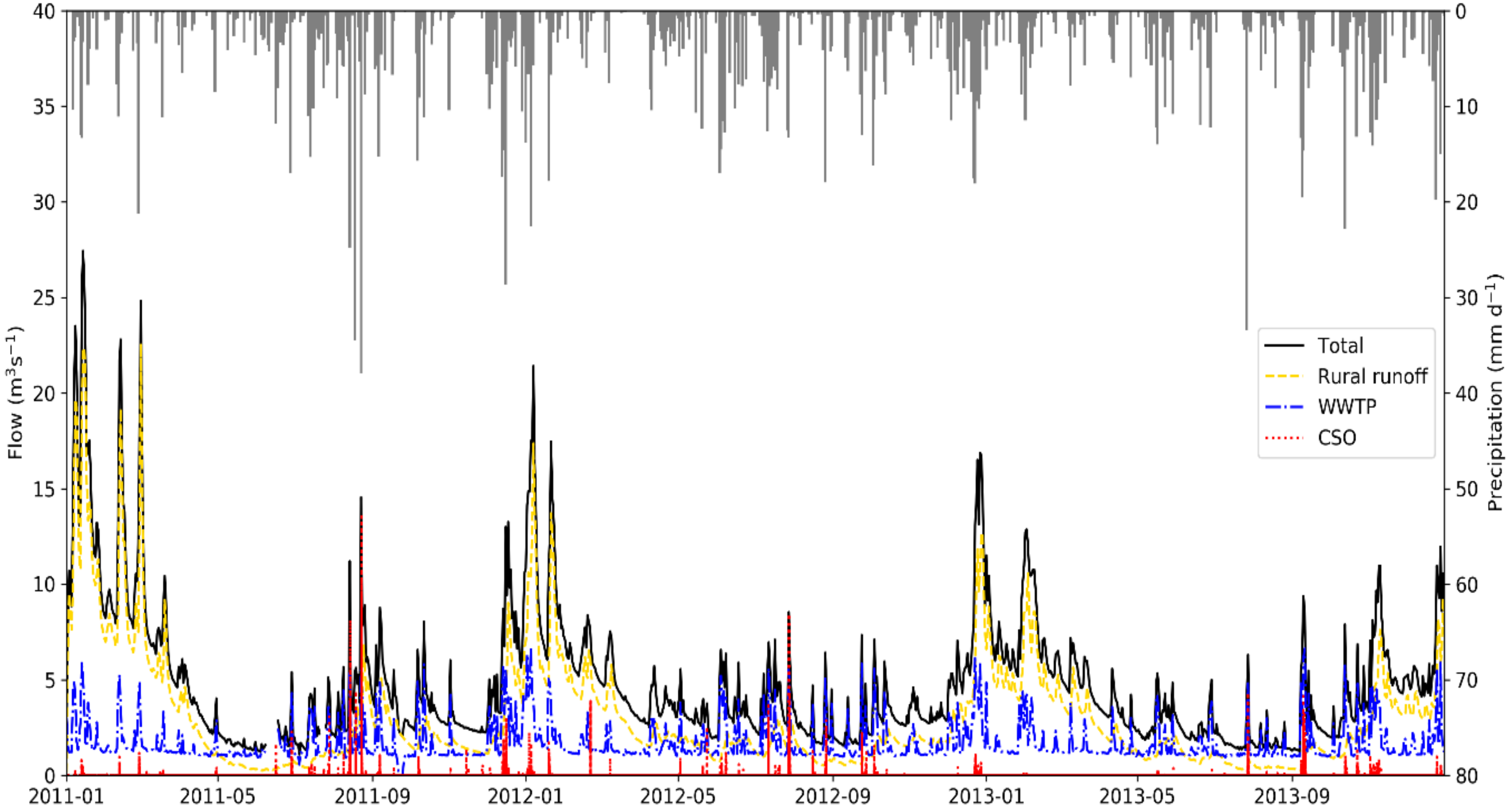

Figure 15. Daily flow average contributions in the River Dommel and Precipitation versus time

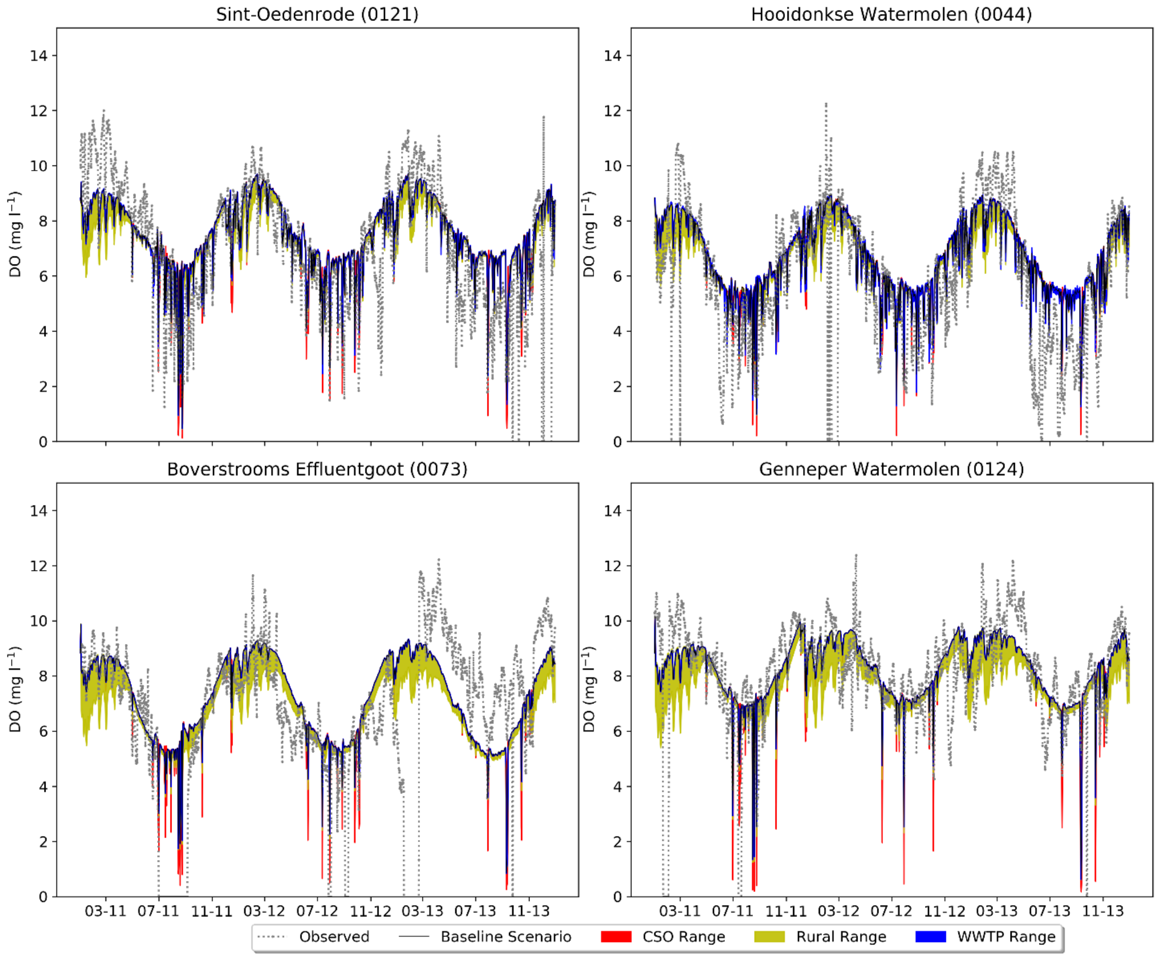

Figure 16. Sensitivity analysis results versus time

The sensitivity analysis results are shown in Figure 16. The baseline scenario represents the 'base' nutrient concentrations for the rural runoff, CSOs, and WWTP. The input concentrations for the rural and CSOs are shown in Table 6. The yellow, red, and blue areas display the ranges between the selected 'high' and 'low' scenarios of rural runoff, CSOs, and WWTP concentration levels, respectively. The seasonal influence of the rural runoff is observed in Figure 16 were the rural flows have a higher influence over the winter months. This effect is more noticeable in the upstream locations (Boverstrooms and Genneper Watermolen) where the catchment is less urbanized. Most of the connected urban area is located in the downstream sections at the Eindhoven city. The influence of the CSOs is visible during precipitation events. The short-term CSO effects are expected since these occur due to excess of drainage capacity during rainfall events. Moreover, the oxygen depletion occurrences due to the CSOs have severe acute effects on the river ecology. The high and low scenarios of WWTP input concentrations have the lowest impact over the DO concentrations as noted by the WWTP blue range which is narrower for the Boverstrooms and Genneper Watermolen locations than the

Sint-Oedenrode and Hooidonkse Watermolen locations. The first two do not receive flow from the WWTP.

5.3.3 Dominant Processes in Oxygen Production and Consumption

The sources and sinks of dissolved oxygen (DO) in the Dommel River at Sint-Oedenrode are shown in Figure 17 and Figure 18. These illustrate the daily production and consumption of DO for the simulated period from 2011 to 2013. The sum of these processes results in the daily concentration contribution that was produced or consumed. In addition, Figure 17 and Figure 18 show the ranges of concentrations obtained when the low and high scenarios of boundary conditions are analysed. The yellow, red and blue correspond to the low-high ranges for the rural, CSOs and WWTP respectively.

Figure 17 reveals that aeration is the main source of DO, followed by the production of oxygen by phytoplankton, and macrophytes production. The contribution of DO from aeration is higher than the contribution of DO from macrophytes production and production by NO_3 uptake by macrophytes by several orders of magnitude. Aeration remains fairly constant throughout the simulation except for when CSOs occur when aeration may increase up to 7 mg $l^{-1}d^{-1}$. This is expected due to turbulent flows entering the river from the CSOs during and after rainfall events.

Figure 18 shows that the dominant consumption processes consist of mineralization and nitrification of detritus (in water and the sediment) and respiration of macrophytes and phytoplankton. The dominant consumption process observed in Figure 18 is the mineralization of detritus in water, followed by the nitrification of detritus in water. Higher mineralization processes are expected in the Dommel due to the high organic loads coming from both rural runoff and CSOs.

