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Nitrogen transformation in horizontal subsurface flow constructed wetlands I: Model development

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Abstract

In this paper a mathematical model for prediction of nitrogen transformation in horizontal subsurface flow constructed wetlands was developed. Two horizontal subsurface flow constructed wetlands were designed to receive organic loading rate below 50 kg/ha/d and hydraulic loading rate of 480 m^3/ha/d from a primary facultative pond. Two rectangular shaped units each 11.0 m long, 3.7 m wide and 1.0 m deep and bottom slope of 1% were constructed and filled with 6–25 mm diameter gravel pack to a depth of 0.75 m. Each unit was planted with *Phragmites mauritianus* with an initial plant density of 29,000 plants/ha. The plants were allowed to grow for about four months before sampling for water quality parameters commenced. Samples were collected daily for about three months. Dissolved oxygen, pH and temperature were measured in situ and ammonia, total Kjeldahl nitrogen, nitrates, nitrite and Chemical Oxygen Demand were measured in the laboratory in accordance with Standard Methods.

The mathematical model took into account activities of biomass suspended in the water body and biofilm on aggregates and plant roots. The state variables modelled include organic, ammonia, and nitrate–nitrogen, which were sectored in water, plant and aggregates. The major nitrogen transformation processes considered in this study were mineralization, nitrification, denitrification, plant uptake, plant decaying, and sedimentation. The forcing functions, which were considered in the model, are temperature, pH and dissolved oxygen. Stella II software was used to simulate the nitrogen processes influencing the removal of nitrogen in the constructed wetland. One of the two-wetland units was used for model calibration and the second unit for model validation. The model results indicated that 0.872 gN/m^2 d was settled at the bottom of the wetland and on gravel bed and roots of the plants. However, 0.752 gN/m^2 d (86.2%) of the settled nitrogen was regenerated back to the water body, which means that only 13.8% of the settled nitrogen was permanently removed. Denitrification and nitrification were responsible for transformation of 0.436 gN/m^2 d and 0.425 gN/m^2 d, respectively. Uptake of nitrogen by plants was 0.297 gN/m^2 d out of which 0.140 gN/m^2 d was returned to the water body as plants decay. It was found that the major pathways leading to permanent removal of nitrogen in a horizontal subsurface flow constructed wetland system in descending order are denitrification (29.9%), plant uptake (10.2%) and net sedimentation (8.2%). A total nitrogen removal of 48.9% was achieved in this study.
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Keywords: Constructed wetlands; Nitrogen transformation; Nitrification; Denitrification; Biofilm; Modelling

1. Introduction

Discharging wastewater effluents rich in nitrogen into receiving rivers has a number of problems including eutrophication in receiving water bodies, impact to human health and marine ecology. Therefore nitrogen must be removed to preserve water environment and protect aquatic life and health of water users downstream.

Activated sludge and biofilm processes have been used successfully for biological removal of nitrogen for over three decades. However, these technologies are rather expensive for use in small communities of developing countries. The use of constructed wetlands (CW) is now recognised as an accepted low cost eco-technology, especially

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beneficial to small communities that cannot afford expensive conventional treatment systems (White, 1995; Billore et al., 1999). Constructed wetlands have demonstrated potential for remove of nitrogen, but variability in performance due to inadequate understanding of the transformation and removal mechanisms is one of its major shortcomings (Mutamba, 2002; Senzia et al., 2003). Currently individual fate processes are known, but little is known about how these processes are influenced by diverse forcing functions and conversely how nitrogen pollutants influence the functioning of wetlands.

