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CWM1 implementation in RetrasoCodeBright: First results using horizontal subsurface flow constructed wetland data

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ABSTRACT

Constructed Wetland Model No. 1 (CWM1) processes were implemented within RetrasoCodeBright (RCB) to simulate hydraulics and reactive transport as well as the main biodegradation and transformation processes in horizontal subsurface flow constructed wetlands (SSF CWs). New values for some stoichiometric and kinetic coefficients were determined in the calibration step in order to obtain more realistic biochemical transformation and degradation processes. The model was checked and then tested for a horizontal SSF CW operating with different hydraulic loading rates [20, 36 and 45 mm/d]. Modifications to the CWM1 formulation had a negligible effect on the good fitting of measured and simulated data. However, changes in stoichiometric and kinetic parameters positively affected performance. Bacterial concentrations defined as initial conditions proved to be a variable requiring attention in the calibration. In terms of pollutant concentrations in effluent, simulated data corresponded well with data measured in most cases evaluated. The quality of the results obtained suggests that CWM1-RETRASO, the resulting model, is a potential tool for studying hydraulics, reactive transport and the main biochemical transformation and degradation processes for organic matter, nitrogen and sulphur in horizontal SSF CWs.

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1. Introduction

The use of subsurface flow constructed wetlands (SSF CWs) for treating urban wastewater in small communities is growing rapidly in many regions of the world [1]. However, some aspects of their performance are still unknown because the degradation of wastewater contaminants within these systems takes place through a large number of physical, chemical and biological processes that occur simultaneously. Interactions between water, granular media, macrophytes, litter, detritus and microorganisms add further complexity [2]. All of this hinders the understanding of SSF CWs and clearly shows that their design must take into account a wide set of components. Some authors have highlighted the importance of a sound conception of systems at the design stage in order to avoid unsuitable treatment and a very short life span of the wetlands [2–6].

Modelling allows us to obtain a better understanding of the performance of wastewater treatment systems and to optimise design [7]. SSF CWs have often been considered as "black boxes" [8–11], in which design is carried out by means of the concept of concentration changes of selected parameters at influent and effluent. The removal mechanisms in these systems are not considered, so they provide a limited understanding of the system performance [12]. Therefore, mechanistic models that describe the transformation and elimination processes taking place within constructed wetlands (CWs) have become a promising tool for understanding parallel processes and interactions occurring in wetlands.

The development of mechanistic models describing processes in SSF CWs is relatively new. Several models of varying degrees of complexity have been developed in recent years [13]. The most advanced of these models applied to horizontal SSF CWs are those developed by Langergraber [14], Rousseau [15], Brovelli et al. [16] and Ojeda et al. [2]. Langergraber [14] developed the Constructed Wetland two-dimensional (CW2D), a multi-component reactive transport model that describes the removal of organic matter, nitrogen and phosphorus in both vertical and horizontal SSF CWs. Rousseau [15] developed a mechanistic and dynamic model of carbon, nitrogen and sulphur transformations in horizontal SSF CWs that reflects the competition between bacteria and plants for nutrient uptake, and the competition between microbial groups

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for substrates and electron acceptors. Brovelli et al. [16] implemented a set of biological and biogeochemical reactions (the same as those considered by CW2D) into the three-dimensional numerical simulator PHWAT [17], which was developed for modelling reactive transport in porous media. Finally, Ojeda et al. [2] developed a two-dimensional model based on the finite element code RetrasoCodeBright (RCB) [18]. In this work, RCB was modified to include the most significant biochemical pathways for organic matter transformation and removal: hydrolysis, aerobic respiration, nitrification and denitrification, sulphate reduction and methanogenesis.

Based on previous experiences, in 2009 a general model named the Constructed Wetland Model No. 1 (CWM1) was published with the aim of providing a widely accepted model formulation for biochemical transformation and degradation processes for organic matter, nitrogen and sulphur in SSF CWs [19].

The main objective of this study was to implement CWM1 processes within RCB, a code designed for hydrogeological studies, in order to simulate hydraulics and reactive transport as well as the main biodegradation and transformation processes in horizontal SSF CWs. The result is a two-dimensional (2D) mechanistic numerical model, CWM1-RETRASO, in which CWM1 provides all knowledge related to biochemical processes and RCB code adds the knowledge related to reactive transport and flow properties. The implementation steps and the results of the calibration and validation are presented here. In the discussion section the limitations of the resulting model are described.

2. Materials and methods

2.1. Model implementation

The resulting 2D simulation model, called CWM1-RETRASO, was obtained from the coupling of RCB code and CWM1. RCB is, in turn, a coupling of the former reactive transport code RETRASO [20] with the multiphase flow and heat code CodeBright [21].

2.1.1. RCB code

RCB is a powerful modelling tool that has been successfully applied in various hydrogeological studies. The code formulates the flow problem in a multiphase approach, which includes porous media composed of solid grains, water and gas. It also enables the simulation of the reactive transport of inorganic dissolved and gaseous species in non-isothermal saturated and unsaturated problems by finite elements [18,22,23]. The transport of solutes in water is modelled by means of advection, dispersion and diffusion, together with chemical reactions. Advective flux and dispersive and diffusive fluxes are computed by means of Darcy's and Fick's laws, respectively. However, it is worth noting that the dispersive term generally dominates in the liquid phase, whereas the diffusive term does so in the gas phase [20,24].

For the numerical solution of the reactive transport equations, RCB uses the direct substitution approach [20], which consists in substituting the chemical reactions in the transport equations and solving them simultaneously, usually by means of the Newton–Raphson method. The code can use one-, two- or three-dimensional finite element grids.

2.1.2. CWM1

CWM1 is a biokinetic model that describes biochemical transformation and degradation processes for organic matter, nitrogen and sulphur that take place in SSF CWs. It has 16 components (8 soluble and 8 particulate) (Table 1) and 17 processes that can occur in aerobic, anoxic and/or anaerobic conditions [19]. CWM1 considers the most relevant biokinetic processes occurring in both horizontal and vertical SSF CWs, which take place depending on wetland characteristics and operation conditions. In general, vertical SSF CWs favour aerobic processes, whereas horizontal SSF CWs favour anaerobic processes [19,25,26].