The macrophytes processes of production and NO_3 uptake display a seasonal pattern in which vegetation suddenly increases during the spring/summer. However, the effect of mowing is highly noticeable by the sudden drop in production and NO_3 uptake on June 1st of each studied year (when mowing occurs). After mowing, the remaining vegetation starts to increase again until winter arrives, and the vegetation reduces once again. Moreover, the peaks of macrophytes production and NO_3 uptake, and dips in macrophytes respiration become progressively smaller over the three years that were simulated, indicating that with the current simulated mowing regime the vegetation appears to be incapable of fully recovering after mowing.

The sensitivity of the system to changes in input boundary conditions (low and high levels of nutrient scenarios) is visible in Figure 17 and Figure 18. The rural runoff (yellow range) has a constant impact over aeration throughout the studied time, while the CSOs (red range) have specific impacts on aeration, which are evident by the aeration spikes that occur during and after precipitation events. The macrophytes processes are more sensitive to CSOs impacts than the other boundary conditions. This is expected to be due to the organic loads within CSOs. Although CSOs occur at daily or sub-daily timescales, the organic loads remain in the system and decompose throughout time, reducing the oxygen available for vegetation. Mineralization and nitrification processes are sensitive to all boundaries. Particularly, rural nutrient input is constantly reflected in nitrification. In addition, sudden drops in nitrification are also noticeable due to WWTP input.

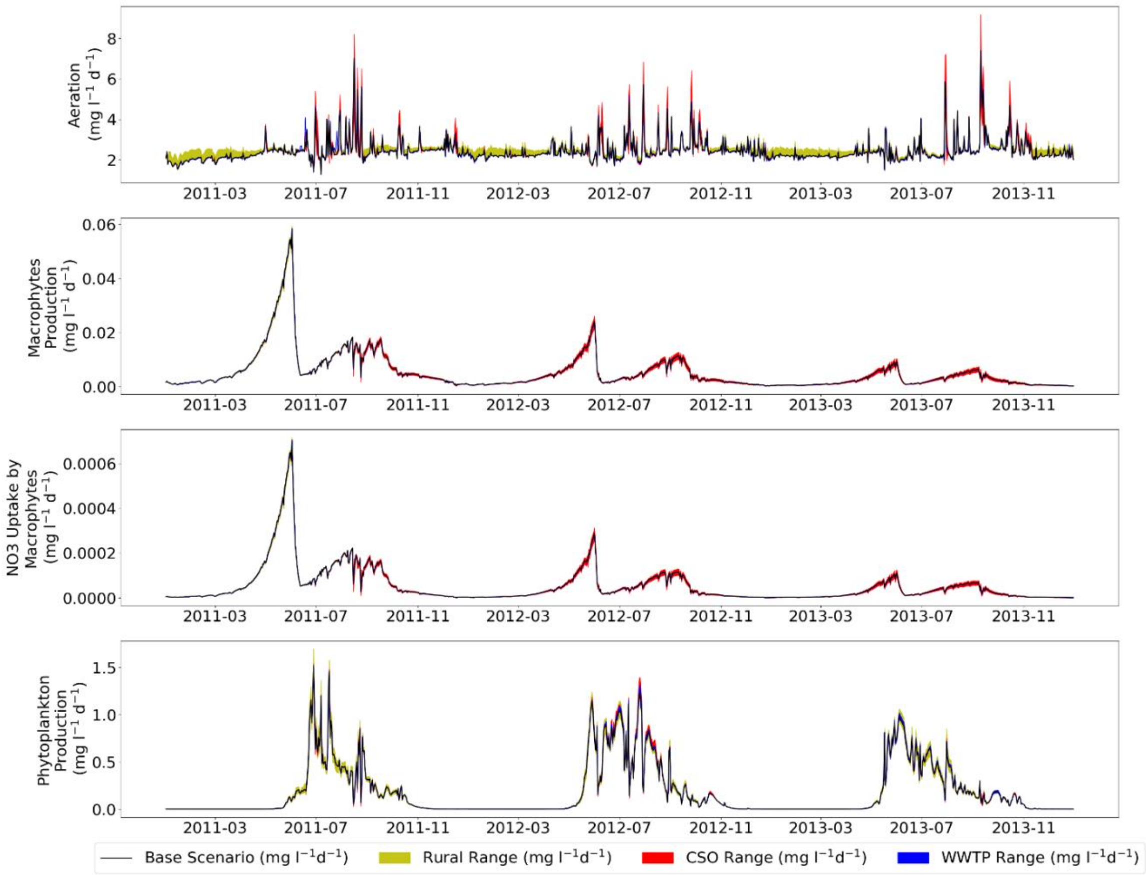

Figure 17. Dissolved Oxygen production processes versus time and sensitivity of boundary input scenarios

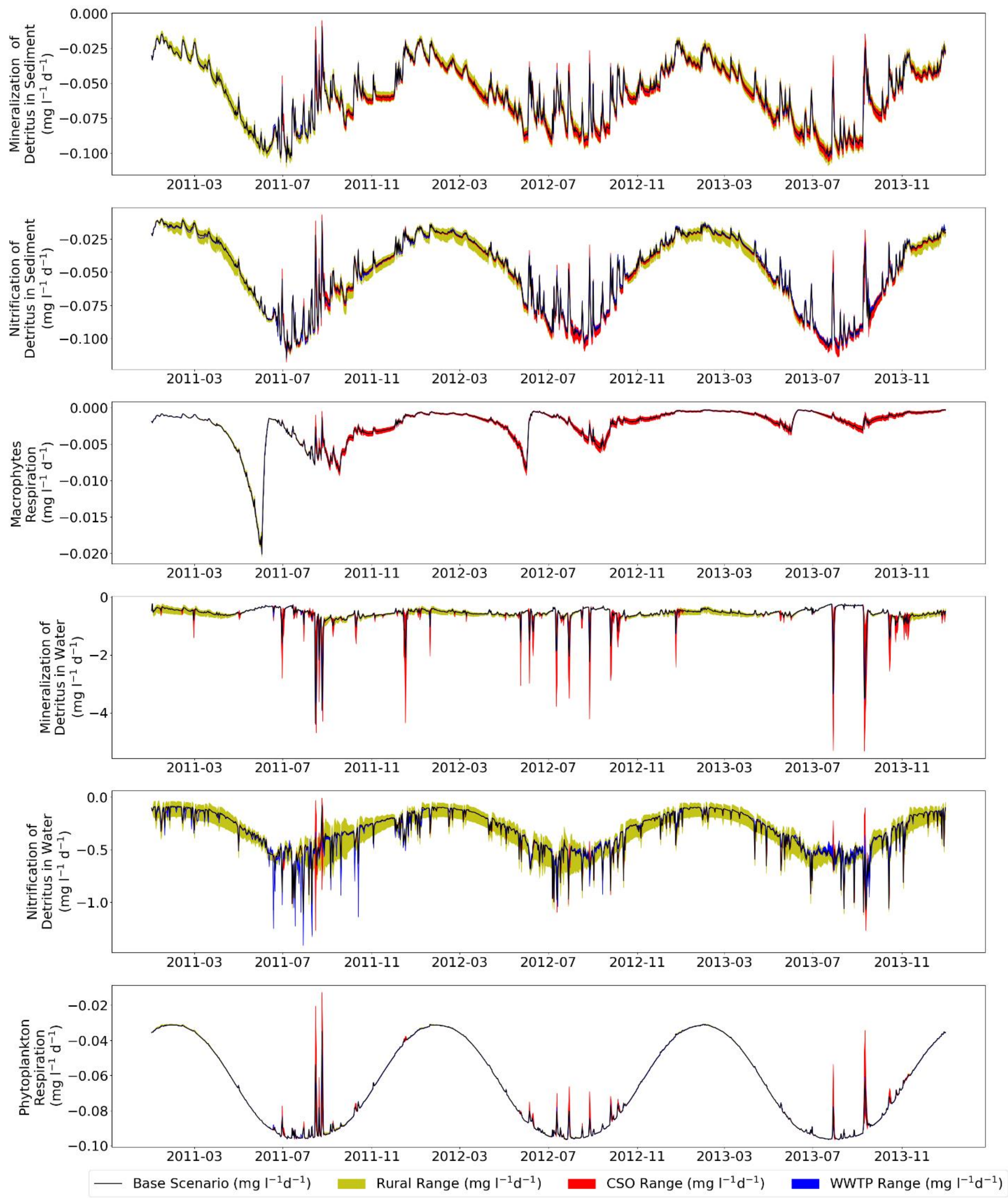

Figure 18. Dissolved Oxygen consumption processes versus time and sensitivity of boundary input scenarios

5.4 Discussion

This study combined a rainfall-runoff model, hydrodynamic model and closed-nutrient cycle model to simulate DO concentrations for the Dommel River, and their sensitivity to low and high scenarios of nutrient inputs. In addition, the oxygen decomposition into the production and consumption processes was carried out along with the sensitivity of these processes to changes in nutrient levels.

The first aim of the paper, to evaluate the combined modelling approach (from now on referred to as 'the model'), demonstrated that the methodology can be used to simulate the seasonal dynamics of DO. The DO concentrations were the highest during the winter months and lowest during the summer months. The model matches this winter/summer dynamic with low values of Root Mean Square Errors ranging from 1.2 to 1.7 mg l^{-1}, and PBIAS values ranging from -11.0% to 1.5% despite some measurement errors in the observed data (Figure 13). Accurately estimating the seasonal behaviour is necessary when evaluating the long-term effects of eutrophication. The model, however, is not as suitable for simulating the short-term dynamics of DO since it cannot fully capture the DO depletion and recovery events (Figure 13). This is partly due to the time step of the ecological model PCDitch, which has a daily time resolution. The lack of representation of these DO falls and their recovery might also be due to the absence of slow degradation of organic matter. Moreover, this modelling approach can be coupled with a higher temporal resolution DO model to simulate shorter periods if this is the main interest or purpose of the user thus providing boundary conditions for higher temporal resolution models. For instance, Moreno-Rodenas et al. (2017) carried out an integrated catchment modelling study in the Dommel River. With a focus on determining the impact of the spatiotemporal effects of rainfall variability, they evaluated the dissolved oxygen concentrations in the Dommel River. Their Integrated Catchment Model (ICM) included a rainfall-runoff model that was complemented with the urban components of CSOs and the WWTP and a water quality module. The processes of fractionation of Biological Oxygen Demand, respiration from macrophytes and nitrification-denitrification were included in the water quality module in a three-phase layout module to account for the atmosphere-water-sediment interactions. In contrast to the study presented in this paper, Moreno-Rodenas et al. (2017) focused on shorter time scales studying particular rainfall events. These allowed the better understanding of the dynamics of the CSOs, and the WWTP in response to the precipitation events. However, such models require more computational resources for a long-term eutrophication study evaluation, have a reduced representation of the modelling system (by integrating less ecological processes and components), and do not provide insights regarding the ecological processes involving the aquatic biota.