The transformation and removal of nitrogen involves a complex set of processes and relations (Metcalf and Eddy, Inc., 1995). The fate of nitrogen in constructed wetlands is understood to involve ammonification, nitrification–denitrification, adsorption, ions exchange, fixation, volatilization and biological uptake (Metcalf and Eddy, Inc., 1995; US EPA, 1993). Decomposition and mineralization processes in the wetlands are believed to convert a significant part of organic-nitrogen, which is associated with particulate matter such as organic wastewater solids and/or algae, to ammonia (Mayo and Mutamba, 2004). Biological nitrification, which is realised by nitrifiers such as *Nitrosomonas*, *Nitropira*, *Nitrosococcus* and *Nitrobacter* followed by denitrification is believed to be the major pathway for ammonia removal in both surface and subsurface constructed wetlands (Gersberg et al., 1985; Reed et al., 1988). The objective of the paper is to develop a mathematical model for prediction of transformation and removal rate of nitrogen in subsurface flow constructed wetlands (SSF CW).

2. Methods and materials

Four field scale horizontal subsurface flow units of constructed wetlands were built (Fig. 1). Three units were planted with different plant species while one unit was used as a control. All units received effluents from the primary facultative pond treating domestic wastewaters from staff houses, student halls and offices at the University of Dar es Salaam. The scheme is located at latitude 6°48′ S and longitude 39°13′ E where the mean monthly air temperature of the site varies between 23 °C and 28 °C with a mean value of 26 °C (Mayo, 1989).

Two units were planted with *Phragmites mauritianus*, with purpose of using the data for model developing and model verification. The other unit was planted with *Typha domingensis* species while the remaining unit was used as a control. Two horizontal subsurface flow constructed wetlands were designed to receive organic loading rate below 50 kg/ha/d and hydraulic loading rate of 480 m^3/ha/d from a primary facultative pond. Two rectangular shaped units each 11.0 m long, 3.7 m wide and 1.0 m deep and bottom slope of 1% were constructed and filled with 6–25 mm diameter gravel pack to a depth of 0.75 m. The porosity of the bed was about 44% and flow rate in each unit was about 2 m^3/d, which filled the gravel bed to a depth of about 60 cm. Each unit was planted with *P. mauritianus* with an initial plant density of 29,000 plants/ha. The plants were allowed to grow for about four months before sampling for water quality parameters commenced. Samples were collected daily for about three months and were analysed for organic-nitrogen, ammonia-nitrogen and