CWM1 is presented in a matrix notation similar to that of Activated Sludge Models (ASMs) [27]. As in the ASMs, kinetic expressions are based on switching functions (hyperbolic saturation terms, inhibition terms and Monod equations). Lysis processes are modelled using first-order decay rates. The values for kinetic and stoichiometric parameters given by the model are mainly obtained from the literature.

The main objective of CWM1 is to predict effluent concentrations without predicting gaseous emissions. Therefore, gases produced in several of the reactions considered, such as methane and dinitrogen, are not considered as model components. Phosphorus is also not considered because microbial reactions play a minor role for phosphorus removal in SSF CWs. As a consequence, phosphorus concentration is assumed to be non-limiting for microbial growth. Neither does the model consider processes with iron and hydrogen as electron acceptors, which can be neglected according to Burgoon [28]. More details on model formulation can be found in the original description of the model [19].

2.1.3. CWM1-RETRASO simulation model

In the present case, in order to implement CWM1 in RCB, the original RCB code was modified to include all the bacterial reactions described in CWM1, which were considered to be the most significant microbial reactions involved in contaminant transformation and removal in horizontal SSF CWs.

The implementation of the biochemical processes within RCB code consisted of adding the rates relevant to CWM1 to the reaction term of the RCB mass balances (Eq. (1)):

$$\frac{\partial C}{\partial t} = -q\nabla C + \nabla(D\nabla C) + r \tag{1}$$

where C is the component concentration [M M$(H_2O)^{-1}$], t is the time [s], the first term refers to the advective flux [M T^{-1} L^{-2}], the second term refers to the diffusive-dispersive fluxes [M T^{-1} L^{-2}] and the third term refers to the reaction term [M T^{-1} L^{-2}].

The reactive transport model of the present study basically consists of 19 reactions or processes instead of the 17 described by CWM1. This is essentially due to the RCB architecture, which only permits kinetic rate law formulation based on Monod kinetics in accordance with Eq. (2):

$$r = \prod_{m=1}^{Nm} fm \tag{2}$$

where r is the rate, Nm is the number of terms of the expression, and fm is a term of the expression. Each fm can be one of the three types described in Eqs. (3)–(5), depending on their function in kinetic rates (p-order, catalysis and inhibition factors, respectively):

$$fm = km \prod_{i=1}^{Ni} Ci^{p_{im}} \tag{3}$$

$$fm = \frac{\prod_{i=1}^{Ni} Ci^{p_{im}}}{km + \prod_{i=1}^{Ni} Ci^{p_{im}}} \tag{4}$$

$$fm = \frac{km}{km + \prod_{i=1}^{Ni} Ci^{p_{im}}} \tag{5}$$

Table 1
Definition and units of the components considered within CWM1. Concentrations of soluble components are characterized by S_i and particulate components by X_i. All different microorganisms are considered particulate components and are referred to as bacteria only. Organic nitrogen is considered as a fraction of organic matter (COD). M refers to mass and L to volume units, respectively.

Components [units]	Definition	Components [units]	Definition
S_O [M(O_2) L^{-3}]	Dissolved oxygen	X_S [M(COD) L^{-3}]	Slowly biodegradable particulate COD
S_F [M(COD) L^{-3}]	Fermentable, readily biodegradable soluble COD	X_I [M(COD) L^{-3}]	Inert particulate COD
S_A [M(COD) L^{-3}]	Fermentation products as acetate	X_H [M(COD) L^{-3}]	Heterotrophic bacteria
S_I [M(COD) L^{-3}]	Inert soluble COD	X_A [M(COD) L^{-3}]	Autotrophic nitrifying bacteria
S_{NH} [M(N) L^{-3}]	Ammonium and ammonia nitrogen	X_{FB} [M(COD) L^{-3}]	Fermenting bacteria
S_{NO} [M(N) L^{-3}]	Nitrate and nitrite nitrogen	X_{AMB} [M(COD) L^{-3}]	Acetotrophic methanogenic bacteria
S_{SO_4} [M(S) L^{-3}]	Sulphate sulphur	X_{ASRB} [M(COD) L^{-3}]	Acetotrophic sulphate reducing bacteria
S_{H_2S} [M(S) L^{-3}]	Dihydrogensulphide sulphur	X_{SOB} [M(COD) L^{-3}]	Sulphide oxidising bacteria

where *km* is the rate constant, *Ni* is the number of species in solution, *Ci* is the concentration of the *i*th species solution and p_{im} is a parameter.

Because the formulation of the term of the heterotrophic bacteria process rates that relates S_F to S_A in aerobic and anoxic conditions in CWM1 does not fit with that of RCB, the implementation of these process rates as described in Langergraber et al. [19] was not possible. The same happened with the formulation of the second and third terms of the hydrolysis process rate. Accordingly, aerobic and anoxic growth of X_H on S_F and on S_A processes were modified to implement them in the model. The solution was to divide the heterotrophic bacteria group into two subgroups according to the substrate they consume in order to grow. Thus, X_H was divided into X_{HF} and X_{HA}, depending on whether they consume S_F or S_A, respectively. The resulting process rates are shown in Table 2. This subdivision subsequently affected the hydrolysis rate related to X_H, which was assumed to be only conducted by X_{HF}. The rate of the X_H lysis process was also modified as shown in Table 2. Therefore, two lysis rates for heterotrophic bacteria are considered within CWM1-RETRASO, one for X_{HF} and the other for X_{HA}. On the other hand, the formulation problem for the hydrolysis process was solved by including two process rates separately: one related to the heterotrophic bacteria (X_{HF}) and one related to the fermenting bacteria (X_{FB}) (Table 2). The variables X'_{HF} and X'_{FB} were defined as constants. A mean value corresponding to the heterotrophic and fermenting bacteria concentrations inside the wetland were obtained by trial and error during calibration [200 mg COD_{BM}/l for both] and were then added to the model.