The sensitivity of the DO concentrations, and the DO consumption and production processes in response to changes in nutrient levels at the boundary conditions was analysed (Figure 16, Figure 17 and Figure 18). The varing influence of the rural runoff over the year is noted in Figure 16, with rural impacts being dominant during winter months. This is in contrast to the influence of CSOs, which are significant during shorter-term rainfall events. Both, short and long-term effects have consequences over the river habitat. The short-term DO depletion caused by the CSOs may have acute effects (lethal for fish/macro fauna) while the while seasonal lowering of oxygen concentration affects the habitat, meaning that oxygen sensitive species will not be abundant in the river basin. The discharge of the WWTP flow in the river appears to have a smaller impact over the DO concentrations at the Hooidonkse Watermolen and Sint-Oedenrode locations, even though the WWTP is a major contributor of flow to the river system (Figure 15).

Figure 17 and Figure 18 illustrate how the sources and sinks of DO behave seasonally and in response to the changes in boundary conditions. The decomposition of dissolved oxygen processes shows that aeration is the main source of DO into the river system with values ranging from 1.5 to 7 mg l^{-1}. Aeration is also sensitive to changes in the boundary conditions of rural runoff and CSOs. When organic loads from both rural runoff and CSO's, enter the water system, water depth is affected, causing increased flows and turbulence in the system which will lead to spikes in aeration.

Figure 18 shows the influence of the rural runoff and the CSOs over the mineralization and nitrification of detritus in the water and also in the sediment. This is due to the inflow of suspended solids contributing to both, organic and inorganic matter into the system. Most of the organic matter in the system will settle into the sediment and decompose contributing to the mineralization and nitrification processes. The mineralization of detritus in the water column is sensitive to the CSO events resulting in spikes of DO depletion. The wastewater treatment plant mainly affects the nitrification processes in the water column by the WWTP discharges of ammonium in the water system. The remaining organic matter mainly consists of humidic acids, which are slowly to not degradable and do not cause a significant and direct oxygen demand in the water column. These interactions between nutrient inputs and oxygen processes show that the system, already loaded by high organic matter content, is likely to tip on to a low oxygen state as observed in a study by Veraart et al. (2011).

Vegetation is significantly affected by mowing. The sharp decrease in macrophytes production in Figure 17 is due to mowing every June 1st. Consequently, the vegetation recovers over the summer but dies during the winter months. It is noted that this particular mowing scenario is removing more vegetation faster than the system can replenish itself. This effect is also visible for the macrophytes respiration and NO_3 uptake. This supports the view that vegetation management strategies can have a substantial effect on water quality and ecological function in river systems. The modelling approach also showed that vegetation is sensitive to CSO events (Figure 17 and Figure 18). A constant influence of the CSOs is noted over the macrophytes DO production.

Overall, the advantages of using PCDitch over other water quality models is noted by this study where the decomposition of dissolved oxygen process and the sensitivity analysis of the boundary inputs revealed critical interactions such as the importance of the CSOs over vegetation, the influence of rural runoff and the WWTP discharge on nitrification, and the sensitivity of the system to the removal of vegetation. This modelling approach is capable of providing an overview of the river processes due to its ability to include the various ecological processes such as the competition of vegetation for nutrient, lights, and temperature. Other models, for instance the Charisma model (van Nes et al., 2003), are also able to model the competition of plants. However, only two types of submerged vegetation are included in the Charisma model (McCann, 2016) while PCDitch incorporates six types of aquatic vegetation. Capturing such vegetation density and its relationship to flow dynamics has been recognized to assist in assessing the ecological quality of the water system (Kuipers et al., 2016), and this is attainable with this modelling approach by coupling the hydrodynamic and ecological models. Furthermore, PCDitch describes the relation between external nutrient loadings, nutrient concentrations and the dynamics of the different types of vegetation (submerged plants, algae, duckweed and helophytes).

5.5 Conclusion

This work evaluates a combined modelling approach to describe hydrologic, hydrodynamic and ecological processes within a catchment in order to provide a holistic view of a river system and its sensitivity to both urban and rural inputs. Such integrated approach is crucial for the full assessment of the catchment and implementation of management measures in response to human pressures. In this study, the modelling approach is evaluated based on a rural and urban catchment (the Dommel River catchment). Precipitation evaporation, and runoff inputs were modelled using a rainfall-runoff modelled designed for low-land areas, followed by the hydrodynamic simulation which included CSOs, the Eindhoven treatment plant and other urban components. The novelty of this study lies in the successful implementation of the extensive closed-nutrients cycle model to the slow flowing river highly impacted by urbanization and rural inputs. PCDitch, which was initially developed for ditches, was used to model DO concentrations for the first time. In addition, this paper studies the decomposition of oxygen processes into production and consumption processes and their sensitivity to low and high levels of nutrient inputs from the different boundaries given mowing and dredging in the river system.

This study found that the seasonal pattern of dissolved oxygen can be well simulated with the combined modelling approach, although some shortcomings are identified when modelling DO recovery following CSO events. Secondly, the sensitivity of the dissolved oxygen processes to changes in nutrient high and low levels from the boundary conditions showed that DO levels are influenced by rural runoff mainly during the winter months. This influence is more notorious in the upstream locations. In addition, it was observed that the CSOs have short-term impacts over DO during and after precipitation events. Thirdly, the separation of oxygen processes into the production and consumption processes and sensitivity analysis revealed: i) a continuous influence of the CSOs input concentrations on the vegetation processes of production, respiration and NO_3 uptake, ii) an influence of rural runoff over nitrification and mineralization processes, iii) a sharp impact of mowing on vegetation processes, and iv) an intermittent effect of the WWTP on mineralization during and after precipitation events.

The model structure of PCDitch using closed nutrient cycles allows for a better understanding of the nutrient dynamics within the ecological habitat allowing the study of important ecological processes affecting the production and degradation of oxygen while implementing vegetation and dredging management practices. This allows for a deeper consideration of such important processes into river management strategies than is currently possible.

These findings are an illustration of the knowledge that can be gained from a modelling approach that incorporated both hydrological, hydrodynamic and detailed ecological processes. With such understanding, specific urban or rural management measures may be more fully considered to improve the overall health of the river system.

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6. Importance of longitudinal dispersion uncertainty in water quality models used for Water Framework Directive (WFD) implementations

This chapter addresses the thesis objective 3, associated with evaluating the impacts of using simple and complex model structures on water quality modelling and duration over threshold analysis. Further assessment is made regarding the scales where longitudinal mixing leads to uncertainty over FIS regulation

6.1 Introduction

The European Union Water Framework Directive (WFD) requires that a holistic approach is taken to evaluate the ecological status of water bodies (European Commission, 2000). This requires a comprehensive understanding of human and natural pressures on aquatic ecosystems. In the United Kingdom, the Fundamental Intermittent Standards (FIS) are used to protect surface water from wet weather discharges as stated in Section 2.3. These Fundamental Intermittent Standards (FIS) are applied to dissolved oxygen (DO) and un-ionised ammonia for specific duration thresholds and for a range of return periods (1 month, 3 months, and 1 year) during wet weather conditions (Foundation for Research, 2012).

Mathematical models are efficient tools for assisting in gaining an overall understanding of the complex dynamics of catchments, providing information in instances were field data collection is not feasible, and predicting the responses of ecosystems to the implementation of measures for the improvement of water resources (Hartnett et al., 2007). The accurate estimation of dispersion processes is key in water quality modelling for the proper estimation of water quality variables (Velísková et al., 2019; Zeng & Huai, 2014). Two-dimensional (2D) models have been proven superior in modelling mixing processes due to their ability to capture the stream-wise variation of the transverse mixing (Baek & Seo, 2016). Seo et al. (2016) studied the river Sum (2.5km reach and varying width between 20m and 77m) in South Korea using a finite element-based model which included the depth-averaged shallow water model, 2D Hydro Dynamic Model (HDM-2D). Their findings revealed a good match between observations and model predictions at locations where secondary currents were negligible. However, 2D models require additional data, thus they are more costly and computationally demanding, particularly at the catchment scale. As a result, water quality practitioners may resort to less complex models such as the advection-only or the one-dimensional advection dispersion equation (1D ADE) model.

Advection-only models are not capable of representing dispersion processes since these models can only transport the pollutant due to the movement of the flow parcel. Despite this, advection-only models such as the SIMulation of CATchments (SIMCAT) model have been widely applied in the United Kingdom for catchment management and evaluation of compliance with the Water Framework Directive (Hankin et al., 2016). The SIMCAT model, created by the Water Research Centre (WRc), is used by the UK Environmental Agency. SIMCAT conceptualizes the river as continuous stirred-tank reactors with perfectly and instantaneously mixed sections (Cox, 2003b; Kayode, 2018). Crabtree et al. (2009) illustrate how SIMCAT was used to support decision making for the River Ribble Catchment in the UK. In their study, they assessed 80 catchment scenarios for the implementation of Programmes of Measures (PoMs) to reduce diffuse pollution and evaluate water industry management options. SIMCAT is still the preferred choice within the River Quality Planning (RQP) software suite by the UK's Environment Agency to evaluate single discharges into a watercourse (Foundation of Water Research, 2014). SIMPOL ICM is another simplified urban pollution model that assists water companies to assess the pollutant loads and investigate the impacts of human pressures on watercourses (Water Research Centre, 2012). SIMPOL represents key urban processes by using surface, sewer, and CSO tanks connected together. Dempsey et al. (1997) used SIMPOL to evaluate the upgrade of the drainage system of an urban area serving approximately 220,000 people in response to extreme rainfall events. Predicted Biological Oxygen Demand and un-ionised ammonia concentrations in the river were evaluated for compliance with water quality standards (Dempsey et al., 1997).

