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Comparison of simple models for total nitrogen removal from agricultural runoff in FWS wetlands

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ABSTRACT

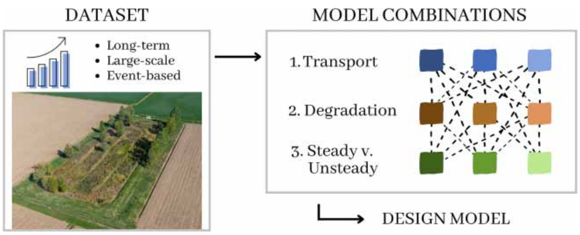
Free water surface (FWS) wetlands can be used to treat agricultural runoff, thereby reducing diffuse pollution. However, as these are highly dynamic systems, their design is still challenging. Complex models tend to require detailed information for calibration, which can only be obtained when the wetland is constructed. Hence simplified models are widely used for FWS wetlands design. The limitations of these models in full-scale FWS wetlands is that these systems often cope with stochastic events with different input concentrations. In our study, we compared different simple transport and degradation models for total nitrogen under steady- and unsteady-state conditions using information collected from a tracer experiment and data from two precipitation events from a full-scale FWS wetland. The tanks-in-series model proved to be robust for simulating solute transport, and the first-order degradation model with non-zero background concentration performed best for total nitrogen concentrations. However, the optimal background concentration changed from event to event. Thus, to use the model as a design tool, it is advisable to include an upper and lower background concentration to determine a range of wetland performance under different events. Models under steady- and unsteady-state conditions with simulated data showed good performance, demonstrating their potential for wetland design.

Key words: agricultural runoff, design models, free water surface wetlands, modelling, treatment wetlands

HIGHLIGHTS

- The most robust model combination: the tanks-in-series model under steady conditions.
- First-order kinetics with non-zero background concentration was the best for degradation.
- The optimal background concentration changed from event to event.
- Potential use of TIS model in unsteady conditions when infiltration and evapotranspiration occur.

GRAPHICAL ABSTRACT



INTRODUCTION

The loss of water-soluble nutrients from agricultural soils through runoff and percolation has made agricultural systems one of the main sources of diffuse pollution of water bodies in recent decades (Robertson & Vitousek 2009; Withers *et al.* 2014). One of the most important pollutant of that origin is nitrogen that can cause negative effects in different environmental matrices, and the progressive increase of nitrates in soils and freshwaters has been recognised as a serious problem (Mancuso *et al.* 2021).

Among aquatic systems, wetland systems are known for their high productivity, as they can transform and accumulate organic matter, nutrients and other incoming compounds (Brinson *et al.* 1981). This results in a high purification capacity, which has led to the development of treatment wetlands (TWs), a nature-based solution used to treat different types of wastewater, including agricultural runoff (Langergraber *et al.* 2019). The most widely used TW type for agricultural runoff are free-water surface flow (FWS) wetlands due to their ability to cope with stochastic runoff events. FWS wetlands require large surface areas that are exposed to precipitation and evaporation. This influences the water balance, e.g. causing the system to dry out if rainfall does not compensate for evapotranspiration. In addition, they usually have a permeable bottom, hence infiltration water losses. Their performance depends on different factors, such as surface area, hydraulic residence time (HRT), hydraulic loading rate (HLR) or ambient temperature, which makes their design more challenging (Kadlec & Wallace 2009; Dotro *et al.* 2017).

The growing interest in FWS wetlands in the 1980s led to the development of mathematical models to predict their behaviour. Since then, various models have been used for design or optimization purposes, ranging from the simplest models, based on empirical equations that establish a relationship between input and output, i.e. linear regression (Kadlec 1994; Stone *et al.* 2004; Kadlec & Wallace 2009), to process-based models (Hammer & Kadlec 1986; Gargallo *et al.* 2017; Aboukila & Deng 2018; Aragones *et al.* 2020). The latter require modelling skills and several parameters to be calibrated, which can only be obtained when the wetland is constructed. In addition, when there is insufficient information for calibration, the complex models tend to propagate uncertainty errors, making them cumbersome and expensive to use for decision-making and upfront design. On the other hand, simple tools can provide an overview of the performance of TWs regarding water quality under different conditions, support their design and increase confidence in their implementation (Langergraber 2011; Meyer *et al.* 2015). As an example of simple models, the reader is referred to the simulation tools developed to support the design of combined sewer overflow wetlands (Meyer & Dittmer 2015; Palfy *et al.* 2018).

Simplified mechanistic models widely used in chemical engineering have been adopted to model the solute transport as well as removal processes in FWS wetlands. The first models used were the continuously stirred tank reactor (CSTR) and the plug-flow (PF) model (Werner & Kadlec 2000). In their basic form, these models represent ideal reactors with a single residence time. In wetlands, by their nature, effects such as irregular geometry or the turbulence caused by vegetation or the presence of animals cause dispersion transport. Their hydraulic behaviour is characterised by non-ideal flow with mixing zones, dead zones and different velocities at different depths, which result in different residence times (Werner & Kadlec 1996; Walker 1998). In order to simulate the residence time distribution observed in FWS wetlands, models such as the tanks-in-series (TIS) or the plug-flow with dispersion (PFD) have been widely used (Kadlec 1994, 2000; Persson *et al.* 1999; Werner & Kadlec 2000). Also, combined or hybrid models have been used, as is the case with the series-parallel network of tanks model by Kadlec (1994). The hydraulic models can include kinetic expressions for predicting the average behaviour of the system, such as first-order degradation kinetics or Monod kinetics. A widely accepted degradation model is the modified first-order model (k-C* model) that includes background concentrations (C*) (Kadlec 2000). In the k-C* model a compound is never completely removed due to various factors such as uncontrolled inputs and outputs, or internal wetland processes. This model was adapted to the TIS model with an apparent number of tanks (P) to consider pollutant weathering, known as P-k-C* or relaxed TIS, and is currently used for sizing FWS wetlands (Kadlec & Wallace 2009). This model, however, assumes constant detention times during an event and does not account for water and mass losses by evaporation and infiltration. The simple degradation models do not differentiate between microorganisms-degradation and plant-absorption. Some reaction rates are affected by temperature, which can be accounted for in models by adding a correction factor, e.g. Arrhenius equation, as nitrogen compounds.