Most of the stoichiometric and kinetic parameter values described in CWM1 were adopted in our model, with the exception of that outlined above and of several related to the growth of fermenting bacteria. In this case, the stoichiometric factor $\nu_{5,9}$ for ammonia was modified (Eq. (6)) because the original expression of the factor $\nu_{5,9}$, once its value was calculated, referred to ammonia generation rather than consumption in the growth of X_{FB} (Table 3). The original expression was modified as follows:

$$\nu_{5,9} = -i_{N,\,BM} \tag{6}$$

where $i_{N,BM}$ refers to the nitrogen content of biomass [0.07 g N/g COD_{BM}]. This value was obtained by trial and error. Moreover, the values of the saturation/inhibition coefficient for S_O (K_{OFB}) and the saturation/inhibition coefficient for S_{NO} (K_{NOFB}) were decreased from 0.2 to 0.002 mg O_2/l and from 0.5 to 0.005 mg N/l, respectively. The original values were checked in the verification and calibration steps and showed that the effects of inhibition terms must be increased because the growth of X_{FB} seemed not to be influenced by the presence of S_O or S_{NO}. With the new values, results from the growth of X_{FB} process verification and calibration tests were satisfactory (Table 3). In these tests only the process of growth of the X_{FB} was considered and the other processes considered in CWM1-RETRASO were switched off in order to avoid interactions among them.

For the sake of simplicity, oxygen leaking from macrophytes, plant uptake, biofilm development and processes linked to clogging (i.e. solids accumulation) were not considered at this stage of the model implementation. Root oxygen release is a continuing subject of debate in SSF CW research [2]. It is widely accepted that aerobic microsites exist in the granular media of horizontal SSF CWs [29]. However, at present it is generally recognised that wetland plants do not generate enough oxygen to fully remove pollutants from standard urban wastewater [30,31]. For this reason, oxygen leaking from macrophytes was not taken into account. The non-consideration of solids accumulation processes resulted in the model overestimating total COD effluent concentrations. Total COD overestimations were addressed by incorporating a multiplicative exponential function similar to that used by Ojeda et al. [2] for the hydrolysis process in their paper ($e^{-kt/(\tau/4)}$), where k is a dimensionless constant with a value of 1.5 (obtained by trial and error during calibration), t is the hydraulic residence time from the inlet to the location along the length of the wetland [s] and τ is the mean hydraulic retention time (HRT [s]). Physical oxygen transfer from the atmosphere to the water was included in the model.

When CWM1's processes had been implemented in the reaction term of RCB (Eq. (1)), reactive transport reactions with kinetic laws were verified and checked for the 2D problem in saturated media.

2.2. Data for calibration and validation

The data used for calibration and validation were obtained from previous studies conducted at a pilot plant located in Les Franqueses del Vallès (province of Barcelona, Catalonia) from 2001 to 2003 [5,6,32–34]. The system was set up in March 2001 and was constituted by 8 horizontal SSF CWs planted with common reed (*Phragmites australis*). Each wetland was fed with urban wastewater previously treated in an Imhoff tank. The wetlands were operated with different hydraulic loading rates (HLR) [20, 36 and 45 mm/d]. Data from one of these wetlands, C1, were used for calibration and validation.

Wetland C1 was designed with an aspect ratio of 2:1 (with a length and width of approximately 10.3 m and 5.3 m, respectively) and coarse granitic gravel as a granular medium (D_{60} = 10 mm, coefficient of uniformity = 1.6, initial porosity = 41%). The average wetted depth of the wetland was approximately 0.5 m.

The influents of the model are primary effluents. An invariable water density of 1.0 kg/l was assumed in order to simplify calculations.

2.3. Hydraulic calibration and validation

In order to solve the flow problem, the model requires the definition of various aspects such as the mesh, initial water pressure in each node, boundary conditions and hydraulic parameters. The 2D mesh consisted of 960 trapezoidal finite elements (80 columns and 12 rows). The length of the mesh was approximately 10 m for upper

Table 2
Definition of the modified heterotrophic bacteria process rates and the modified hydrolysis process rates within the CWM1-RETRASO model, where μ_{HF} is the maximum aerobic growth rate of X_{HF} on S_F [6 d^{-1}], K_{SF} is the saturation/inhibition coefficient for S_F [2 mg COD_{SF}/l], K_{OH} is the saturation/inhibition coefficient for S_O [0.2 mg O_2/l], K_{NHH} is the saturation/inhibition coefficient for S_{NH} [0.05 mg N/l], K_{H_2SH} is the saturation/inhibition coefficient for S_{H_2S} [140 mg S/l], η_g is the correction factor for denitrification by heterotrophs [0.8], K_{NOH} is the saturation/inhibition coefficient for S_{NO} [0.5 mg N/l], μ_{HA} is the maximum aerobic growth rate of X_{HA} on S_A [6 d^{-1}], K_{SA} is the saturation/inhibition coefficient for S_A [4 mg COD_{SF}/l], b_H is the rate constant for lysis [0.4 d^{-1}], X_{HF} and X_{HA} are the concentrations of the heterotrophic bacteria that consumes S_F and S_A [M(COD) L^{-3}], respectively, k_h is the hydrolysis rate constant [3 d^{-1}], X'_{HF} is the heterotrophic bacteria concentration inside the wetland [200 mg COD_{BM}/l], K_X is the saturation/inhibition coefficient for hydrolysis [0.1 g COD_{SF}/g COD_{BM}], η_h is the correction factor for hydrolysis by fermenting bacteria [0.1], and X'_{FB} is the fermenting bacteria concentration inside the wetland [200 mg COD_{BM}/l]. The description of the other components not discussed here can be found in Table 1.