One-dimensional advection dispersion models (1D ADE) have been popular as shown in Section 2.2.4 for estimating water quality variables and are widely implemented in commercial software such as Infoworks ICM (Innovyze, 2017) the D-Water Quality Suite (Deltares, 2018) and MIKE11 (DHI, 2017). These models typically use empirical formulations for the estimation of longitudinal dispersion. For instance, Infoworks ICM estimates dispersion as a result of the shear velocity and the river width (Innovyze, 2017). MIKE11 can include estimates of dispersion coefficient using the mean flow velocity, and suggests to use dispersion coefficients of 1-5 $m^2 s^{-1}$ for small streams and 5-20 $m^2 s^{-1}$ for rivers, but the default setting of dispersion coefficient is 0 $m^2 s^{-1}$ (i.e. advection only) (DHI, 2017). Additional information of commercial software is provided in Appendix A, and examples of the use of commercial software for evaluation of water regulation compliance are provided in Section 2.2.4.

As pointed out in Chapter 4, the use of empirical equations for estimating dispersion potentially leads to large uncertainty intervals in water quality concentrations and estimations of durations that the pollutants exceeded a water quality threshold. Another deficiency of the 1D ADE is its inability to reproduce the observed skewness in pollutant concentration profiles (van Mazijk & Veling, 2005). This skewness has been attributed to several reasons including the effects of vertical and transverse shear velocities over turbulent diffusion (more dominant in the advective zone) (Schmalle & Rehmann, 2014) and trapping areas and zones of hyporheic exchange where pollutant mass is stored and slowly released (Nordin & Troutman, 1980; Zaramella et al., 2016).

In order to include the effects of pollutant exchange with storage and hyporheic zones, transient storage models, which include a first order mass exchange mechanism between the main flow and the storage areas were proposed (Bencala & Walters, 1983; Zaramella et al., 2016). The Aggregated Dead Zone model was introduced conceptualizing the river as an imperfect mixed reach dominated first by advection and then by dispersion (Lees et al., 2000). Moreover, transient storage models have been further developed and improved over the years. Some examples include the Continuous Time Random Walk model (CTRW) introduced by Boano et al. (2007), the Multi Rate Mass Transfer model (MRMT) (Haggerty et al., 2002) and the Solute transport in rivers (STIR) model by Marion et al. (2008).

Although there is evidence that simpler models potentially lead to larger sources of uncertainty (Blumensaat et al., 2014), simpler models can still resemble experimental data when modelling urban effects on receiving water bodies. G. Mannina and G. Viviani (2010b) compared the differences between a more complex Saint-Venant equations along with 1D advection-dispersion approach to a simplified reservoir model approach. Both methodologies lead to a good fit to the experimental data. However, the simpler reservoir model lead to larger uncertainty intervals than the more complex model. Nevertheless, simpler models (e.g. nutrient export coefficient or regression models) can be used for an overall characterization of nutrient loads in the catchment, and assessing the risk that the water body may fail to meet the WFD requirements (Hartnett et al., 2007).

Moreover, a disconnection between researchers and practitioners still exists when applying appropriate water solutions to freshwater systems (Brown et al., 2010). Water quality practitioners and modellers are still limited by insufficient input data (Rode et al., 2010) that are often required by more complex models. Another challenge raised by UK water practitioners is the lack of scientific knowledge of biological, physical and socio-economic processes required for the proper management of freshwater ecosystems (Brown et al., 2010). This example illustrates the timeliness of understanding the impact of utilising complex and simple water quality models on predicted river water quality variables and implications on water regulation evaluation, as well as, the need for practical studies that look into uncertainty in the light of water quality regulation.

This chapter studies the impacts of uncertainty in the dispersion coefficient on modelled water quality concentrations and regulation when the Fundamental Intermittent Standards are applied. Two types of modelling approaches are studied: 1) a complex integrated water quality modelling approach, and 2) simpler pollutant transport models. The first study introduced in Chapter 5 focuses on the integrated water quality model of the Dommel River that is highly influenced by diffuse pollution, a wastewater treatment plant and combined sewer overflows. The second case study focuses on point source pollution from CSO discharges in the UK where simpler but widely used pollutant transport models are used to describe the trajectory of pollution along the stream reach. This analysis addresses the questions of the impact of structural uncertainty on water quality concentrations and the impact on water quality regulation.

6.2 Impact of dispersion uncertainty on water quality concentrations in an integrated water quality model

This section evaluates the impact of diffuse nutrients (e.g. nitrates and phosphorus) originating from agricultural rural runoff on the predicted river Dissolved Oxygen (DO) concentrations. The Dommel River (described in Section 5.2.1) is highly impacted by agricultural runoff at the upstream regions of the catchment and urban discharges (CSOs and a wastewater treatment plant) at the downstream region.

Using the integrated water quality modelling approach described in Sections 5.2.2, 5.2.3, and 5.2.4, the sensitivity of the modelled DO concentrations to changes in dispersion coefficients was analysed. To represent the longitudinal dispersion for the Dommel Case Study, a linear relationship of the concentration gradient between the river segments was implemented as this is one of the user options within the Delwaq/PCDitch interface (the concentrations at each river segment are obtained from the pollutant load over the segment volume) (Deltares, 2014b). Moreover, the calculated model dispersion resulted in a zero dispersion coefficient. This indicates that in the Dommel River, the concentration gradients are negligible representing a network of fully mixed river segments. This is potentially because the mixing processes within the river are only significant at sub-daily time scales. In order to check this assumption, the effect of dispersion has been further evaluated on the Dissolved Oxygen (DO) concentrations by setting a constant longitudinal dispersion coefficient for the river network as shown in (Figure 19) where a set dispersion coefficient of 8.1 m^2s^{-1} was implemented. This dispersion coefficient was obtained using Deng et al. (2001) equation and applied to the river sections. Deng et al. (2001) equation was selected because visually it matched the concentration peaks better than the other studied equations in Section 4.3.1. Figure 19 shows that when including dispersion, the DO concentrations do not vary considerably for the downstream locations at St.-Oedenrode and Hooidonkse Watermolen. The RMSE increased by 0.3 mg l^{-1} and 0.1 mg l^{-1} at the mentioned locations when dispersion was included, respectively. Moreover, at the outlet of the catchment (Sint-Oedenrode), a poorer fit between observations and predictions is obtained, especially over the summer months, during periods of low flow. For the upstream locations, no change in the RMSE of the concentrations was obtained when including dispersion into the model. This indicates that especially in the upstream locations, the model is not sensitive to the inclusion of dispersion, and that dispersion does not have a major influence over the DO concentrations when a daily time step is evaluated.

Under FIS Standards for ecosystem suitability for sustainable salmonid fishery (most strict FIS Standard), thresholds are based on 1-hour, 6-hour and 24-hour durations and 1-month, 3-month and 1-year return periods (Foundation for Water Research, 2012). When applying these FIS thresholds to the Dommel case study, the resolution of the model is not detailed enough to apply the sub-daily standards (1-hour and 6-hour). However, if evaluation is required for the 24-hour/1-year return period event, the integrated modelling approach presented in this study allows observing that there are instances where the DO concentrations fail to meet the minimum DO concentrations of 5.0 mg l^{-1} during the summer months as observed in Figure 19. Thus, at the daily scale, this tool can be used by water managers for evaluation of water quality compliance. Moreover, by including dispersion in the model, there is a reduction in the model prediction accuracy. This inclusion of dispersion for this particular case and at the daily scale would result in no differences when complying with FIS standards for the upstream locations of the catchment where rural agricultural runoff dominates. However, when looking at the outlet of the catchment (Sint-Oedenrode) during the winter months of 2013, the modelled concentrations considering dispersion show erroneous spikes of higher DO concentrations in the summer months. This could lead to situations of compliance when in reality; concentrations were lower than the acceptable limits.

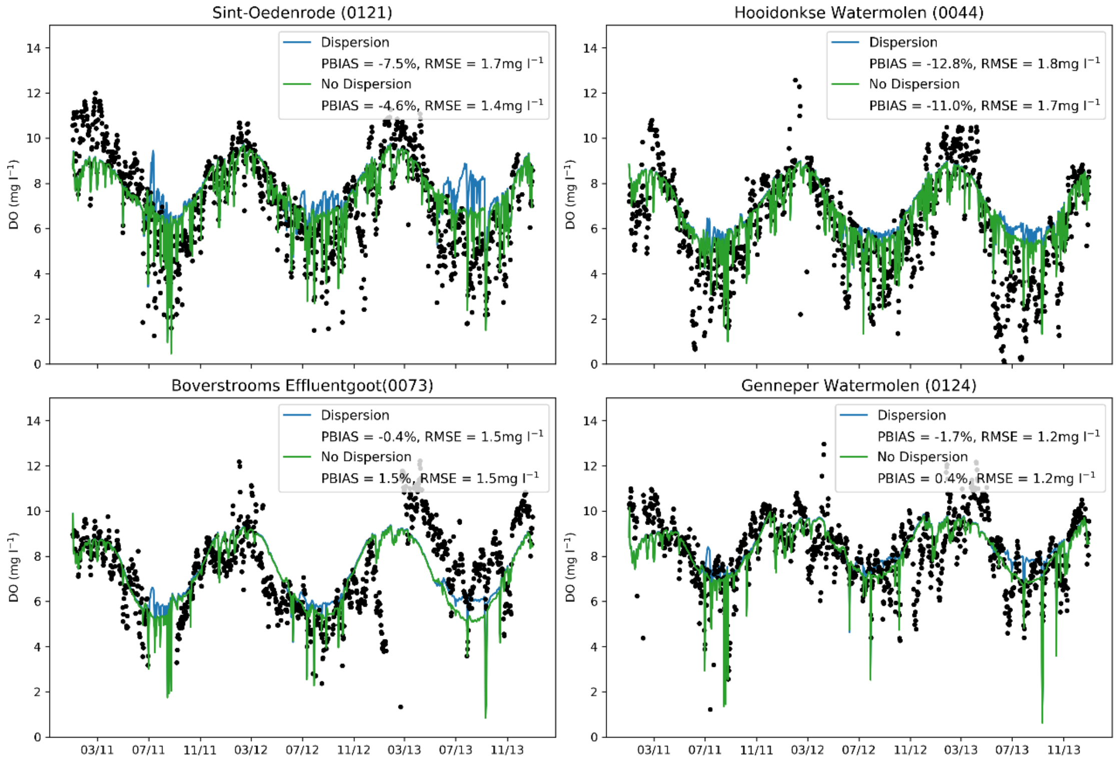

Figure 19. Dommel River model. Sensitivity of DO concentrations to inclusion of longitudinal dispersion

6.3 Impacts in river dominated by CSOs

To evaluate the impact of dispersion when using simple advection-dispersion water quality models for representing the transport of pollution from CSO discharges on FIS (Foundation for Water Research, 2012), a case study from an urban catchment in the United Kingdom is presented. Flow and quality data describing a CSO spill has been collected as part of a wider integrated model verification study as shown in Figure 20 (Norris et al., 2014). Within the integrated model, the receiving water is modelled using the DUFLOW package to evaluate the potential use of Event Mean Concentrations (EMC) models to predict CSO spills. Data from the model is extracted to provide boundary river conditions immediately upstream of the CSO, as well as the receiving water characteristics during the monitored spill event (Table 7). The evolution of un-ionised ammonia concentrations was evaluated in accordance to the Fundamental Intermittent Standards (FIS) for ecosystem suitable for sustainable salmonid fishery, establishing that the concentration should not exceed 0.105 mg Nl^{-1} unionised ammonia for 1-hour/1-year event (Foundation for Water Research, 2014).