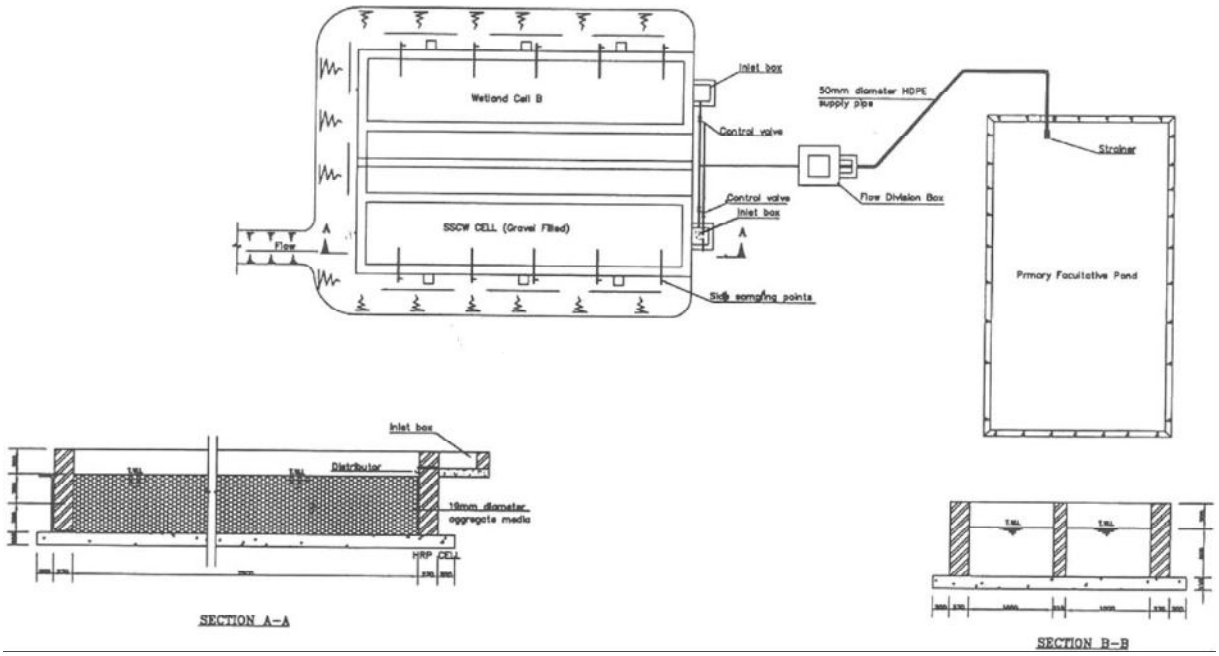


Fig. 1. Layout of experimental wetlands.

nitrate-nitrogen. Other parameters measured were flow rate, temperature, pH, total suspended solids (TSS) and dissolved oxygen (DO).

3. Development of a mathematical model

A conceptual model that encompasses the suspended and biofilm biomass activities governing the nitrogen transformations and removal was developed. Fig. 2 illustrates the conceptual model used in this research. The model shows the material flow in and out of the state variables (indicated by boxes in Fig. 2) represented by subscript "i" and "e", respectively. This model incorporates the activities of both suspended and biofilm biomass on nitrogen transformation and removal in a horizontal subsurface flow constructed wetland. The conceptual model has considered organic-nitrogen, ammonia nitrogen and nitrate ammonia as the major forms of nitrogen in the wetland. The transformation mechanisms considered in model include mineralization, nitrification, denitrification, plant uptake, sedimentation and decaying processes and uptake of ammonia and nitrates by microorganisms. All these transformation processes are carried out by both suspended and biofilm biomass. Therefore, mathematical equations developed in this study will incorporate the suspended and attached biomass activities.

3.1. Nitrogen mass balance

The system was considered to be continuous flow and plug flow type. In determining the governing mathematical expressions a complete materials balance including all forms of substances produced and consumed in biochemical reactions, inflows, accumulations and depletion were considered. The mass balance around the state variables was done based on Eq. (1).

$$V\sum_{j=1}^{m}(r_c)_j + Q_iC_i = Q_oC + V\frac{dC}{dt} \quad (1)$$

where C is substrate concentration in mg/l, V is reactor volume in m^3, r_c is volumetric reaction rate (g/m^2 d), C_i is influent concentration in mg/l, m is number of reactions that involve the substrate, $V(dC/dt)$ is volumetric rate of change of substance in the reactor (mg/l d), Q_i is influent flow rate in m^3/d, Q_o is effluent flow rate in m^3/d l. During mass balance of state variables in the system units of gN/m^2 d was used for the transformation and transport processes while gN/m^2 was selected for storage. The various equations used in balancing the storages in the system are discussed in the following sections.

3.1.1. Suspended biomass

The organic-nitrogen (ON) mass balance shown by Eq. (2) was used to model the mass balance of organic-nitrogen in the system.

$$\frac{d(ON)}{dt} = \left(\frac{Q_i}{A}ON_i\right) - \left(\frac{K_S \times S}{L}ON\right) + r_{dc} + r_{g1} + r_{g2} - r_m - r_s \quad (2)$$

where r_{dc} is rate of decay of plants (g/m^2 d), r_{g1} is rate of ammonia uptake by microorganisms for growth (g/m^2 d), r_{g2} is rate of nitrate uptake by micro organisms for growth (g/m^2 d), r_m is mineralization rate of organic-nitrogen (g/m^2 d), r_s is settling rate of organic-nitrogen to the soil (g/m^2 d), K_S is hydraulic conductivity (m/d), S is slope of the bed (%), L is length of the bed (m).

In mass balancing of the ammonia nitrogen, Eq. (3) was used to model the mass balance of ammonia in the system.