Processes	Process rates
Aerobic growth of X_{HF} on S_F	$\mu_{HF} * \left[\frac{S_F}{K_{SF}+S_F}\right] * \left[\frac{S_O}{K_{OH}+S_O}\right] * \left[\frac{S_{NH}}{K_{NHH}+S_{NH}}\right] * \left[\frac{K_{H_2SH}}{K_{H_2SH}+S_{H_2S}}\right] * X_{HF}$
Anoxic growth of X_{HF} on S_F	$\eta_g * \mu_{HF} * \left[\frac{S_F}{K_{SF}+S_F}\right] * \left[\frac{K_{OH}}{K_{OH}+S_O}\right] * \left[\frac{S_{NO}}{K_{NOH}+S_{NO}}\right] * \left[\frac{S_{NH}}{K_{NHH}+S_{NH}}\right] * \left[\frac{K_{H_2SH}}{K_{H_2SH}+S_{H_2S}}\right] * X_{HF}$
Aerobic growth of X_{HA} on S_A	$\mu_{HA} * \left[\frac{S_A}{K_{SA}+S_A}\right] * \left[\frac{S_O}{K_{OH}+S_O}\right] * \left[\frac{S_{NH}}{K_{NHH}+S_{NH}}\right] * \left[\frac{K_{H_2SH}}{K_{H_2SH}+S_{H_2S}}\right] * X_{HA}$
Anoxic growth of X_{HA} on S_A	$\eta_g * \mu_{HA} * \left[\frac{S_A}{K_{SA}+S_A}\right] * \left[\frac{K_{OH}}{K_{OH}+S_O}\right] * \left[\frac{S_{NO}}{K_{NOH}+S_{NO}}\right] * \left[\frac{S_{NH}}{K_{NHH}+S_{NH}}\right] * \left[\frac{K_{H_2SH}}{K_{H_2SH}+S_{H_2S}}\right] * X_{HA}$
Lysis of X_{HF}	$b_H * X_{HF}$
Lysis of X_{HA}	$b_H * X_{HA}$
Hydrolysis of X_{HF}	$k_h * \left[\frac{X_S}{K'+X_S}\right] * X_{HF}$ where $K' = X'_{HF} * K_X$
Hydrolysis of X_{FB}	$k_h * \eta_h * \left[\frac{X_S}{K''+X_S}\right] * X_{FB}$ where $K'' = X'_{FB} * K_X$

and lower bases (with a slope of 1%) and its height was 0.6 m and 0.7 m at the inlet and outlet, respectively. Simulations with a mesh of 480 elements (40 columns and 12 rows) were also conducted for comparison.

The values of hydraulic conductivity [14.76 m/d] and water depth at the inlet [0.540 m] and outlet [0.578 m] in the model were determined by trial and error from known water levels. Once the flow model was calibrated, the results of the conservative transport of a solute (bromide) were employed to validate the flow model. The data used came from a tracer test conducted in June 2002 by means of a single-shot injection of KBr into the wetland inlet [33]. During the tracer test the flow to the wetland was set at 2 m^3/d (HLR was approximately 36 mm/d).

2.4. Reactive transport model calibration and validation

The model requires the values of 51 kinetic parameters (16 first-order kinetic constants, 22 half-saturation coefficients and 13 inhibition constants) and 14 stoichiometric parameters. The values of these parameters are available in Langergraber et al. [19]. As reported in the CWM1-RETRASO simulation model section, only 5 of them were modified (K', K'', $v_{5,9}$, K_{OFB} and K_{NOFB}). Their new values were calculated by calibrating the reactive transport model.

The reactive transport model was calibrated using data from 2001 and it was then validated using different sets of data from the experimental campaigns carried out from 2001 to 2003. For each set the influent concentrations were averaged and then used as input for the model. A maximum and minimum for the effluent were determined in order to define a range of data for each variable in each set and to determine whether simulated effluent values fell within these ranges. Due to the low number of sulphate measures available for wetland C1, only two sets of data were considered, corresponding to two experimental campaigns carried out in the summer and winter of 2003 [5]. The reactive transport model was calibrated in a quasi steady-state due to RCB limitations, which only permit the simulation of a constant influent (constant flow and constant composition).

3. Results

3.1. Simulation of hydraulic factors

The outlet was defined by three nodes, whose flux problem boundary conditions were determined by partial pressures [0.1058871, 0.1051778 and 0.1044685 MPa]. Together with the partial pressures of each node in the meshes, these were essential for calibrating the hydraulic problem, as they led to water level depth definition [a mean value of 0.56 m] and hydraulic conductivity calculation [14.76 m/d].

The next step consisted in checking the flow model using results from the conservative transport of bromide. Parameters such as longitudinal and transversal dispersion coefficients required calibration, which proved to be very sensitive. All parameters were calibrated by trial and error. Longitudinal dispersion coefficient (L_d)

Table 3
Some results from the verification and calibration tests of the modified stoichiometric and kinetic parameters of the fermenting bacteria growth process.

Components	Influent	Case A	Case B	Influent	Case C	Case D	Influent	Case E	Case F	Influent	Case G
S_F [mg O_2/l]	163.2	0.0	0.0	16.3	0.0	15.1	16.3	11.6	16.3	16.3	16.3
S_{NH} [mg N/l]	44.9	47.4	42.8	44.9	43.3	43.4	44.9	43.4	43.4	44.9	43.4
S_O [mg O_2/l]	0.0	0.0	0.0	7.0	7.0	7.0	0.0	0.0	0.0	7.0	7.0
S_{NO} [mg N/l]	0.0	0.0	0.0	50.4	50.4	50.4	50.4	50.4	50.4	50.4	50.4
S_{H_2S} [mg S/l]	0.0	0.0	0.0	34.0	34.0	34.0	0.0	0.0	0.0	34.0	34.0
S_A [mg O_2/l]	18.3	59.0	58.8	18.3	22.3	18.6	18.3	19.4	18.3	18.3	18.3

Case A: $v_{5,9} = (i_{N,SF}/Y_{FB}) - i_{N,BM}$; K_{OFB} = 0.2 mg O_2/l; K_{NOFB} = 0.5 mg N/l.
Case B: $v_{5,9} = -i_{N,BM}$; K_{OFB} = 0.2 mg O_2/l; K_{NOFB} = 0.5 mg N/l.
Case C: $v_{5,9} = -i_{N,BM}$; K_{OFB} = 0.2 mg O_2/l; K_{NOFB} = 0.5 mg N/l.
Case D: $v_{5,9} = -i_{N,BM}$; K_{OFB} = 0.002 mg O_2/l; K_{NOFB} = 0.5 mg N/l.
Case E: $v_{5,9} = -i_{N,BM}$; K_{OFB} = 0.2 mg O_2/l; K_{NOFB} = 0.5 mg N/l.
Case F: $v_{5,9} = -i_{N,BM}$; K_{OFB} = 0.2 mg O_2/l; K_{NOFB} = 0.005 mg N/l.
Case G: $v_{5,9} = -i_{N,BM}$; K_{OFB} = 0.002 mg O_2/l; K_{NOFB} = 0.005 mg N/l.