Several studies have tested simple models to investigate their hydraulic behaviour using performance distributions generated by Monte-Carlo simulations (Werner & Kadlec 2000) or using tracer experiments of existing wetlands (Holland *et al.* 2005; Wong *et al.* 2006; Bodin *et al.* 2012). Many studies performed pilot and large-scale experiments to evaluate the nitrogen removal performance and calculate removal rate coefficients in FWS wetlands (Sun *et al.* 2005; Tuncsiper *et al.* 2006). However, no studies have been found that have compared the models over the entire event using real long-term datasets from large-scale FWS wetlands to identify the limitations of the combined models.

This study aimed to evaluate different FWS wetland models for total nitrogen removal by a full-scale FWS wetland. Various simple models have been applied and evaluated for their ability to predict steady- and unsteady-state conditions.

MATERIALS AND METHODS

Experimental data and boundary conditions

The data used have been collected from a full-scale FWS wetland located at an experimental farm of the Canale Emilio Romagnolo Land Reclamation Consortium in the village of Budrio, Emilia-Romagna region, Italy. It has been in operation and monitored since 2001. According to the Köppen climate classification (Kottek *et al.* 2006), the climate is sub-humid, with an annual average precipitation of 771 mm and an annual average air temperature of 13.7 °C. The wetland has a surface area of 0.4 ha and was fed by a water pump from a channel that collects agricultural runoff from a farm of approximately 12.5 ha in area. The vegetation cover is mostly composed of *Phragmites australis*, *Typha latifolia* and *Carex spp*. The length to width (L:W) aspect ratio was 52, the system being 470 m long and 9 m wide on average. As it can be seen in Figure 1, the FWS wetland has four meanders and the width is not constant. The average depth is 0.4 m, and its total volume is about 1,477 m^3. The bed is permeable, with an infiltration rate ranging between 6.72 and 7.92 mm/d. (Lavrnic *et al.* 2020a).

A number of the inflow events have been recorded by Lavrnic *et al.* (2020b) between 2018 and 2019. Two of these produced outflows and were considered for this study. These are: Event 1, from 1st Feb 2018 to 29th Mar 2018 (56 days), and Event 2, between 17th Nov 2019 and 24th Dec 2019 (37 days). Daily monitoring of precipitation, air temperature, water level, inflow and outflow volume was done during both events. Water samples were taken to measure water quality parameters using two automatic samplers, one at the inlet and one at the outlet. Samples have been collected flow- and time-proportional (Lavrnic *et al.* 2020b). From February to April 2018, additional flow and water level measurements were carried out on an hourly frequency. Additionally, a tracer test was conducted in the wetland using NaCl as a non-reactive tracer to obtain more information on the wetland hydraulics. For more details on the tracer experiment, the reader is referred to Lavrnic *et al.* (2020a).

Water balance

The hydrological behaviour of the FWS wetlands was evaluated using a water balance approach during and shortly before and after Event 1 and Event 2. The water balance was computed as follows:

$$\frac{dV_{(i)}}{dt_{(i)}} = Q_{in(i)} - Q_{out(i)} - I_{(i)} + A\ (P_{(i)}) \tag{1}$$

Figure 1 | Aerial photo of the FWS wetland located in the experimental farm of the Canale Emilio Romagnolo Land Reclamation Consortium, in the village of Budrio, Italy.

where i is the time step, V is the wetland volume over time t, Q_{in}, Q_{out} and I are the inlet flow, outlet flow and infiltration rate in m^3/h, respectively, and P the precipitation in m/h on the wetland area A in m^2 (subsequently called 'direct precipitation', P_{direct}).

A variant of the unsteady-state conditions with simulated data was added to avoid overflow in the model and reduce inconsistencies in the measured values. This also provides an overview of the hydrology depending on the size of the FWS to be constructed. To this end, the water level (h) and the outflow (Q_{out}) in the wetland were calculated for each time step from the water balance according to the following set of equations:

$$V_{(i)} = V_{(i-1)} - I_{(i-1)} + P_{direct(i-1)} + Q_{in(i-1)} - Q_{out(i-1)} \tag{2}$$

$$Q_{out(i)} = \begin{cases} 0, & (V_{(i-1)} \leq V_{max}) \\ Q_{in(i-1)}, & (V_{(i-1)} > V_{max}) \end{cases} \tag{3}$$

$$h_{(i)} = \frac{V_{(i)}}{A*\varepsilon} \tag{4}$$

where P_{direct} is the direct precipitation in m^3/h, V_{max} is the maximum volume in m^3, calculated as A multiplied by the water level at which outflow occurs (i.e. 0.40 m), and ε, the fraction accessible for water flow, i.e. area not occupied by vegetation, which was 0.9, as estimated by Lavrnic *et al.* (2020a).

Both periods were considered to have negligible evapotranspiration because the events are between November and March, months with very low evapotranspiration. An extension of the simulation of Event 1 was carried out for the month of April in which crop evapotranspiration was considered, calculated from the reference evapotranspiration and the crop coefficient for *Phragmites australis* (Cav.), the most widespread crop in the wetland, assuming standard conditions (Allen *et al.* 1998).

Residence time distribution

The tracer test data were used to determine experimentally the residence time distribution (RTD), i.e. the probability distribution of the time a compound remains in the system (Levenspiel 1999). Its function was used to calculate the average hydraulic retention time and adjust the RTD to different hydraulic models in order to find the best-fit parameter values. Finally, the RTD was used to model solute transport in the PFD model with varying input concentrations and volumes.

Simulation study/model combinations

The hydraulic models were set up for steady- and unsteady-state conditions. For each hydraulic model three degradation models have been applied to simulate the removal of total nitrogen (TN) in the FWS wetland using the experimental data of Events 1 and 2, except for Monod kinetics which was only applied to the CSTR and TIS models. The performance of the models was assessed with root mean square error (RMSE) comparing simulated and observed output concentrations, as it has been proven to be more suitable than other goodness-of-fit measures for simulations comparing concrete data points with simulation results (Ahnert *et al.* 2007).

The following hydraulic models were set up to model different hydraulic behaviours that defined the transport of water and solutes in the wetland:

- **CSTR:** The CSTR model assumes instant and complete mixing within, where the concentration at the outlet was the same as in the wetland (Levenspiel 1999). The transport model consisted of a mass balance performed that considered all inputs and outputs of the system.
- **TIS:** The TIS model consists of several CSTRs in series, emulating dispersion and creating a gamma distribution of residence times (Fogler 2016). HRT and N determine the residence time distribution, where N represents the mixing degree. The estimation of N was done in two ways: (1) by minimising RMSE of the RTD curve with the tracer test, and (2) by dividing the square of the HRT by the variance of the RTD curve as described in Bodin *et al.* (2012).
- **PFD:** The plug-flow model was extended to account for the effect of dispersion using the Peclet number (Pe), a dimensionless term that describes the rate of transport by convection in relation to the rate of transport by diffusion or dispersion (Kadlec 1994; Levenspiel 1999). The effect of dispersion introduced different residence times of the compound in the system. Pe was determined by minimising the RMSE of the RTD curve with the tracer test data.