Table 7. River and pollutant information

Parameter	Value
River mean velocity (m s^{-1})	**0.11**
River mean shear velocity (m s^{-1})	**0.0495**
Un-ionised ammonia initial concentration (mg L^{-1})	**5.10**
River average depth (m)	**2.5**
River cross section area (m^2)	**50.0**
Longitudinal dispersion (m^2 s^{-1})	**2.35**
Transverse dispersion (m^2 s^{-1})	**0.01**

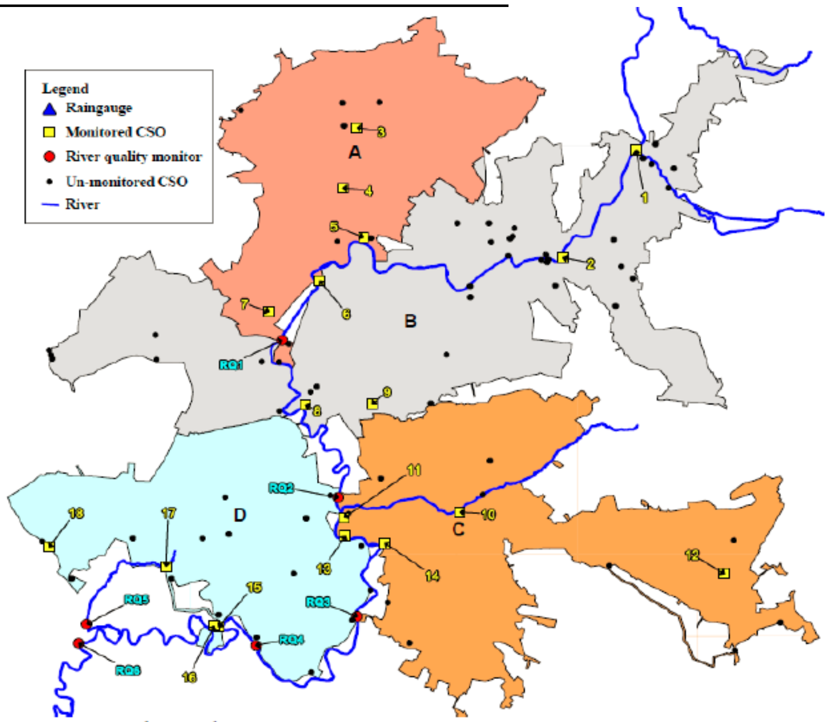

Figure 20. Study catchment (courtesy of Thomas Norris from United Utilities)

The CSO is modelled using the initial Event Mean Concentration (EMC) of 5.1 mg L^{-1}, assuming an instantaneous discharge. The propagation of the pollution events was simulated using four models implemented within the modelling framework as described in Camacho Suarez et al. (2017). The models included were: 1) Advection-only: based on the advective velocity, it does not include dispersion. 2) 1D ADE, using the one-dimensional advection dispersion equation includes both, advection and dispersion in the longitudinal direction. 3) Semi 2D ADE, where dispersion is considered in both, transverse and longitudinal directions. However, only the longitudinal advective velocities are considered, and the 4) ADZ (aggregated dead zone) model which is a simplified model that assumes imperfect mixing. These less complex models were selected for this study since they are commonly used for water quality estimations as first indicators of water compliance (Hartnett et al., 2007). The longitudinal dispersion coefficient was calculated using Deng et al. (2001) equation for consistency with the study in Section 6.2, and the transverse longitudinal dispersion coefficient was obtained from the summary of field measurements of transverse dispersion coefficients for a rivers of similar conditions shown in Rutherford (1994).

Figure 21 shows the predicted concentration versus time profile at 25m, 50m, 75m and 100m downstream of the CSO release using the four models. As expected, the concentrations modelled using the advection-only model remain constant. The differences between the 1D ADE and the semi 2D ADE model predictions reduce with increasing distance from the CSO discharge. The predicted concentrations using the ADZ model for this case take longer to attenuate than the 1D ADE and semi 2D ADE models.

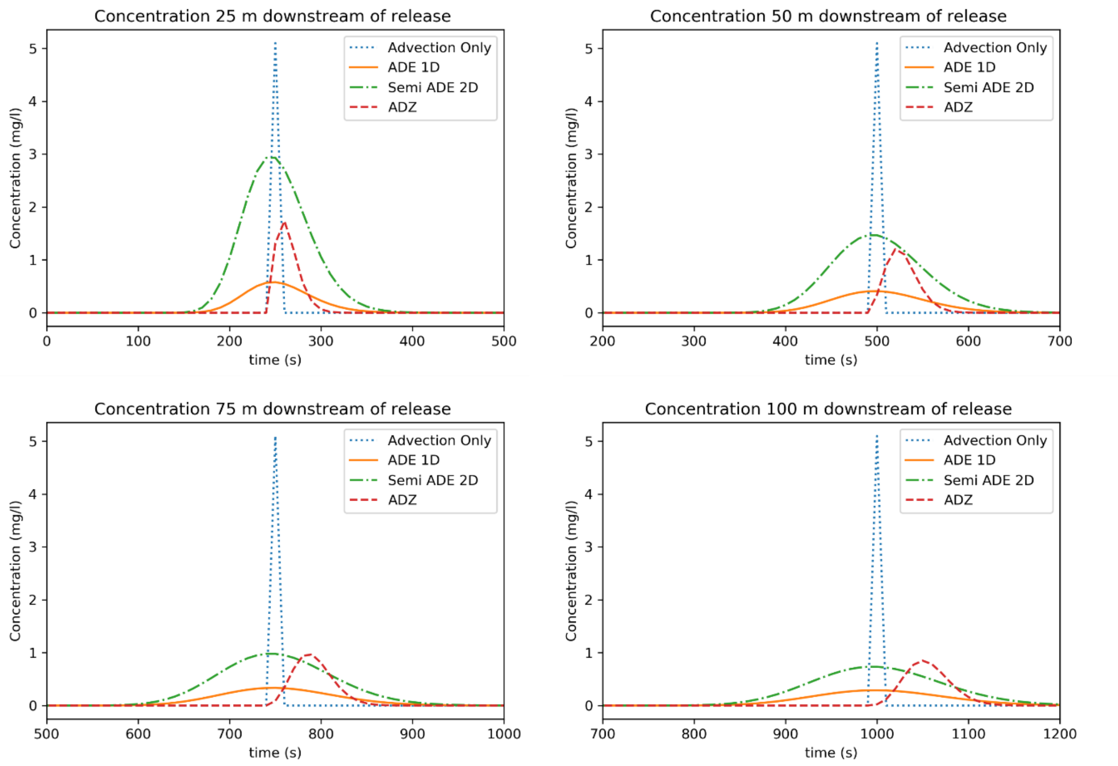

Figure 21. Modelled river NH_4 concentration profile in (mg l^{-1}) after CSO discharge at various times and distances after release at the centreline of the river width. Blue dotted line shows advection processes only, solid orange line uses one-dimensional advection dispersion equation, semi-dotted green displays the use of semi 2D advection dispersion assuming the pollutant has been released at the centre of the stream and the transverse velocities are negligible, and red dashed line uses aggregated dead zone model (ADZ) where advection occurs before dispersion. Please note that y-axis has different scales for the four plots.

To further evaluate the impact of using the various models on comparing model results against water regulation, the durations that the un-ionised ammonia concentrations exceeded the Fundamental Intermittent Standards of 0.105 mg Nl-1 unionised ammonia for Salmonid Fishery were calculated for the first 500m after the CSO release. Figure 22 shows that the advection-only model constantly exceeds the threshold by 12 seconds over the modelled spatial range. The other models exceed the threshold for approximately 410m (semi 2D ADE), 180m (ADZ) and 60m (1D ADE). Although none of the models exceed the 1hr duration (therefore complying with FIS), the estimations of the durations over the threshold vary considerably between the models selected.

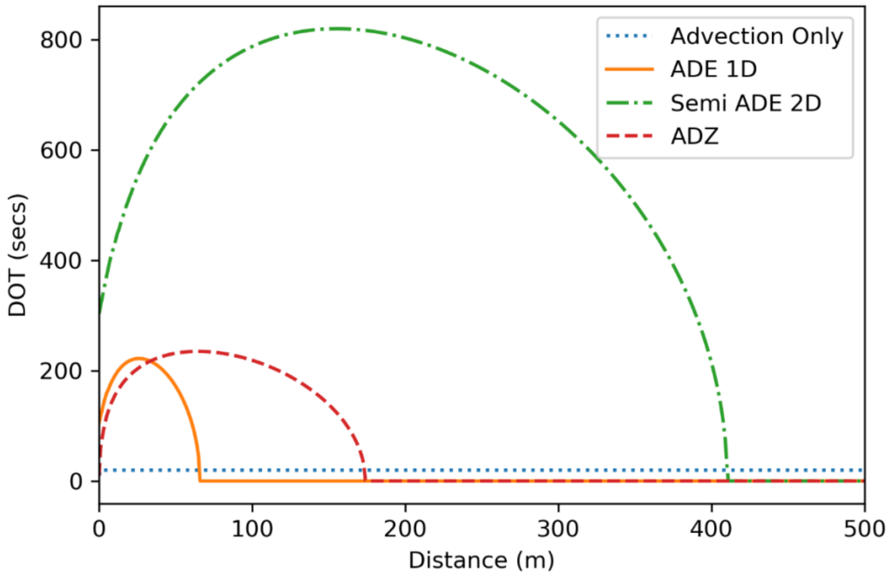

Figure 22. Duration over threshold (DOT) versus distance downstream of the CSO release. DOT values are based on the Fundamental Intermittent Standards of 0.105 mg Nl-1 unionised ammonia for Salmonid Fishery.