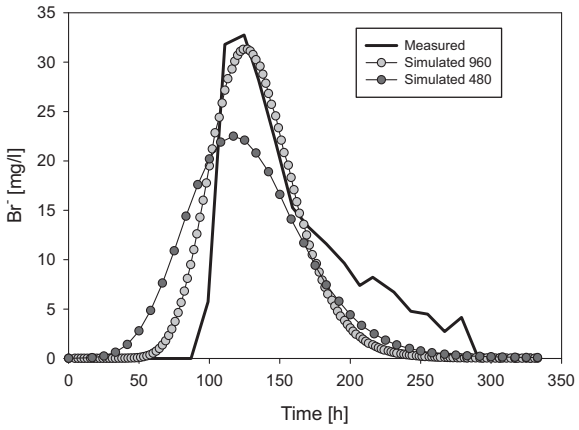

Fig. 1. Experimental data (line) and numerical simulation (dots) for the tracer test with a mesh of 480 and 960 elements.

values were 0.15 and 0.14 m in the mesh of 480 and 960 elements, respectively. The transversal dispersion coefficient values [0.08 and 0.30 m] had little effect on the tracer test simulation results, possibly because the concentration did not vary much in depth, i.e. it was transversal to the flow direction.

Fig. 1 shows the variation in the experimental tracer concentration for a flow rate of 2 m^3/d [HLR = 36 mm/d] and the simulation of the tracer behaviour with a mesh of 480 and 960 elements. The results from the mesh of 960 elements coincide more with the experimental ones observed than with those provided by the mesh of 480 elements. The variations given seem to be linked to the L_d values given to each mesh. Differences in element numbers of the meshes did not allow us to work with the same L_d values, because the mesh with the lowest elements gave some numerical stability problems at certain values. This fact required the use of a higher L_d value in the hydraulic calibration of the mesh of 480. The experimental HRT was 132 h, whereas the simulated HRT was 129 h with a mesh of 480 elements and 133 h with a mesh of 960 elements. On the other hand, normalized variance was slightly affected, being 0.11 for 480 elements (L_d of 0.15 m) and 0.05 for 960 (L_d of 0.14 m), whereas the experimental variance was 0.09. These results indicate that the use of a mesh of 960 elements is reasonable in order to simulate dispersion processes in the wetland.

3.2. Reactive transport simulation

After flow simulation had been checked, the reactive transport model was calibrated using data from summer 2001, when the system had been completely vegetated (Table 4).

During the calibration step, initial bacterial concentration values were defined by trial and error considering a quasi steady-state and were 170 mg COD_{BM}/l for X_{HF}, X_{HA}, X_A and X_{FB}, 1700 mg COD_{BM}/l for X_{AMB}, 576 mg COD_{BM}/l for X_{ASRB}, and 355 mg COD_{BM}/l for X_{SOB}. Bacteria activity distribution patterns and effluent contaminant concentration predictions obtained after these concentrations had been defined were in reasonably good agreement with the results of several other studies [5,35]. The modified parameters were also calibrated (K', K'', $\upsilon_{5,9}$, K_{OFB} and K_{NOFB}) (Table 3). Both the K' and K'' values were 21.28 mg O_2/l, $\upsilon_{5,9}$ was −0.07 g N/g COD_{BM}, K_{OFB} was 0.002 mg O_2/l and K_{NOFB} was 0.005 mg N/l. The remaining values of the kinetic and stoichiometric parameters were the same as those defined in CWM1 [19].

After calibration, the model was validated using different data from the wetland than those used in the calibration step. Eleven cases operating with different HLRs were evaluated. Table 5 shows the influent concentrations and the HLR of each case study. Organic matter, nitrogen and sulphur degradation and transformation were simulated through several biochemical processes, some of them taking place at the same time but at different locations and others occurring in parallel along the wetland (Fig. 2), in accordance with the observations of several studies [5,25,35]. Figs. 3–5 show the measured and simulated effluent concentrations of total COD, ammonia and sulphate in the eleven validation simulations. The bounds (maximum and minimum value) of each range of effluent measured concentrations are shown for each validation case. In most cases, values obtained from simulations corresponded well with measured data (simulated concentrations were within the range, between the upper and lower bounds). The model slightly underestimated the effluent total COD by an average of 8 mg O_2/l. The maximum differences for total COD were observed in cases 8 and 10, which were approximately 40 and 34 mg O_2/l, respectively, from the minimum value of the total COD range of data to the value provided by simulations. For ammonia, the simulated data of most cases were within the range of effluent ammonia data. In cases 3, 6, 7 and 9 data were outside the range (differences from the lower and upper bounds were 3, 24, 4 and 6 mg N/l, respectively). Accord-