Three variants were used to compare different flow conditions:

- **Steady-state conditions (#1):** For this variant, the outflow was equal to inflow, whereas infiltration and precipitation on the wetland area were neglected. There was no change in volume. For each event, the nominal HRT was calculated by dividing the average volume and flow rates over the whole event.
- **Unsteady-state conditions with measured data (#2)**: This variant used measured water level and outflow data for each time step and included infiltration and direct precipitation on the wetland area. The unsteady state conditions of the PFD model were modelled using the RTD approach, where each time step was treated as a pulse emission (Holland *et al.* 2005).
- **Unsteady-state conditions with simulated data (#3):** A water balance was performed in order to simulate the water level and the outflow in the wetland as explained in the *Water balance* section. The RTD approach was used in the PFD model as in #2.

The degradation models used were:

- **First-order kinetics:** This model is used for removal processes in which the reaction depends linearly on the pollutant concentration (C), where the reaction rate coefficient k determines the velocity of the reaction. C was calculated by dividing the mass (g) by the volume (m^3) of the previous time step to account for volume variation in simulations under unsteady conditions (#2 & #3). We used the median degradation rate at 20 °C (k_{20}) value for TN degradation given by Kadlec & Wallace (2009), i.e. 21.5 m/yr.
- **First-order kinetics with non-zero background concentrations:** A background concentration (C^*) was used to set a limit to the degradation reaction. This approach considers processes that prevent complete removal, such as the transformation of some compounds into others, desorption or washing out of particles from the bottom (Carleton & Montas 2010). We compared C^* of 1.5 mg/L as a reference value (Kadlec & Wallace 2009), and 3.7 mg/L, the lowest measured value of TN at the outlet of Event 1. An additional simulation with a background concentration of 6.3 mg/L was done for Event 2.
- **Monod kinetics:** The Monod equation assumes non-linear growth limited, for example, by a finite substrate or the presence of inhibitory substances. It was used only for CSTR and TIS models. The saturation coefficient (k_s) was set to 0.5 g/m^3 as in the model developed by Langergraber & Simunek (2005), and the maximum reaction rate ($k_{o,\ max}$) they used for denitrification ($k_{o,\ max} = 1\ d^{-1}$) was used to calculate the areal rate constant of total nitrogen degradation as indicated by Kadlec & Wallace (2009).

The effect of temperature was considered in the first-order kinetics with zero and non-zero background concentration using the Arrhenius equation with a temperature correction factor (θ) of 1.056 (Kadlec & Wallace 2009).

RESULTS AND DISCUSSION

Hydrological behaviour

A water balance approach was used in order to evaluate Events 1 and 2. Figure 2 shows the measured data during both events whereby the white areas represent the period considered for the evaluation. Rainfall before Event 1 raised the water level to 10 cm height (Figure 2(a)). Subsequently, the recorded water level in Event 1 rose to 50 cm for 5 days, although the theoretical maximum water level in the wetland was 40 cm. However, no outflow was observed until about 10 days after the inflow began. This was due to changes in the operation of the FWS wetland during this period, which resulted in changes in the outflow and water level. Unexpected outcomes are common in long-term data sets of real systems, as it is difficult to have absolute control, compared to systems under controlled conditions in the laboratory or at a small scale in the field. This led us to use the water balance to simulate the water level and the outflow as another model variant (#3: unsteady-state conditions with simulated data). Before Event 2, the FWS wetland was completely dry and took some time to respond to the inflow as expected (Figure 2(b)).

The outflow/inflow ratio, i.e. the proportion of input water leaving the FWS wetland through the outlet, for Event 1 was 77%, and the mass retention rate of TN was about 36%. During Event 2 the outflow/inflow ratio was only 36%, while the mass retention rate of TN was 74%. This can be explained by the fact that in Event 2 there were days with no outflow between water inflows, increasing the hydraulic retention time in the wetland and therefore TN removal. In their study, Lavrnic *et al.* (2018) reported an irregular water flow in the wetland with yearly outflow/inflow ratios between 9 and 65%. They attributed the water losses to high evapotranspiration during the summer months and infiltration through the bottom and the wetland walls. A considerable amount of water could be retained in the soil matrix. This is particularly important in large wetlands, such as the one used for this study. Being a nature-like system, there may also be present preferential flows formed by the root

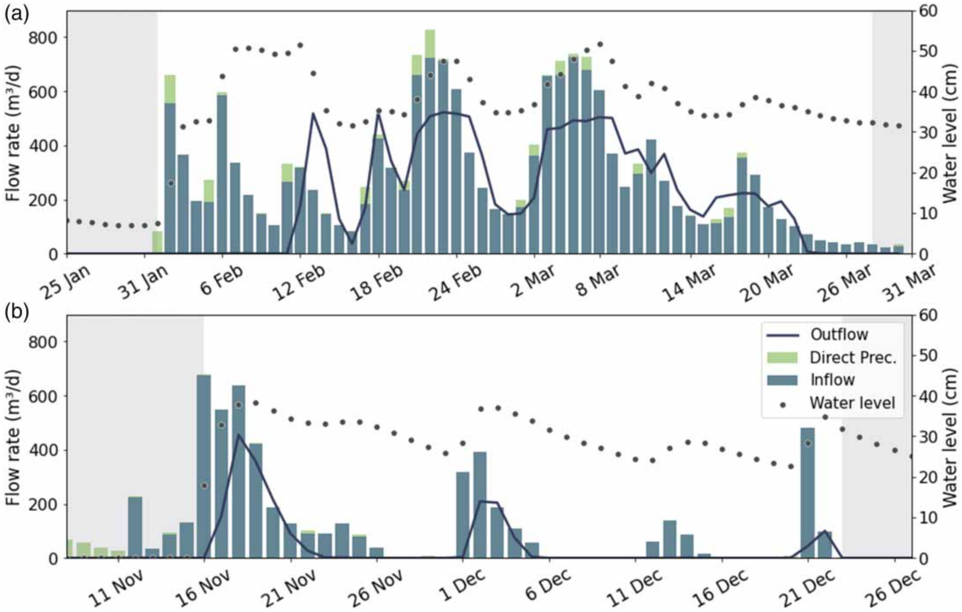


Figure 2 | Overview of measured inflows (inflow and direct precipitation) and outflows (m^3/d) and water level (cm) in the wetland during Event 1 (a) and Event 2 (b). The white area represents the period considered in the models (Event 1: 01st Feb 2018–29th Mar 2018; Event 2: 17th Nov 2019–24th Dec 2019).

system, by the presence of macroinvertebrates in the soil or by cracks formed during dry periods. However, soil storage capacity and preferential flows were neglected in our study to keep the model simple.