Commercial software such as SIMCAT and SIMPOL can only represent the advective pollutant transport. As seen in Figure 21, this type of models tends to overestimate the pollutant concentrations, but underestimate the time that the concentration has exceeded the threshold when compared to the semi 2D ADE model. The commonly used models such as MIKE11, Infoworks ICM and D-Water Quality, by integrating the dispersion component, they potentially underestimate the concentration peaks (Figure 21) and the durations that the pollutant exceeded the threshold when compared to the semi 2D ADE (Figure 22). Moreover, this study is based on an instantaneous pollution discharge. In reality, wet weather discharges have longer durations and are subject to the effects of varying hydraulic and geomorphological features, transient storage and hyporheic zones, which will alter the dynamics of the pollutant transport. Even more so when secondary currents are present requiring a 3D model representation (Seo et al., 2016).Moreover, the spatial and temporal scales of this study (<500 m reach length and sub-hourly time step), demonstrated the importance of a 2D representation of the pollutant transport problem in order to capture the effects of transverse mixing (Seo et al., 2006) at these shorter time and space scales..

6.4 Discussion

In the Dommel study, the dispersion analysis (Section 6.2) shows that dispersion is not a dominant process affecting the dissolved oxygen (DO) concentrations and water quality conditions in the river at the seasonal scale. In order to determine the dominant processes driving the DO concentrations, and the largest sources contributing to overall uncertainty, a sensitivity analysis of the DO production and consumption processes was carried out as discussed in Section 5.3.3. Results showed that aeration and macrophytes production processes were the dominant sources of oxygen while mineralization and nitrification processes were the dominant sinks of oxygen. The oxygen depletion concurs with Wheaton et al. (1994) whom suggest that a minimum dissolved oxygen concentration of 2.0 mg l^{-1} needs to be maintained for nitrification to occur.

The macrophytes production and respiration processes drive the seasonal behaviour observed in the concentration versus time plots (Figure 13). Accurately modelling these processes is key for the estimation of dissolved oxygen and the reduction of uncertainty at these longer time scales. It is important to note that additional uncertainty from input data may affect the concentrations considerably. The sensitivity analysis of input boundary conditions on dissolved oxygen concentrations (Figure 16) showed that despite the high variability of water quality concentrations in the input variables shown in Table 6 (e.g. organic matter content, total suspended solids), the seasonal dynamics of DO concentration still visually matched DO observations. Figure 16 also revealed that the input data from the rural areas resulted in a seasonal influence over the DO concentrations while the Combined Sewer Overflow (CSO) input data lead to more acute sudden effects on the DO estimations.

Contrasting results were found when using a simplified integrated water quality model by Moreno-Rodenas et al. (2019) when evaluating DO dynamics in the Dommel River. Their study found that the CSO water quality parameters, which included Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), ammonia, and DO, accounted for approximately 20% of the variance in the DO predictions in the river water. The reason of these opposing results regarding the influence of pollutant concentrations may be due to the differences in model structures. In contrast to the catchment model used by Moreno-Rodenas et al. (2019), the hydrodynamic-ecological model used in this study included the closed-nutrient dynamics, management practices (mowing and dredging), respiration, production and nutrient uptake for several groups of macrophytes and phytoplankton. A more detailed description of the modelled processes can be found in Janse (2005). The Duflow water quality model used in Moreno-Rodenas et al. (2019) uses the pre-defined EutroF1 model, which includes cycling of nitrogen, phosphorus and oxygen. It only includes one phytoplankton species. DO is estimated from the oxidation of carbon through the biological oxygen demand, algal respiration, nitrification and sediment oxygen demand (EDS, 1995).

Moreover, from the integrated water quality model presented in this thesis, it was found that the thorough and complete representation of the seasonal processes and management practices, while accounting for the nutrient ratios within the food chain of the ecological system, is necessary for the accurate seasonal estimations of DO.

Furthermore, the Dommel integrated water quality model presented in this thesis was not able to capture the short-term (lasting up to a few days) DO depletion events and their recovery during and after precipitation events. This deficiency in representing the short-term dynamics of DO due to CSO events might be due to the time resolution of the ecological model. With a daily time step, the model is not capable of capturing the fast degradation processes of organic matter, the oxygen consumption and the mixing processes, which may explain the insensitivity of the model to changes in dispersion coefficient.

The case study presented in Section 6.3 evaluates the impact of using simple models on estimated pollutant concentrations and water quality regulation in light of Duration over Threshold (DOT) analysis. By using models with different characterizations of dispersion, we can further understand the impact of dispersion on water quality concentrations and consequently, on water quality regulation. The semi 2D ADE model can represent longitudinal and transverse dispersion processes while the 1D ADE and the ADZ can only represent longitudinal dispersion. When compared to the semi 2D ADE, the 1D ADE and the ADZ models underestimate the durations over the threshold and the distances where the pollutant has exceeded the water quality threshold (Figure 22). This example illustrates the implications of using an inappropriate dispersion model for water quality assessment related to CSO discharges.

Although one-dimensional models may be limited by only representing longitudinal dispersion , Ge and Boufadel (2006) highlight that by using the 1D ADE, the high values of the concentration profiles (peaks) can be better represented when compared to transient storage or dead zone models such as TSM or ADZ which better represent the tail of the concentration profiles. When testing for compliance using DOT analysis, the representation of the peaks is more important given that the Fundamental Intermittent Standards (FIS) focus on the high values that have exceeded a water quality threshold. Therefore, the 1D ADE is a preferable choice of model for DOT compliance given the importance of accurately representing the concentration profile peaks. However, the application of the 1D ADE should be implemented after the cross section has fully mixed as also suggested by previous studies (Rutherford, 1994).

The use of 2D or 3D models is recommended to reduce uncertainty for the region near the pollutant release. However, higher dimensional modelling requires the representation of 2D or 3D hydrodynamics. This is also subject to additional parameter uncertainty if calibration data is not available as illustrated by Baek and Seo (2016) who developed a two-dimensional routing procedure to estimate the longitudinal and dispersion coefficient from empirical observations. Previous studies have also proposed empirical models to estimate the transverse dispersion (Boxall & Guymer, 2001; Fischer, 1969). Moreover, the need for 3D models increases for lakes, estuaries and the subsurface as mixing in the three directions becomes important. This is illustrated by studying the effects of heterogeneity on aquifers (Chen et al., 2018), wind currents and circulation patterns on the transport of substances in lakes (Cimatoribus et al., 2019), sediment initial conditions and pelagic processes (Amunugama & Sasaki, 2018), and river-borne particles spreading over estuary systems (Legorburu et al., 2015).

6.5 Conclusion

This chapter studied the effects of dispersion on water quality models of different complexity and different sources. The first study focussed on a complex integrated water quality model with dominant diffuse pollution where dispersion processes are less significant than other physical and ecological processes (e.g. aeration and mineralization of organic matter). This is potentially due to the coarser temporal and spatial resolutions covered by the model. In contrast, the second study demonstrated how when using simple pollutant transport models, the role of dispersion becomes considerable in the estimation of water quality concentrations and when complying with concentration-duration-threshold type water regulation. By including both, longitudinal and transverse dispersion coefficients by means of the semi 2D ADE model, the durations that the pollutant exceeded the established water quality threshold were larger than when using one-dimensional models by several 10s of meters. This could make the difference between whether compliance has been demonstrated or not. Moreover, as the distance from the pollutant release increases, the differences between the predictions by the 1D ADE and semi 2D ADE models reduce and the 1D ADE model can be used with more confidence for water regulation purposes.

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7. Summary, Conclusions and Outlook

This PhD thesis studied one-dimensional river water quality models to determine the impacts of parameter, input and structural uncertainties on water quality predictions made to check compliance with concertation duration frequency type regulation such as the Fundamental Intermittent Standards (FIS; FWR, 2012). The study also provided insights regarding the importance of longitudinal mixing for models of different complexity and varying spatial and temporal scales. The first study (Chapter 4) evaluated the impact of the longitudinal dispersion coefficient on the 1D ADE water quality predictions at the sub-daily time scales for checking compliance with the Fundamental Intermittent Standards for discharges (Foundation for Water Research, 2012). Chapter 5 presented an integrated water quality model using a closed-nutrients cycle at daily timescales for the prediction of seasonal dissolved oxygen processes. Chapter 6 evaluated the impact of longitudinal dispersion on water quality variables used to check compliance with the Fundamental Intermittent Standards regulation for models of varying complexity. Below a summary of each chapter is provided along with conclusions and recommendations for future work.

7.1 Parameter uncertainty from the conceptualization of longitudinal dispersion

Chapter 4 presented a statistical analysis carried out on six of the latest longitudinal dispersion equations. Regression equations, based on hydraulic and geomorphological river properties for the estimation of longitudinal dispersion equations are abundant in the literature. However, understanding the impact of implementing such methods for the quantification of dispersion in advection dispersion models is crucial for the proper estimation of water quality variables and their impact on evaluating compliance with water quality standards.

By studying the distributions of predictive ratios (predicted over measured longitudinal dispersion coefficients), information regarding the behaviours of the goodness of fit of the longitudinal dispersion equations was gained. Probability distributions of predictive ratios were derived and propagated using Monte Carlo analysis to estimate confidence intervals for time-concentration profiles for an independent study (Chillan River), and four rivers of different characteristics. For four rivers of different mean to shear velocity ratios and aspect ratios, confidence intervals of concentration profiles were derived, and compared to water quality standards by estimating the duration that the pollutant had exceeded a water quality threshold under the Fundamental Intermittent Standards (Foundation for Water Research, 2012). The duration over threshold analysis demonstrated that the uncertainty from the longitudinal dispersion coefficient extends up to 100s of meters from the pollutant release. This demonstrates that uncertainty in the longitudinal dispersion coefficient can have a major impact in determining how compliance with water quality regulation can be achieved following simulation of different water quality improvement strategies. The parameter uncertainty study in this thesis was limited to the longitudinal dispersion coefficient given its importance within the 1D ADE, and the wide use of the 1D ADE. However, further work should include the evaluation of parameter uncertainty and its propagation over water quality regulation from other transport models such as the transient storage and hyporheic exchange models.