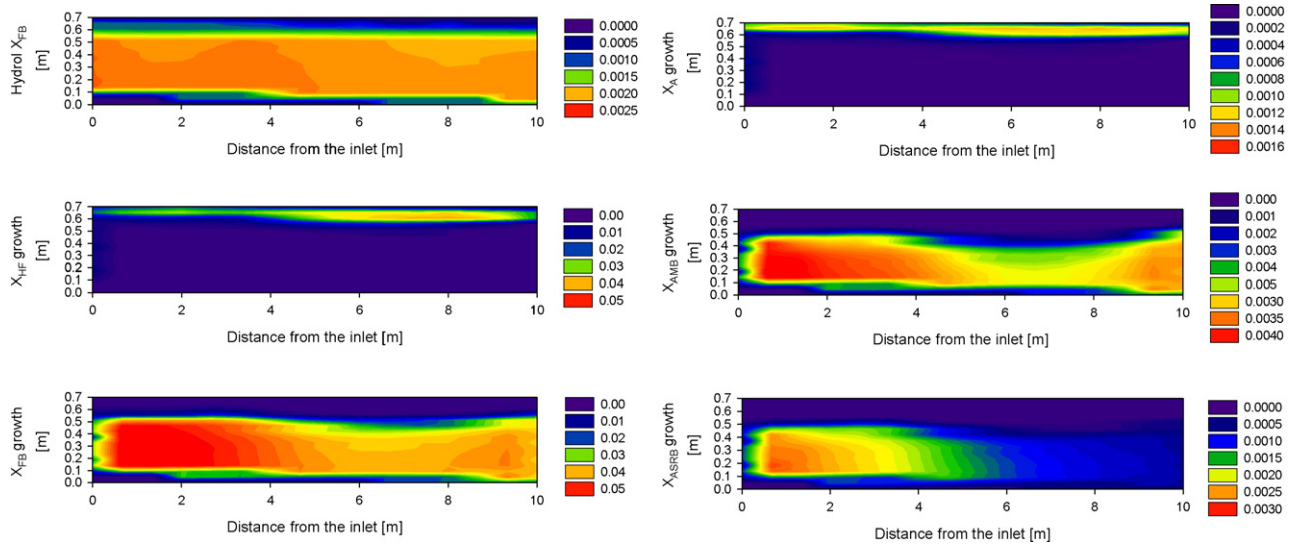

Fig. 2. Simulated changes along the wetland length of the rates [mol substrate/4.8E5 s kg water] of hydrolysis of X_{FB} (Hydrol X_{FB}), aerobic growth of X_{HF} on S_F (X_{HF} growth), fermenting bacteria growth (X_{FB} growth), nitrification (X_A growth), methanogenic bacteria growth (X_{AMB} growth) and sulphate reduction (X_{ASRB} growth) for case 4. Each image represents a longitudinal profile of the wetland, with a length of 10 m and a depth of 0.6 m at the inlet and 0.7 m at the outlet (vertical axis).

Table 4
Measured (±SD) and simulated concentrations at the influent and effluent of the horizontal SSF CW during calibration. Wetland operated at a flow rate of 2 m^3/d (HLR of 36 mm/d). Measured data from July to August 2001 [n = 3].

Type of water	Total COD [mg O_2/l]	NH_4^+–N [mg N/l]	NO_3^-–N [mg N/l]	SO_4^{2-}–S [mg S/l]	H_2S [mg S/l]
Influent measured (used for simulation inputs)	280 ± 47	50 ± 7.8	0	20 ± 9.2	0
Effluent measured	64 ± 14	36 ± 2.0	n.a.	13 ± 17	n.a.
Effluent simulated (simulation outputs)	77	34	0	11	0.78

n.a. means not available. [n] refers to the number of samples for the calibration case.

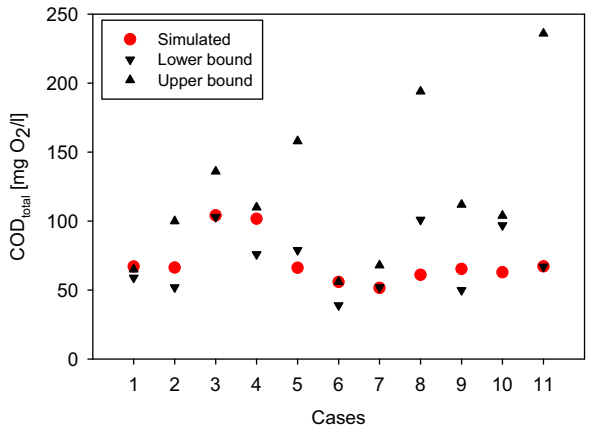

Fig. 3. Measured and simulated total COD concentrations at the outlet of the horizontal SSF CW from the eleven cases evaluated during validation. Black triangles indicate the maximum and minimum measured values. Red dots refer to the values provided by the model. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

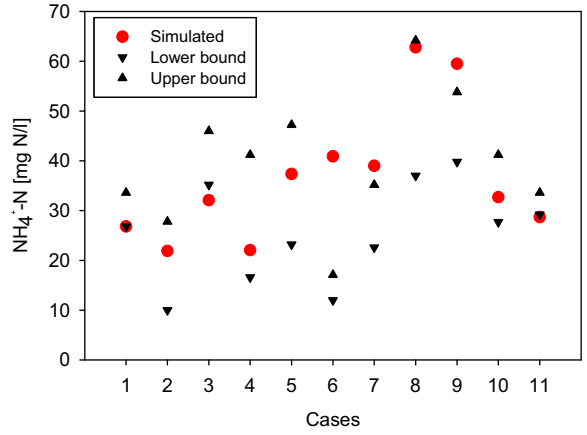

Fig. 4. Measured and simulated ammonia concentrations at the outlet of the horizontal SSF CW during validation. Black triangles indicate the maximum and minimum measured values. Red dots refer to the values provided by the model. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