The measured and simulated values of the water level and outflow during and after Event 1 are plotted in Figure 3. The measured water level has more fluctuations than the simulated water level, which remains below the maximum wetland level, i.e. 40 cm. From the 24th of March onwards, no further inflows or rainfall were measured, and the steady decline in water level was due to infiltration and evapotranspiration in April, when the growing season of *Phragmites australis* began. The decrease was very similar in measured and simulated water levels, and when evapotranspiration was considered, the simulated water level reached the measured values. It is therefore important to take evapotranspiration into account in simulations during warm periods of year.

As shown in Figure 3(b), the simulated outflow started earlier, correlating with the rise in water level. Additionally, the peaks are higher than those of the measured outflow. This can be explained by the fact, that soil storage and other infiltration

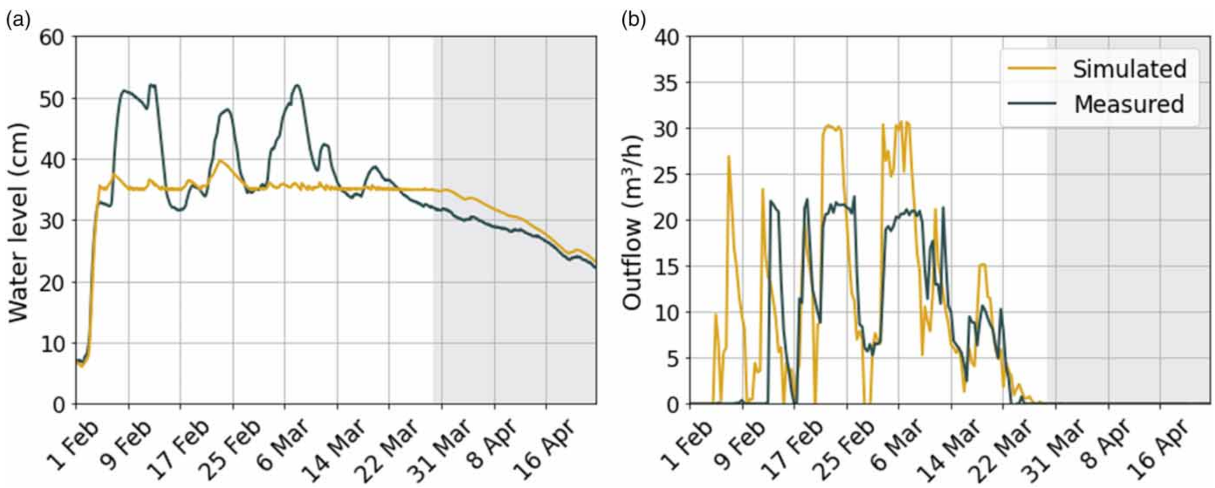


Figure 3 | Measured and simulated water level (a) (cm) and outflow (b) (m^3/h) in the wetland during and after Event 1. The white area represents the period included in the models: 01st Feb 2018–29th Mar 2018.

through preferential flows have not been accounted for, the recovery rate using the simulated data would be 100%. Since the simulated outflow of Event 1 started earlier and ended later than the measured values, the evaluation period for this event was extended by a few days for a model comparison covering the whole event.

Figure 4 shows the measured and simulated water level and outflow during Event 2. At the beginning of the event, there was a rapid rise in water level followed by a drop of more than 10 cm in 13 days in the measured values. In contrast, the decline is not as pronounced in the simulated water level. This indicates that in the water balance some processes have not been considered or have been underestimated, such as water storage in the soil or the infiltration rate. It is unlikely that the decrease was due to evapotranspiration since the event occurred between November and December. The simulated outflow was also higher than the measured outflow and lasted longer, similar to Event 1.

Residence time distribution in the hydraulic models

The use of RTD was threefold; (1) to calculate the HRT from the tracer experiment, (2) to find the best-fit parameter values for the transport models, and (3) to model the degradation of pollutants under unsteady conditions in the PFD model. The HRT estimated by the tracer experiment was 6.7 days, as indicated by Lavrnic *et al.* (2020a). This value was used to determine the best-fit parameters in the hydraulic models; the number of tanks-in-series (N) for the TIS model and the Peclet number (Pe) for the PFD model.

TIS model

For an HRT of 6.7 d, the estimated number of tanks was 14, when calculated with the HRT and the variance of the RTD curve. Minimising the RMSE of the RTD curve resulted in an HRT of 8.4 d (RSME of 14.23 mg/L). However, Lavrnic *et al.* (2020a) reported a better fit with 3.78 tanks in series. The mean values reported in the literature for N values in FWS wetlands are 4.1 ± 0.4 (Kadlec & Wallace 2009). In their study, Persson *et al.* (1999) reported N values between 1.3 and 10, depending on the wetland configuration. In our study, we included 4, 8 and 14 tanks in series to evaluate the model performance with different N in both events.

Figure 5 shows the RTD curves created for different N and the tracer concentrations measured during the experiment. The result for $N = 14$ was more similar to the measured tracer data, although the HRT does not fit the peak of the curve. This tends to occur in wetland systems, where there may be flows with different retention times. In their study, Lavrnic *et al.* (2020a) reported a hydraulic efficiency (e_v) of 0.79 and an effective volume ratio of 0.71, indicating that approximately one-quarter of the wetland did not participate in the active flow.