7.2 Input uncertainty in integrated water quality modelling

A combined modelling approach involving a rainfall-runoff, hydrodynamic and ecological model was used for determining the sensitivity of input water quality concentrations on dissolved oxygen concentrations. An emphasis was made on input data as it is challenging to obtain accurate input data to describe the biochemical factors driving the ecosystem ecological response. A sensitivity analysis was carried out in order to evaluate the river system's response to changes in pollution inputs. This analysis was carried out for a case study on the River Dommel catchment in the Netherlands, for which water quality data was available. Scenarios of high and low input water quality concentrations incoming from rural and urban flows were simulated to assess their effect on total Dissolved Oxygen (DO) and find out the dominant DO production and consumption processes. These variables included concentrations of NH_4, NO_3, total nitrogen, organic nitrogen, PO_4, total suspended solids, organic matter content and chlorophyll-a.

The impact over DO processes originating from the variability of input concentrations originating from rural runoff, CSOs and the Eindhoven wastewater treatment plant (WWTP) discharges is visible at the four studied locations in the Dommel River. This analysis assisted to identify both short-term and long-term effects. CSOs impacts are visible by the sudden drops and spikes of DO and DO production processes that occur in response to precipitation events. Such oxygen depletion events can be lethal for the aquatic habitat. The sensitivity analysis results showed that the rural runoff input concentrations have a larger influence over DO concentrations over the winter months than the summer months, while CSO input concentrations have sudden short-time impacts over DO. The impact of the WWTP input water quality concentrations shows both, short-term and long-term effects over DO concentrations.

Aeration is sensitive to both, rural runoff inflows and CSOs inflows. The results of the sensitivity analysis (Figure 17) studying then influence of varying input boundary conditions on aeration showed that the changes in input concentrations (shown in Table 6) of the rural boundary flows had a noticeable impact on aeration throughout the entire simulation time while the CSOs impacted aeration only during CSO discharge events. It is noted that the CSOs and the rural runoff input boundary conditions have an effect over the mineralization and nitrification processes on the sediment over the longer time scale while for the mineralization of detritus in the water, CSOs, have more sudden effects over shorter time scales. Similarly, the WWTP has acute short time effects over nitrification in water while the rural runoff has a constant effect over nitrification in water.

This study found that although uncertainty in the values of input data has influence over the simulation results, it is not a deterrent for obtaining reasonable seasonal DO predictions in the Dommel River. Despite the wide ranges of input boundary conditions, as shown in table 6, the seasonal behaviour of DO is still well represented. Furthermore, this analysis can be used to further evaluate the influence of individual pollution sources over the oxygen production and consumption processes, including ecological processes. This allows for testing of a wider range of water quality management options, such as mowing or dredging. Although the model runs at daily timescale and is therefore not suitable for testing sub-daily concentration-duration-frequency regulation, the effect of CSO spills is still visible, so the impact of considerable spills could still be seen. Future would should use this modelling approach for longer term (decades) of simulation, to see if the model would be capable of studying detrimental effects of build-up of pollutants in the river sediments over time.

7.3 Importance of dispersion in water quality models

Chapter 6 evaluated the impacts of longitudinal dispersion on models of varying complexity used for compliance with water regulation under the Fundamental Intermittent Standards (FIS). The first study (Section 6.2) focused on an integrated water quality model, which included the impacts of diffuse pollution from agricultural areas and urban pollution from wet weather discharges of combined sewer overflows and a wastewater treatment plant. No substantial influence on the dissolved oxygen concentrations was observed by varying the longitudinal dispersion coefficient, especially in the upper locations of the catchment where rural agricultural runoff is dominant. Moreover, the root mean square error between the observed and predicted DO concentrations increased by including the dispersion component in the downstream regions of the catchment indicating a mismatch between observed and predicted concentrations of DO. One potential reason for the low influence of dispersion in this study may be due to the daily time step resolution of the model. This coarse time resolution (daily) may not capture the effects of dispersion that usually occur at the sub daily time scale. The second study of a river reach within the UK focused on studying the impact of pollutant transport model structures: Advection-only, 1D ADE, ADZ, and semi 2D ADE (commonly implemented within commercial water quality software) on water quality concentrations and compliance with FIS regulation. The model structure selection resulted in wide differences of durations over the thresholds extending over 100s of meters between the different models. This indicates that the model selection has a substantial influence when estimating water quality concentrations as it affects the shape of the peaks of pollutant concentrations. Further analysis integrating the impacts of continuous pollution discharges as well as non-conservative substances is still required to further assess the impact of such discharges on river water quality parameters.

7.4 Overarching conclusions and recommendations

The longitudinal dispersion coefficient propagates substantial uncertainty at the sub-daily time scales and up to 100s of meters from the pollutant release when using the 1D ADE equations, which are often included in industry standard software packages. It is therefore recommended that in water quality studies where accurately simulating water quality parameters at sub-daily scales and within 100s of meters of the pollutant release, tracer tests are carried out to establish the specific longitudinal dispersion coefficient for the river reach studied.

At larger space and time scales (daily/seasonally and catchment scale), the mixing processes become less evident. It would therefore be recommended for larger space-time scale studies, that some initial exploratory sensitivity analysis be done to see if water quality parameters simulated are sensitive to varying longitudinal dispersion coefficients. If they are, local tracer tests would be recommended, if not then other types of water quality processes should be simulated.

Hence, for every proposed water quality modelling study, it is important to first establish which type of water quality processes are thought to be dominant at the space and time scales studied, and select an appropriate model type and structure accordingly. If there is a mismatch between the space and time scales at which water quality parameters are simulated, and the model type and resolution used, model results could contain considerable uncertainty.

There also appears to be a mismatch between more and more sophisticated water quality models developed by researchers, and the water quality models used in practice by industry to show compliance with regulations. More work should be done to study and quantify the implications of uncertainty related to the use of industry standard models on investment in water quality management strategies.

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Appendix A: Review of water quality modelling software

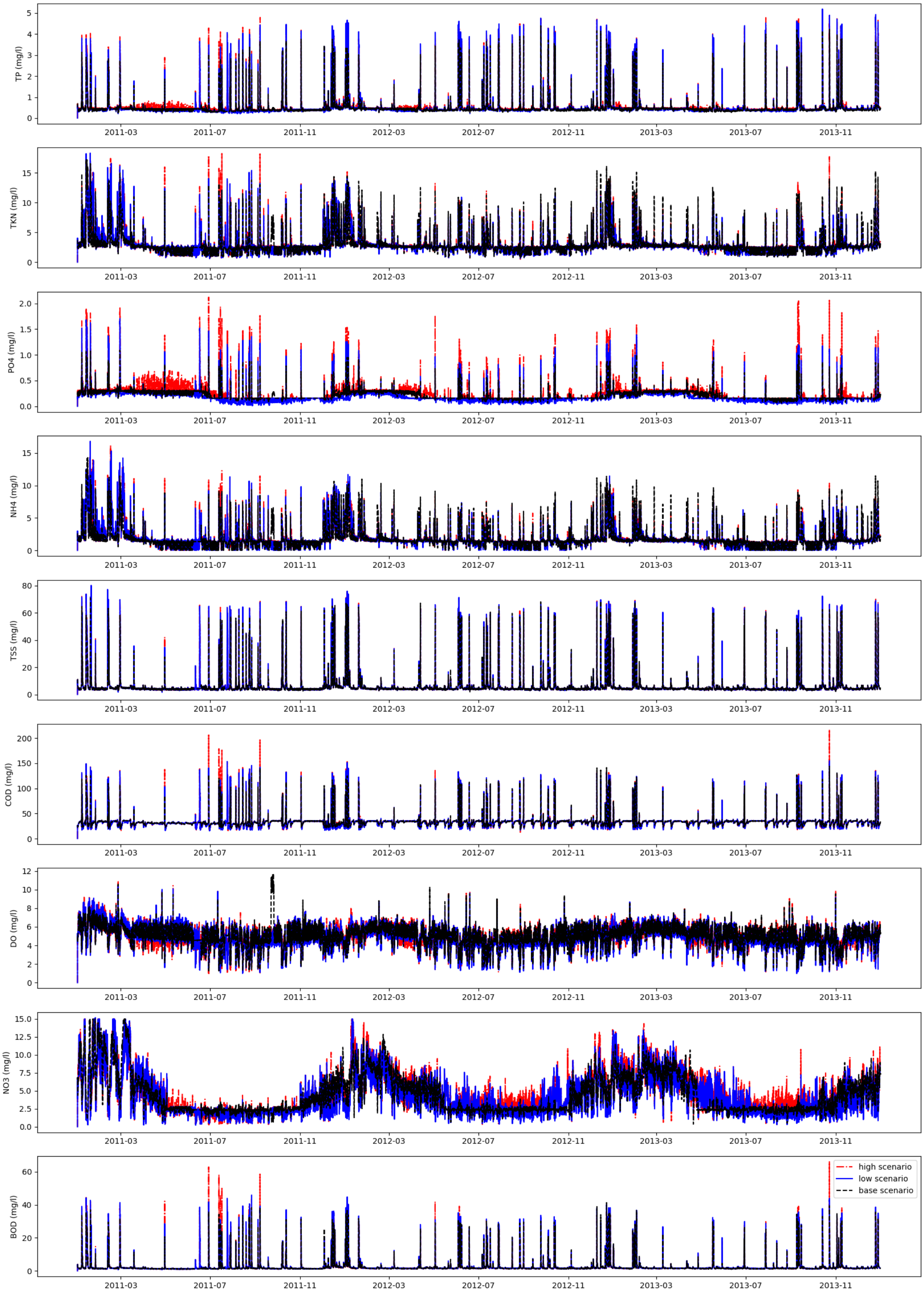
WATER QUALITY MODEL	VARIABLES MODELLED	GOVERNING EQUATIONS	DIMENSION	ASSUMPTIONS	UNCERTAINTY ANALYSIS	REVIEW FROM	DEVELOPED BY
Simulation Catchment (SIMCAT)	BOD, COD, DO, NH_4	Mass balance including tributary, effluent discharges, abstractions, and upstream conditions. Solute: for conservatives - only advection, for non-conservative - first order decay (BOD and NO_3), DO uses decay, temperature and reaeration	1D	fully instantaneous mixing throughout the reach	Monte Carlo simulation Summary Statistics	Kannel et al 2011, B. A Cox (2003)	Water Research Centre (WRc)
QUAL2EU	waste loads in-stream water quality and non-point source waste loads DO, N, P, and algae,	advective transport is within mean flow and dispersive transport is proportional to concentration gradient, first-order decay water balance for finite difference elements, uses a implicit backward difference numerical scheme	1D	Steady state, completely mixed along cross section	uncertainty analysis, sensitivity analysis, first order error analysis, Monte Carlo simulation	Kannel et al 2011	US EPA
QUASAR	pH, N,P, E Coli, algae, BOD, DO, Conservative pollutants	ADZ Model	1D				developed as part of the Bedford Ouse Study
MIKE-11	flow and quality in rivers	St Venant equations (diffusive wave and kinematic wave) allows to add ADE module	1D	Assumes the substance is completely mixed over the cross-section, the substance is conservative and Fick's diffusion law applies	Includes data assessment tool to evaluate uncertainties on boundary conditions in the river network, and ensemble Kalman filter to implement Monte Carlo simulations	DHI (2017)	DHI