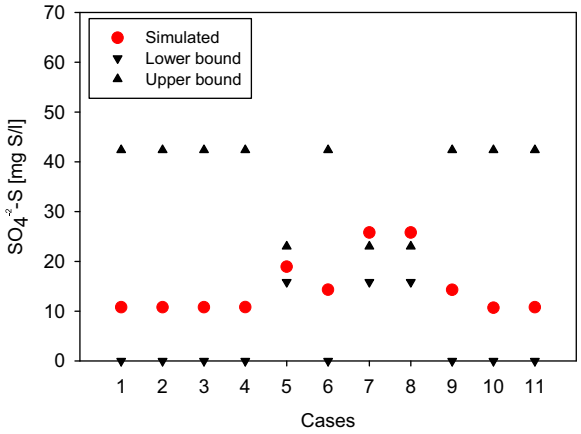

Fig. 5. Comparison of the observed effluent sulphate concentration results in the horizontal SSF CW with the sulphate values predicted by the model during validation. Black triangles indicate the maximum and minimum measured values. Red dots refer to the values provided by the model. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

ingly, the model slightly overestimated the effluent ammonia by an average of 8 mg N/l when it simulated HLRs of 20 mm/d. The simulated sulphate data corresponded well with those measured (maximum difference of 3 mg S/l from the upper bounds of the data ranges). Effluent sulphate concentrations were lower than or similar to those of the influent. Nitrate effluent concentrations given by the model were low and did not change along the length of the wetland, being very close to 0. These results agreed with those observed in four sampling campaigns carried out in the same wetland in 2003 [5], where no changes in nitrate concentrations were observed from the influent to the effluent. Simulations indicated that dihydrogen sulphide was produced in the wetland in concentrations in the effluent ranging from 0.53 to 1.77 mg S/l. Simulations of dissolved oxygen concentration along the depth at different locations throughout the length of the wetland (Fig. 6) reflected field observations quite well: a sharp decrease in concentration in the first centimetres of depth [32]. Changes in concentrations of different components inside the wetland matched the behaviour observed in the field reasonably well (Fig. 7). Dissolved COD decreased mostly near the inlet zone, while ammonia remained quite constant, only

Table 5
Influent mean concentrations (±SD) and HLR values of each case study simulated during validation. Concentrations and HLR values correspond to measured values of different experimental campaigns from 2001 to 2003. The number of samples for each case study is shown in brackets.

Case	Total COD [mg O_2/l]	NH_4–N [mg N/l]	NO_3–N [mg N/l]	SO_4–S [mg S/l]	H_2S [mg S/l]	HLR [mm/d]	Time period [n]
1	123 ± 27	36 ± 19	0	20 ± 9.2	0	36	October–November 2002 [5]
2	138 ± 37	27 ± 11	0	20 ± 9.2	0	36	April–June 2003 [6]
3	230 ± 24	56 ± 6.5	0	20 ± 9.2	0	45	May–June 2001 [4]
4	249 ± 25	39 ± 11	0	20 ± 9.2	0	45	June–July 2003 [5]
5	254 ± 68	57 ± 6.9	0	35 ± 4.2	0	36	February–April 2002 [5]
6	151 ± 32	36 ± 6.5	0	20 ± 9.2	0	20	October–November 2003 [4]
7	118 ± 10	33 ± 5.9	0	35 ± 4.2	0	20	November–January 2003 [5]
8	335 ± 125	66 ± 7.0	0	35 ± 4.2	0	20	November–January 2002 [6]
9	263 ± 82	62 ± 3.6	0	20 ± 9.2	0	20	September–October 2001 [5]
10	257 ± 30	48 ± 8.2	0	20 ± 9.2	0	36	August 2003 [3]
11	184 ± 22	40 ± 13	0	20 ± 9.2	0	36	September–October 2003 [5]

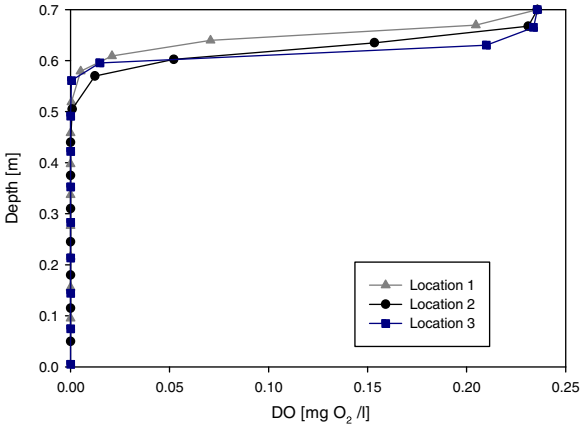

Fig. 6. Simulated dissolved oxygen concentration along the depth of the wetland at the three different locations uniformly distributed throughout the length of the wetland. Location 1 is at 0.5 m from the inlet, location 2 at the middle [5 m] and location 3 near the outlet [9.5 m]. The bottom of the wetland is located at 0 m in the *Y* axis. Operation and influent characteristics as well as simulation results are those of case 4 from validation.

decreasing when the COD concentration was low. Sulphate diminished near the outlet, suggesting that fermentation was a major organic matter biodegradation pathway. The peak of dissolved COD observed near the inlet seems to be the result of organic matter production by hydrolysis and microbial lysis processes. All these assumptions are in agreement with the results presented in Fig. 2.

4. Discussion

Tracer behaviour simulations with a mesh of 960 elements coincided more with experimental observations than those provided with a mesh of 480. Major differences between simulations and experimental observations might be due to the facts that: (1) RCB considers granular medium as homogeneous and (2) evapotranspiration was not included in CWM1-RETRASO. In RCB, dispersive and diffusive fluxes are computed by means of Fick's laws, which are described for a homogeneous medium, that is, it does not consider mass exchange between mobile zones (e.g., bulk pores and high permeability zones) and immobile zones (e.g., dead end pores and low permeability zones). The consideration of non-Fickian laws could solve the heterogeneity of the medium. However, considerable difficulty is involved in programming the integration of these laws into RCB and thus into CWM1-RETRASO. The inclusion of an evapotranspiration term in the model seems to be more feasible. For this reason, future work will focus on this direction.

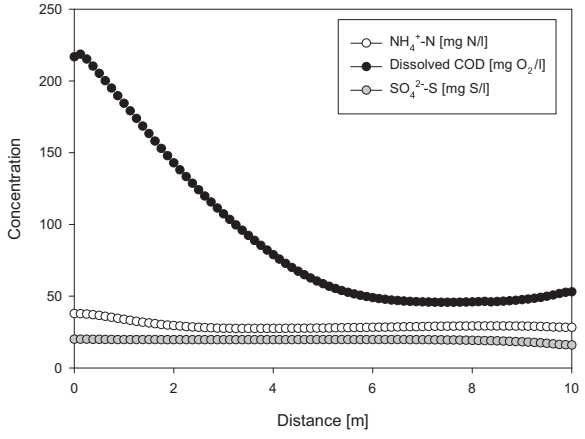

Fig. 7. Simulated dissolved COD, ammonia and sulphate concentrations along the wetland at a water depth of 0.25 m above the bottom in case 4 from validation.