Plug-flow with dispersion model

The calibration of the PFD model resulted in a Pe of 25 ($D/uL = 0.04$) for an HRT of 6.7 d, with a RMSE of 10.99 mg/L, the minimum among all hydraulic models applied. The RTD curve fits best at the peak and at the end of the tracer concentration

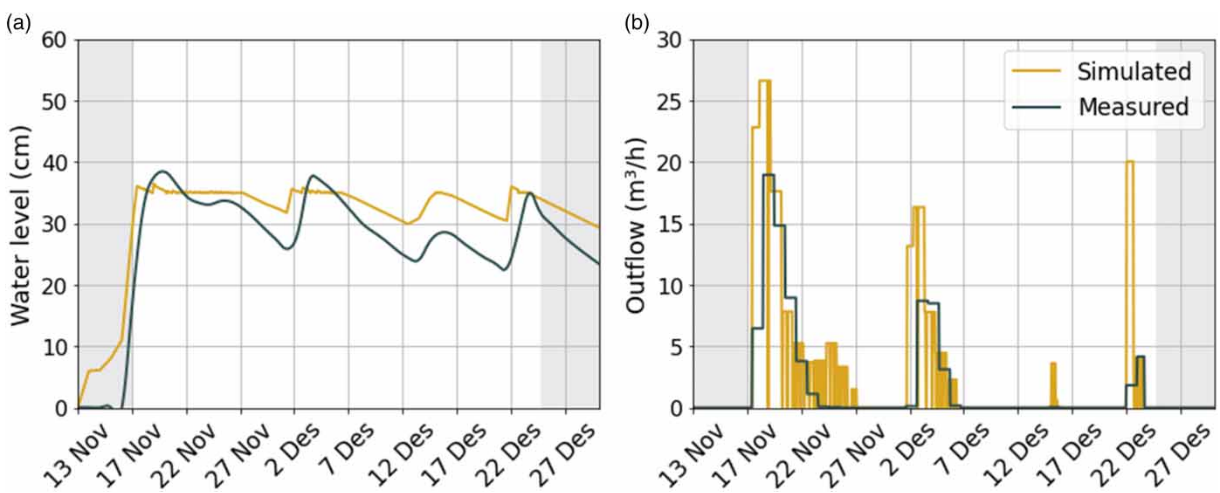


Figure 4 | Measured and simulated water level (a) (cm) and outflow (b) (m^3/h) in the wetland in Event 2. The white area represents the period included in the models: 17.11.2019–24.12.2019.

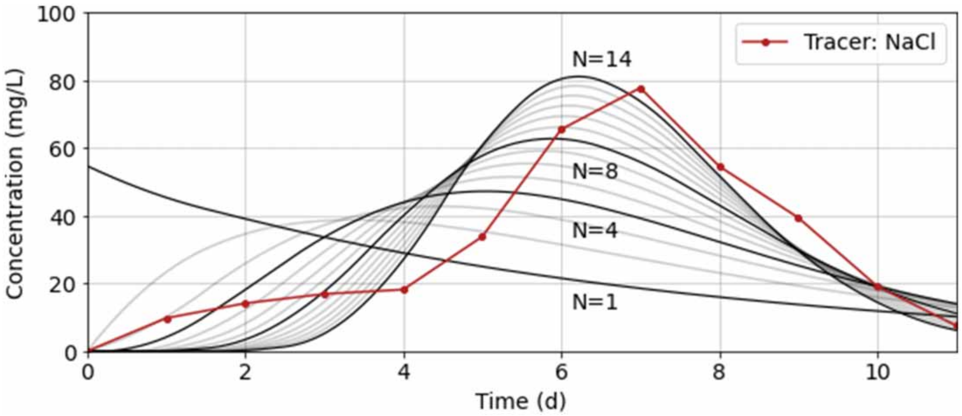


Figure 5 | Residence time distribution curves for the tanks-in-series (TIS) model with different numbers of tanks (N) and the measured tracer concentration.

curve but does not seem to fit well at the beginning of the experiment (Figure 6). The results of both models indicate that the wetland had two distinguishable flows: one that arrived earlier to the outlet and could be emulated by a TIS model and another with a longer retention time that could be described as a near-plug flow.

Performance of models for total nitrogen removal

Comparison of hydraulic models

Table 1 gives the RMSE values obtained from the comparison of measured and simulated data for Event 1 and Event 2. All hydraulic models were able to model Total Nitrogen transport with RMSE values between 2.06 and 5.48 mg/L for Event 1 and between 3.17 and 10.62 mg/L for Event 2. The nominal HRT for Event 1 and 2 were 4.7 d and 5.1 d and were used in the PFD model under steady-state conditions (#1). The measured values are represented in the figures as *plateaus* because they were flow- and time-proportional.

When comparing the CSTR and TIS models, CSTR always had higher RMSE values in the first-order degradation kinetics during Event 1. The difference could be attributed to the sharp increase of effluent TN concentration in the CSTR model at the beginning of the event (Figure 7(a)). CSTR models a single tank and assumes instantaneous, complete mixing, and hence the concentration increased immediately at the beginning of the event. This occurred regardless of the degradation model used. By contrast, during Event 2, the modelling of solute transport with a single tank led to better results in most simulations compared to TIS with 4, 8 and 14 tanks-in-series. However, a visual analysis shows that the difference is very small. A better fit was obtained with the TIS models, particularly with $N = 14$ and non-zero background concentrations (Figure 7(b)).

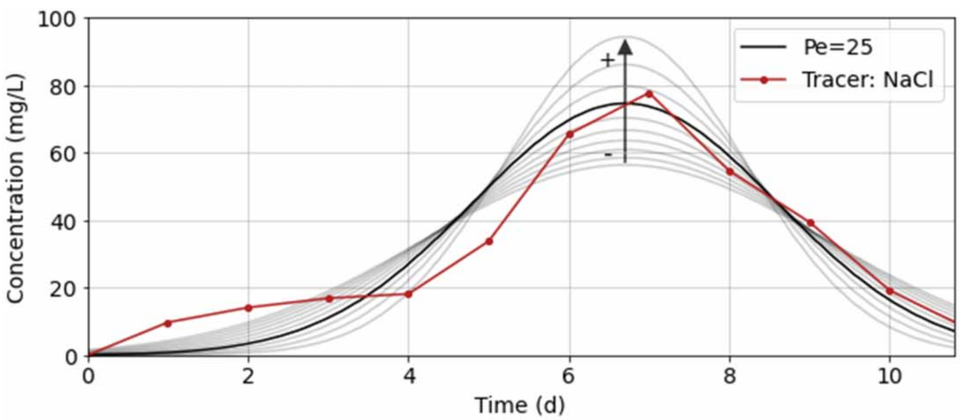


Figure 6 | Residence time distribution curves for the plug-flow with dispersion (PFD) model with a hydraulic retention time of 6.7 d and the measured tracer concentration. The black line indicates the curve with the best fitting Peclet number ($Pe = 25$). The arrow points out the change in the shape of the distribution curve as Pe increases.