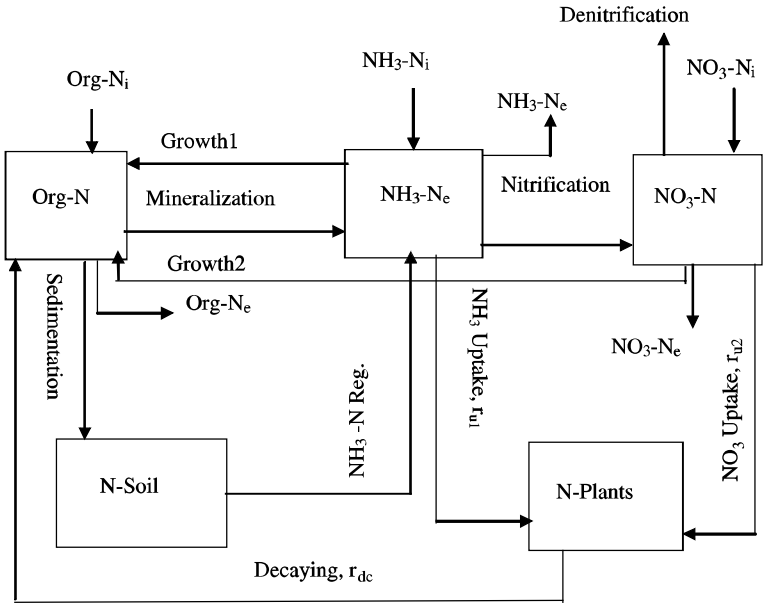


Fig. 2. Nitrogen transformation and removal in the wetland.

$$\frac{d(NH_3_N)}{dt} = \frac{Q_i}{A}(NH_3_N_i) - \frac{K_S \times S}{L}(NH_3_N) - r_n - r_{u1} - r_{g1} + r_r + r_m \quad (3)$$

where r_n is rate of nitrification of ammonia (g/m^2 d), r_{u1} is rate of ammonia utilization by plants for growth (g/m^2 d), r_{g1} is rate of ammonia uptake by microorganisms for growth (g/m^2 d), r_r is rate of ammonia regeneration (g/m^2 d), r_m is mineralization rate of organic-nitrogen (g/m^2 d).

The major processes considered in modelling the mass balance of nitrate–nitrogen in the system include; nitrification, denitrification, nitrate uptake by plants and nitrate uptake by microorganisms for growth. Eq. (4) was used to model the nitrate transformation.

$$\frac{d(NO_3_N)}{dt} = \frac{Q_i}{A}(NO_3_N)_i - \frac{K_S \times S}{L}(NO_3_N) + r_n - r_{u2} - r_{dn} - r_{g2} \quad (4)$$

where r_{dn} is rate of denitrification of nitrate (g/m^2 d), r_{u2} is rate of nitrate utilization by plants for growth (g/m^2 d). The first term $(NO_3_N)_i$ on the right-hand side of Eq. (4) represents nitrate influent concentration while the second term (NO_3_N) represents the nitrate effluent concentration. The remaining terms represent the reaction rates that either increase or decrease nitrate-nitrogen concentration in the system.

Sedimentation and ammonia nitrogen regeneration were the only processes used in modelling the mass balance of nitrogen in the aggregates (N_{aggr}) and it is shown by Eq. (5)

$$\frac{d(N_{aggr})}{dt} = r_s - r_r \quad (5)$$

where r_s is settling rate of organic-nitrogen to the gravel bed (g/m^2 d).

Mass of organic-nitrogen in plants (N_{plants}) was modelled by assuming that it is influenced by nitrate and ammonia uptake by plants, and plants decaying processes. The symbolic representation of mass balance is given by Eq. (6).

$$\frac{d(N_{plants})}{dt} = r_{u1} + r_{u2} - r_{dc} \quad (6)$$

Various processes as described below influenced nitrogen transformations in the system and its ultimate removal out of the system. Mineralization of organic-nitrogen, which is the biological transformation of organically combined nitrogen to ammonia through degradation, was modelled using first order kinetics (Eq. (7)) with respect to organic-nitrogen concentration (Martin and Reddy, 1997).

$$r_m = ON \times R_{min} \quad (7)$$

where R_{min} is mineralization rate constant of organic-nitrogen (d^{-1}).