The experience showed that simulation results closely matched the measured concentrations. In most cases, simulated values in the calibration and validation steps revealed good correspondence with measured data. The biggest differences observed between simulated and measured concentrations were those related to total COD. The effluent concentration of case 8, the worst for this variable, differed by 40 mg O_2/l. Bearing in mind the high variability of COD data, the way the experimental campaigns were carried out and the fact that the model does not consider particle accumulation, these differences must be regarded as acceptable at this stage of the study. Fewer differences were observed for the other cases and the other simulated variables. HLR variations did not affect the good correspondence between simulated and measured concentrations for total COD and sulphate, but the simulation results showed that the model could slightly overestimate effluent ammonia values when simulating HLR of 20 mm/d. This fact could be linked to an ammonia production increase by hydrolysis and microbial lysis when HLR is low.

The modification of the formulation of hydrolysis (divided into two process rates, one for heterotrophic bacteria and one for fermenting bacteria) and heterotrophic bacteria processes (divided according to the substrate S_F or S_A that they consume) allowed these processes to be included in the model. However, no modification effects were expected as the hypothesis stated that these modifications were other ways of representing those processes without changing their meaning. On the other hand, the constant values provided to the variables X'_H and X'_{FB} of the model [200 mg COD_{BM}/l] were very close to the mean simulated concentration of X_{HF} and X_{FB} inside the wetland once a quasi steady-state was reached [270 mg COD_{BM}/l]. Due to this similarity, the effects of X'_H and X'_{FB} constants were considered negligible. On the contrary, modifications of the stoichiometric factor $\nu_{5,9}$ for ammonia and changes in the saturation/inhibition coefficient values for S_O (K_{OFB}) and for S_{NO} (K_{NOFB}) (from 0.2 to 0.002 mg O_2/l and from 0.5 to 0.005 mg N/l, respectively) were shown to greatly affect the concentration results from simulations. The modification of the original expression of the factor $\nu_{5,9}$ entailed ammonia consumption rather than generation being considered in X_{FB} growth. Changes in the above-mentioned saturation/inhibition coefficient values led to an increase in the influence of oxygen and nitrate inhibition terms and restricted the growth of X_{FB} in aerobic and anoxic conditions. Therefore, it is clear that changes in the formulation of the CWM1 processes in RCB could be made without interactions in the model outcomes, providing that the changes are only in mathematical terms and do not entail the introduction or removal of kinetic/stoichiometric parameters or the modification of any of their values.

Experiences from calibration suggested that the bacterial concentrations defined as initial conditions are a variable requiring attention. The values found in the calibration phase to be used in the simulations were higher for the initial anaerobic bacteria concentrations than for the aerobic ones. The simulated results provided good bacteria activity distribution patterns, suggesting the predominance of anaerobic microorganisms in agreement with findings by Ojeda et al. [2], García et al. [5], Huang et al. [6] and Langergraber [26], who conclude that anaerobic reactions play a greater role in horizontal SSF CWs than anoxic and aerobic reactions.

In its present state, CWM1-RETRASO is not able to handle porosity reduction due to the entrapment of suspended solids, plant root development and biofilm growth over time, and is thus not able to handle longitudinal variations in hydraulic conductivity. Some studies have highlighted the need to address all these aspects in order to provide a reliable design tool for CWs [26,36]. Future work will be conducted in this direction in the expectation that,

for example, COD and ammonia results will improve once clogging phenomena have been included in the model.

The non-inclusion of the plant effect into the model assumptions was considered acceptable at this stage of the study. However, the effect of plants on wetlands is another point to be addressed in our future research. Root oxygen release, nutrient uptake and litter decomposition rates are a continuing subject of debate in SSF CWs. In all likelihood, oxygen release – and hence redox potential and the diversity of the rhizosphere microbial community – varies according to macrophyte plant species and environmental conditions, but results are not consistent from study to study [35,37]. Results from experiments dealing with quantification of oxygen release rates by plants have led to the generally accepted statement that aerobic microsites exist in the granular medium of horizontal SSF CWs [29]. However, it is now widely recognised that the amount of oxygen given off by plant roots is insufficient in comparison with oxygen demand for pollutant removal in a typical primary effluent [30,31]. Furthermore, seasonal variations as well as plant species selection seem to affect plant uptake processes [35,37]. It is therefore widely accepted that plant uptake is a minor nitrogen removal mechanism, as microbial transformations provide most total nitrogen removal [8].

Finally, the calibration and validation results indicated that the model behaviour is good, coinciding with another attempt at CWM1 implementation [38] using AQUASIM 2.1d (EAWAG, Switzerland). However, the results from both studies are preliminary and more simulations drawing from different scenarios are therefore needed to better evaluate the performance of the two implementations.

5. Conclusions

We present CWM1-RETRASO, a numerical model resulting from the implementation of CWM1 in RCB. It has 17 components (8 soluble and 9 particulate) and 19 processes, which occur in aerobic, anoxic and/or anaerobic conditions.

The implementation of some processes in a different way to that described in CWM1 in RCB entailed modifying their formulation and increasing the number of reactions from 17 to 19. Results from simulations suggested that these modifications did not affect the good performance of the model when they only consisted of mathematical variations. On the other hand, modifications of one or more kinetic and stoichiometric parameter values led to major differences among simulated data. Initial bacterial concentrations were also seen to be a variable requiring attention in the calibration.

Physical oxygen transfer from the atmosphere to the water was added as a new process in CWM1-RETRASO but other processes – such as plant influence, biofilm growth and particle/suspended matter transport, which must be considered for the formulation of a full model for CWs – were not. However, the quality of the results obtained suggests that CWM1-RETRASO is a potential model for horizontal SSF CW simulation. Further research will be conducted in order to test new scenarios and to include processes not considered at the present stage of the study.

Acknowledgements

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