Table 1 | Root mean squared error (RMSE) values during Event 1 and Event 2 with the combinations of hydraulic and degradation models

				Event 1			Event 2		
				#1	#2	#3	#1	#2	#3
Degradation model	**Hydraulic model**	**C* mg/L**	**N –**	**RMSE (mg/L)**					
1st order kinetics	CSTR	0	1	2.72	4.95	2.95	4.90	4.13	5.15
	TIS		4	2.36	3.31	2.55	5.19	4.34	5.85
	TIS		8	2.38	2.92	2.59	5.33	4.60	6.19
	TIS		14	2.42	3.28	2.64	5.52	4.82	6.48
	PFD		∞	2.10	5.19	4.78	7.96	10.44	10.62
1st order with non-zero background concentration	CSTR	1.5	1	2.79	5.13	2.96	4.41	3.99	4.68
	TIS		4	2.30	3.51	2.43	4.51	3.67	5.09
	TIS		8	2.28	2.91	2.43	4.60	3.77	5.37
	TIS		14	2.29	3.00	2.46	4.76	3.89	5.64
	PFD		∞	2.06	5.16	4.72	7.14	10.22	10.36
	CSTR	3.7	1	2.99	5.48	3.12	3.88	4.19	4.17
	TIS		4	2.48	4.00	2.48	3.69	3.37	4.14
	TIS		8	2.43	3.22	2.42	3.68	3.21	4.32
	TIS		14	2.40	2.98	2.42	3.78	3.17	4.53
	PFD		∞	2.13	5.21	4.72	6.02	9.90	9.99
Monod kinetics	CSTR		1	2.14	4.11	2.74	5.09	7.44	5.28
	TIS		4	2.17	3.50	2.56	4.94	4.97	5.86
	TIS		8	2.38	3.78	2.69	5.06	5.60	6.21
	TIS		14	2.52	4.46	2.76	5.30	6.26	6.55

C^* is the background concentration; N is the number of tanks-in-series.
Hydraulic models: Continuous-stirred tank reactor (CSTR), tanks-in-series (TIS), plug-flow with dispersion (PFD).
Model variants: steady (#1) and unsteady-state conditions using measured (#2) and simulated (#3) water level and outflow data.

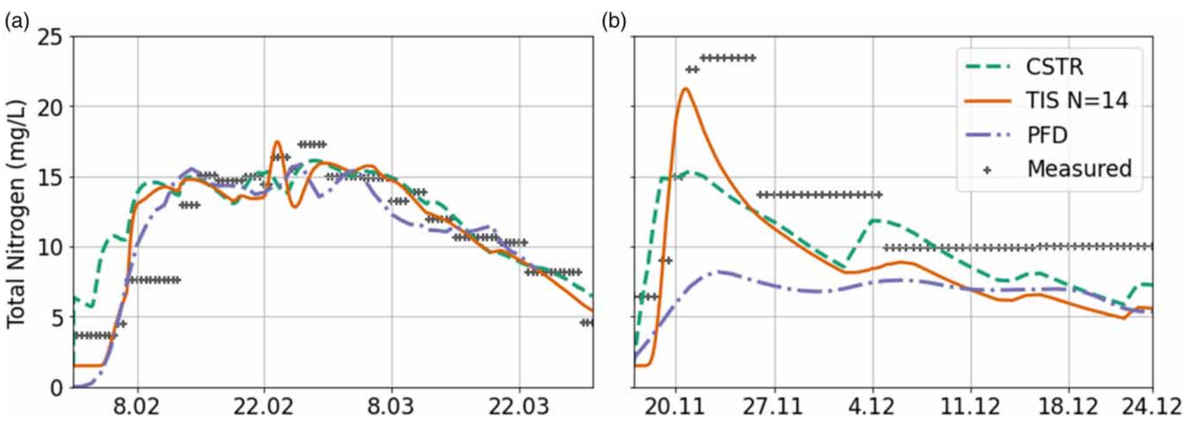


Figure 7 | Measured and simulated total nitrogen effluent concentrations during Event 1 (a) and Event 2 (b) with continuous-stirred tank reactor (CSTR), tanks-in-series (TIS) ($N = 14$) and plug-flow with dispersion (PFD) models, under steady-state conditions, and first-order degradation kinetics with a background concentration of 1.5 mg/L.

As for the TIS model, a gradual improvement in the simulations was expected to be observed as N increased due to the large length to width ratio of the wetland. However, the number of tanks-in-series in the TIS model did not significantly improve in Event 1. At the beginning of the event, the simulated effluent concentration increased faster than the measured concentration in all simulations. In contrast, the simulated concentrations were close to the measured values during and at the end of the event (Figure 7(a)). Likewise, the differences in RMSE values between 4, 8 or 14 tanks-in-series in Event 1 were small, with standard deviations of 0.02 mg/L, 0.29 mg/L and 0.03 mg/L for variants #1, #2, and #3, respectively. During Event 2, the differences with different N in TIS, and in hydraulic models, in general, are more pronounced. The standard deviations were also slightly larger than in Event 1 (0.09 mg/L, 0.13 mg/L and 0.22 mg/L), with the lowest RMSEs in the models with $N = 4$. However, in both events, it was observed that with a background concentration of 3.7 mg/L, the RMSE value decreased with an increase of N. The FWS wetland used for this study had an elongated shape (L:W = 52), resulting in good hydraulic efficiency ($e_v = 0.79$), so it was expected to perform better for a $N = 14$. In the design of newly constructed or modified FWS wetlands, the hydraulic efficiency can be improved by lengthening the wetland or by adding barriers or other elements within the wetland (Persson *et al.* 1999). Depending on the wetland configuration, a different N could be assumed in the TIS model (Wong *et al.* 2006).