Flood modeller Pro (Former ISIS)	flow and quality	St Venant equations, finite difference approximation to 1 ADE, transformation equations				B.A. Cox (2003)	
AQUATOX	organic chemicals, suspended and sediments, DO fluctuations, toxicity from low oxygen and ammonia	Mass balance of nutrients ,Uses 4th and 5th Runge-Kutta integration method, divides river into equal segments	1D	Assumes segments are uniformly mixed	Latin hypercube uncertainty analysis, nominal range sensitivity and time-varying process rates analysis	Sharma, D. & Kansal, A. (2013)	
One dimensional Riverine Hydrodynamic and Water Quality Model (EPD-RIV1)	16 variables including water temperature, N, P, DO, CBOD, algae, Fe, MN, Coliform bacteria, macrophytes, varying point and non-poin source pollution, cycling of nutrients, and fate, effect of toxic materials	1D advection - dispersion with decay and sinks ,2 point, 4th order accurate, Holly-Preissman scheme. It has hydrodynamic and water quality modes	1D	River is homogenous		Sharma, D. & Kansal, A. (2013)	
QUAL2Kw	pathogens as a function of temperature, light settling velocity, temp, pH,	first order decay, mass balance, 1D Steady state, water quality simulated in dynamic mode with diel water quality kinetics and heat budget, river is collection of reaches	1D	steady flow	provides uncertainty analysis component	Sharma, D. & Kansal, A. (2013); Kannel et al 2011	Pelletier & Chapra

	conductivity, inorganic suspended solids, DO, CBOD, N, Ammonia, P, biomass, algae, alkalinity					
WASP 7	DO, N, P, C, Temp, salinity, bacteria, soloca, sediments, heavy metals, mercury, inorganic loads	ADE and kinetic transformation, Conservation of mass, fluid dynamics, ADE, based in QUAL2K algorithm	1D, 2D, 3D (Wool et al. 2001)	Assumes complete mixing in river, requires hydrodynamic component for advection, user specifies dispersion coefficient, may have significant numerical diffusion	does not provide uncertainty analysis component	Sharma, D. & Kansal, A. (2013)
Water Quality for River - Reservoirs Systems (WQRRS)	water quality conditions in rivers and reservoirs	Conservation of heat and mass spatially and temporal, hydrologic routing, kinematic routing, steady flow, or full St Venant equations	1D	Instantaneous dispersion, 1D homogenous (longitudinal and lateral variations neglected)		Sharma, D. & Kansal, A. (2013)
Branched Lagrangian Transport Model (BLTM)		1st order decays, 1D advective dispersion equation (Lagrangian reference frame) divides into sub-reaches, uses finite difference solution of mass transport and reactions equations. Five levels: QULTMP, SOLAR, INTRP, MRG BBLTM, BQUAL2E, CTPLT, CXPLT	1D	Uniform hydraulics, but when coupled with BLTM, limitation is reduced, assumes solutes are completely mixed across cross section and dispersive transport is proportional to concentration gradient		Sharma, D. & Kansal, A. (2013)

Compliance Assessment Tool	**E.coli and intestinal enterococci (IE)**	**Uses database of hydrographs, pollutographs and unit impacts to assess environmental standards and solution designs**				**Verghetta and Taylor (2019)**
SIMPOL	BOD, un-ionised ammonia	Uses surface, sewer and CSO tanks connected to each other	0	perfectly mixed tanks		Dempsey et al., (1997)

Appendix B: Simulated WWTP nutrient input scenarios



Appendix C: WALRUS model results and calibration

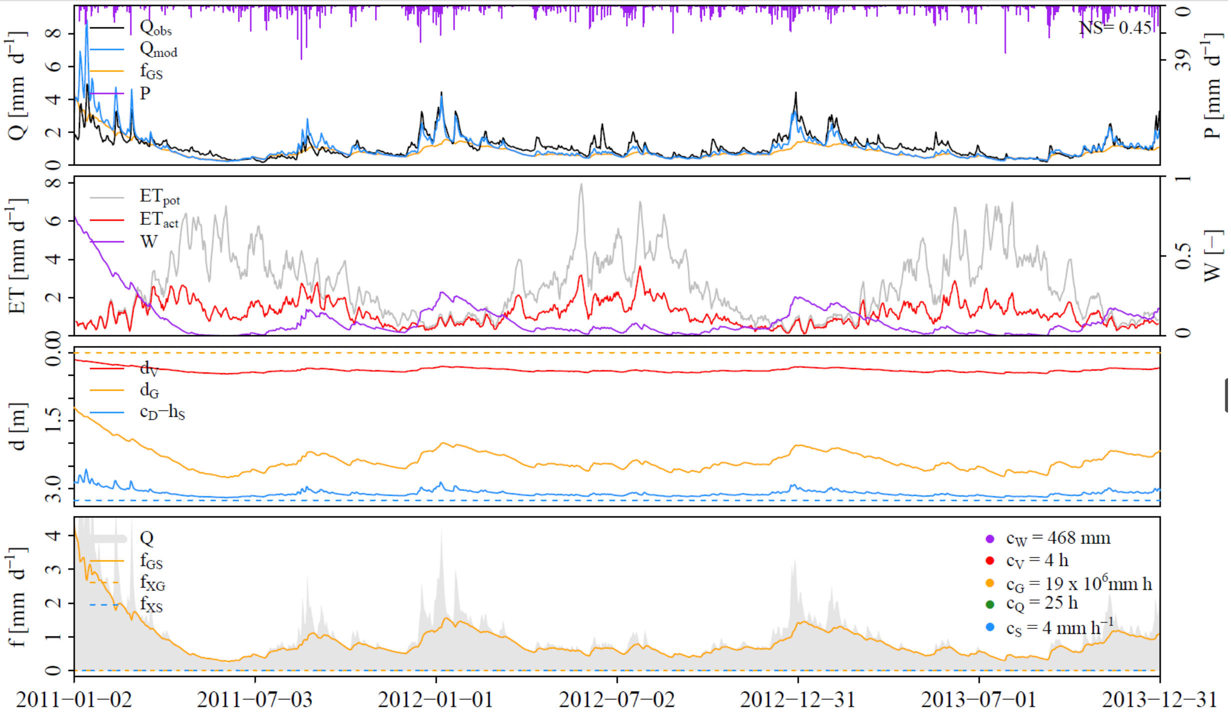


Figure C1. Walrus model results and calibration for Keersop catchment

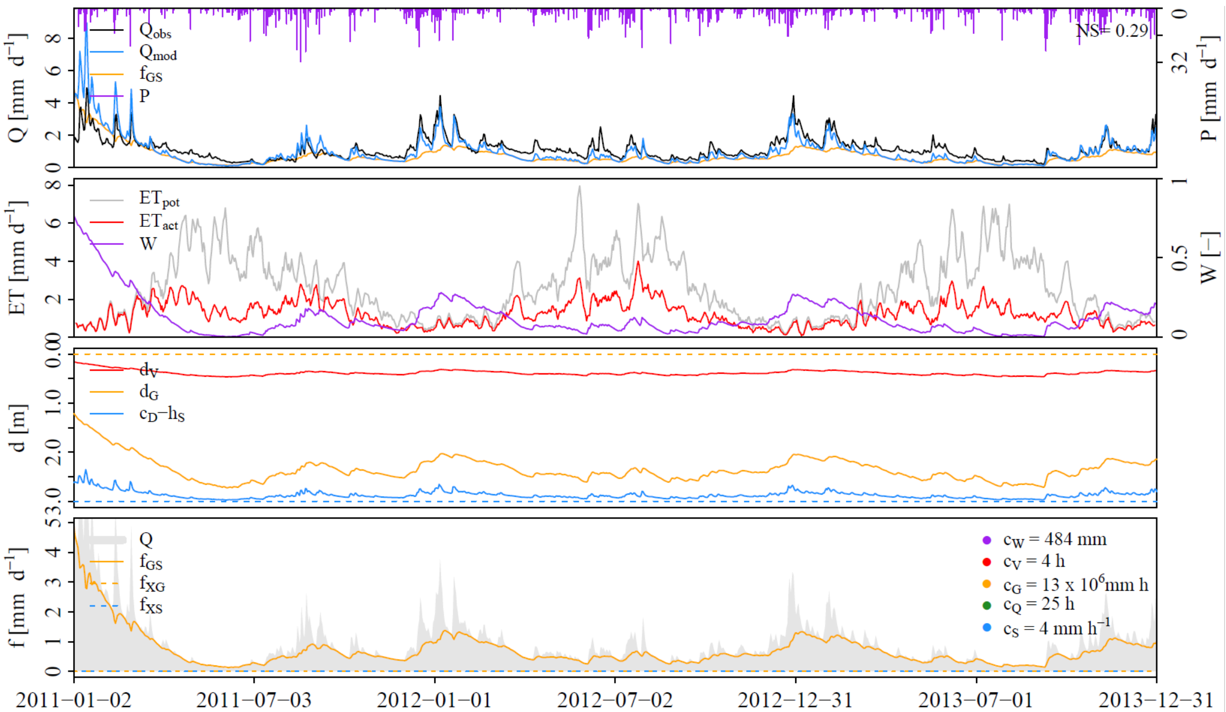


Figure C2. Walrus model results and calibration for Tongelreep catchment

Appendix D: Observed and predicted flow using Sobek hydrodynamic model