The differences in the PFD model are more noticeable between the events. During Event 1, the PFD model under steady-state conditions (#1) was able to simulate the TN concentration at the wetland outlet with RMSE values of 2.10 ± 0.03 mg/L, the lowest of all combinations and of both events, whereas in Event 2, the PFD model showed the worst performance for all variants and degradation models with RMSEs of 9.18 ± 1.60 mg/L. As shown in Figure 7(b), the simulated output concentration in Event 2 was much lower than the measured concentration and did not even follow sits pattern. The difference between events lies in the outflow rate and intermittency that were a consequence of different precipitation. As seen previously, the outflow in Event 1 was continuous, while in Event 2 it was intermittent. It is precisely the stochastic inputs to the FWS wetlands that treat agricultural runoff that pose a constraint to the PFD model. Irregular inflows lead to different flow velocities affecting dispersive transport, which differ greatly from event to event. This was noticeable when comparing the RTD curve of the tracer experiment with the events. In the tracer test, the lowest RMSE (10.99 mg/L) was obtained for a HRT of 6.7 d with a Pe of 25. However, in Event 1, a better fit could be achieved for a Pe of 1.02 (HRT = 4.7 d; $C^* = 3.7$ mg/L), resulting in RMSE of 1.27 mg/L. Conversely, during Event 2 the Pe resulting from the tracer test was too small, and the RMSE decreased to 3.92 mg/L for a Peclet number of 1335 under steady-state conditions. This confirms that the use of PFD would not be appropriate to model intermittently fed FWS wetlands, even when their configuration resembles a channel.

Steady and unsteady state conditions

The differences between the models depended largely on the state conditions. Under unsteady-state conditions, as opposed to steady-state, fluctuations increased and were not able to simulate the outflow concentration. In Event 1, all models showed better performance under steady-state conditions (#1), followed by unsteady state conditions with simulated water level and outflow (#3), and unsteady conditions with measured data (#2) (Figure 8(a)). In the TIS model, #2 variant had a sharp increase at the beginning, which could not resemble the concentration observed in the wetland. The great peak of TN corresponded to a drastic decrease in the measured water level in the wetland that lead to the concentration of this element in available water volume. Although we used an areal rate constant k_A in the degradation models, the concentration in #2 and #3 was calculated as the mass divided by the volume, which was determined by the water level. Thus, the decrease in water level reduced the degradation of TN and increased the concentration at the outlet. Compared to #1, variant #3 had a slightly lower outflow concentration, which can be attributed to the mass infiltrating into the ground.

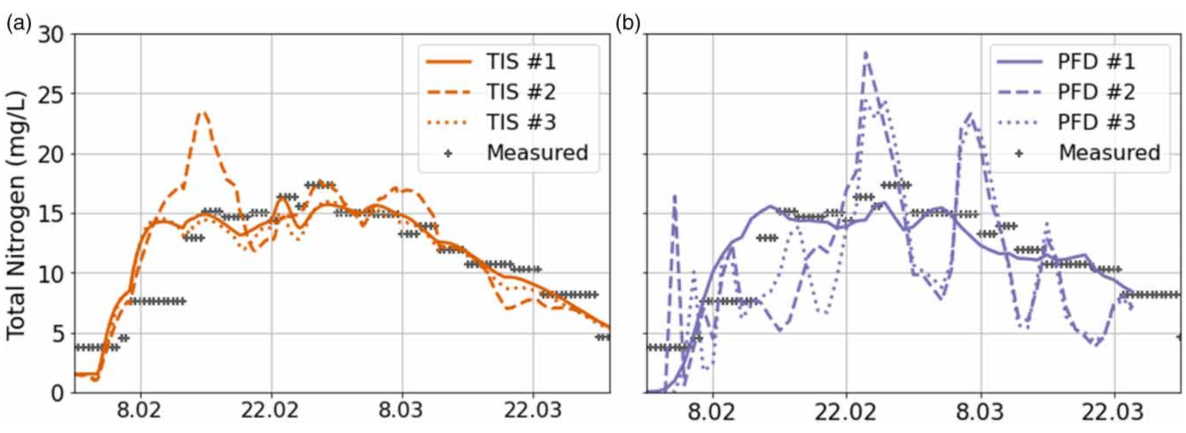


Figure 8 | Measured and simulated total nitrogen effluent concentrations in Event 1 with tanks-in-series (TIS) ($N = 4$) (a) and plug-flow with dispersion (PFD) (b) models under three variants of state conditions: steady-state (#1), unsteady-state with measured (#2) and simulated water level and outflow (#3). The degradation kinetics is first-order with a background concentration of 1.5 mg/L.

In TIS model variant #3, the simulated wetland water level values smoothed the curve and minimised the changes in water level. Nevertheless, this improvement was not as pronounced in variant #3 with the PFD model (Figure 8(b)). In fact, all PFD model simulations under unsteady-state conditions (#2 & #3) resulted in large fluctuations in the effluent concentration that correlated with the input volumes. This can be explained by the influence of the inflow rate on the HRT calculated at each time step, where high inflow rates resulted in lower HRT, entailing a reduction in TN degradation. This supports the findings of Kadlec (2000), who concluded that the calibrated k values tend to increase in the PFD model as HRT decreases.

In contrast to Event 1, the TIS model under unsteady-state conditions (#2) in Event 2 resulted in lower RMSE values for the TIS model (Table 1). However, Figure 9(a) shows the numerical instability in variant #2. This may be due to the high hydraulic variability of this event, with three main discharges and zero outflow in between. Reducing the time step would likely lead to a more stable numerical solution.

Concerning the PFD model in Event 2, none of the variants could model the TN concentration at the wetland outlet, as seen in Figure 9(b). The steady-state variant #1 could simulate output concentrations of the same order of magnitude by increasing Pe. Increasing Pe in #2 and #3 increased the oscillation of the curve, further worsening the result (data not shown).

Comparison of degradation models

All degradation models were able to simulate the increase in concentration, the peak platform and the decrease in Event 1. However, in Event 2, total nitrogen degradation was overestimated in all simulations. The first-order rate constant k was shown to be valid for different events when the effect of temperature was corrected with the Arrhenius equation, even if only air and not water temperature data were available.

Among the degradation models, the Monod-type kinetic gave the best results for Event 1, with the lowest RMSEs in CSTR and TIS with $N = 4$ under steady conditions (Table 1). This was due to a less pronounced increase of the output concentration in the first part of the event compared to the first-order kinetics, as observed in Figure 10. The first-order degradation model, with and without background concentration, simulated a rapid increase in TN concentration at the wetland outlet at the beginning of the event. During the event, an increase of 1 mg/L in the background concentration translated into an increase of approximately 3% in the output concentration. However, the most noticeable difference in the simulated TN concentration was observed rather after Event 1 (since the 29th of March). In Figure 10, the simulations were extended by one month (shaded area). It shows that the combined effect of the first-order degradation kinetics with a background concentration of 3.7 mg/L reproduced the behaviour of the FWS wetland during the latter part of the event, while Monod-type kinetics dropped to zero a few days after the event. In this case, we took the minimum concentration observed in the data set as the background concentration (3.7 mg/L), but this data is not always available. Even so, adding a C^* of 1.5 mg/L resulted in lower RMSE values than the first-order kinetics with zero background concentration.

In Event 2, the first-order degradation model gave better results regardless of the hydraulic model and state conditions, especially when the background concentration was 3.7 mg/L. Interestingly, an additional simulation for Event 2 with a

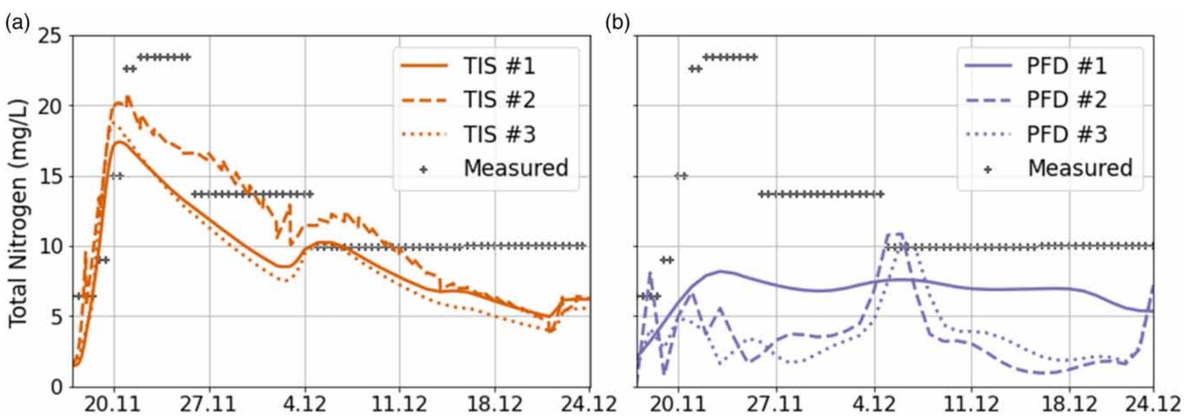


Figure 9 | Measured and simulated total nitrogen effluent concentrations in Event 2 with tanks-in-series (TIS) (a) ($N = 4$) and plug-flow with dispersion (PDF) (b) models under three variants of state conditions: steady-state (#1), unsteady-state with measured (#2) and simulated water level and outflow (#3). The degradation kinetics is first-order with a background concentration of 1.5 mg/L.

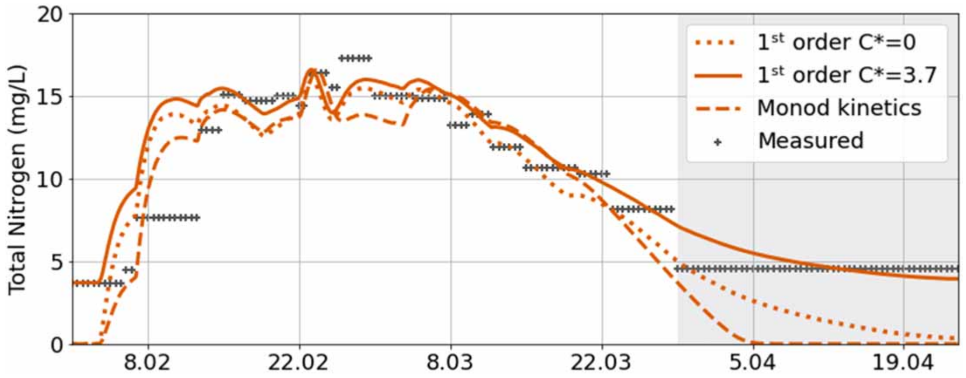


Figure 10 | Measured and simulated total nitrogen effluent concentrations in Event 1 with first-order degradation kinetics with zero and non-zero background concentrations (C^*) and Monod kinetics. The hydraulic model is a tanks-in-series (TIS) model under steady-state conditions ($N = 4$). The shaded area indicates the extended period.

higher background concentration ($C^* = 6.3$ mg/L, the lowest concentration during the event) in the TIS model was shown to improve the performance of the model by 20%. The best fit in the TIS model was observed when $N = 14$ (RMSE = 3.08 mg/L). The above shows that the optimal background concentration was different for each event, which could be considered a limitation of the model. Nevertheless, it can be exploited in the model by setting performance limits at different loading conditions using different background concentrations.

In his study, Kadlec (2000) reported that C^* was very close to zero for compounds such as ammonium and nitrate but not for organic nitrogen. In our study, total nitrogen was modelled, which encompasses both nitrogen compounds, so the high C^* value could be due to the proportion of organic nitrogen. Indeed, in the water samples analysed from the inlet, nitrate accounted for 50–90% of the total nitrogen. The highest percentage (90%) was observed when TN concentration was higher, and the lowest (50%) at the end, when TN concentration was lower and the influence of C^* was greater (Figure 10).

CONCLUSIONS

Based on the results of evaluating the model combinations for Events 1 and 2, the following conclusions can be drawn:

- The TIS model proved to be more robust than the CSTR and the plug-flow with dispersion models. Thus, the TIS model is recommended for wetland design, even if the wetland has a large aspect ratio (e.g., as in this study, 52:1).
- The number of tanks, N, will depend on the configuration of the FWS wetland to be designed. The TIS model with $N = 14$ was able to simulate both events well in the FWS wetland modelled in this study, which was quite long. For rather rectangular or uneven FWS wetlands, N close to 4 can be used.
- Although the system has event-dependent inputs (i.e. unsteady-state conditions), the models under steady-state conditions were able to better simulate the total nitrogen outlet concentration of the FWS wetland. The use of simulated outflow and water level data also gave very good results with the TIS model, with an hourly time discretisation.
- Depending on the environmental conditions and purpose, it may be appropriate to use steady or unsteady-state conditions for design purposes. For example, if we expect large evapotranspiration losses or a high infiltration rate, it is desirable to use unsteady-state conditions with simulated data (as in #3 of this paper).
- The first-order kinetics with non-zero background concentration showed the best performance among the degradation models.
- Optimal background concentration varied between events for the same FWS wetland. For the design model, an appropriate background concentration should be included, or a range with lower and upper thresholds can be defined to describe the variability of treatment performance of the FWS wetland.
- The background concentration thresholds should be further explored, as both the current and previous environmental conditions of the FWS wetland (e.g. long periods of drought previous to the event) may influence the background concentration. A background concentration of 1.5 mg/L can be used as a lower limit.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST STATEMENT

The authors declare there is no conflict.

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