The rate of nitrification was modelled by considering both suspended and biofilm biomass activities in the system. The biofilm biomass was assumed to be composed of *nitrosomonas* bacteria, which are attached on the surfaces of aggregates and plant roots. The Monod model was used to model the suspended bacteria nitrification and the biofilm nitrification was modelled using the model developed by Polprasert and Agarwalla (1994). A combined nitrification model equation is given in Eq. (8).

$$r_n = \left[(\mu_n/Y_n + rb_1 + rb_2) \times \left(\frac{NH_4}{KN + NH_4 - N}\right) \times \left(\frac{DO}{KNO + DO}\right) \times C_T \times C_{pH} \times ON\right] \quad (8)$$

where μ_n is maximum *Nitrosomonas* growth rate (d^{-1}), Y_n is yield coefficient for *Nitrosomonas* bacteria in mg VSS/mg N, KN is ammonia *Nitrosomonas* half saturation constant (g/m^3), KNOis oxygen *Nitrosomonas* half saturation constant (g/m^3), C_T is temperature dependent factor, C_{pH} is *Nitrosomonas* growth-limiting factor for pH, rb_1 is biofilm reaction rate constants for aggregate (d^{-1}), rb_2 is biofilm reaction rate constant for plants (d^{-1}).

The growth of nitrifying bacteria depends on temperature, pH, dissolved oxygen concentration and ammonia concentration. The influence of temperature on *Nitrosomonas* bacteria is explained by the empirical relationship shown by Eq. (9) in accordance with Downing (1966).

$$C_T = \exp\cdot\varphi(T - T_0) \quad (9)$$

where T_0 is the reference temperature (15 °C) and φ is an empirical constant (0.098/°C). Downing (1966) also studied the influence of pH on growth of *Nitrosomonas* bacteria and came up with the relationship shown by Eq. (10). However, in this study, the variation of pH was insignificant because pH value varied from 7.01 to 7.33.

$$C_{pH} = \begin{cases} 1 - 0.833(7.2 - pH) & \text{for } pH < 7.2 \\ 1.0 & \text{for } pH \geqslant 7.2 \end{cases} \quad (10)$$

3.1.2. Biofilm

The role played by biofilm biomass attached on aggregates (rb_1) on nitrification process, was modelled using Eq. (11) in accordance with Polprasert and Agarwalla (1994). For nitrogen transformation and removal by biofilm, a diffusion process in which material is transported because of the existence of concentration gradient was assumed. Once the nitrogen reaches the biofilm surface, its concentration is determined by diffusion term and a reaction term.

$$rb_1 = a_s \frac{\alpha\beta}{(\alpha + \beta)} \quad (11)$$

$$\alpha = \frac{D_w}{L_s} \quad (12)$$

where rb_1 is rate of reaction of aggregate-biofilm biomass (d^{-1}), a_s is specific surface area of biofilm per unit volume in m^2/m^3, α is a sticking coefficient, D_w is diffusion coefficient in liquid sublayer in m^2/d, L_s is liquid sublayer thickness in m.

The liquid sublayer is the layer adjacent to biofilm and was assumed to have a constant thickness of 1.19×10^{-4} m. Diffusivity of a substrate through a stagnant liquid sublayer (D_w) is equal to its diffusivity in water (Williamson and McCarty, 1976a). The diffusivity of a substrate in biofilm (D_f) (m^2/d) is usually considered constant or independent of concentration. Williamson and McCarty (1976b) found a D_f/D_w ratio of 0.8 for aerobic biofilm while the D_f/D_w ratios for solutes inside methanogenic aggregates under anaerobic conditions were found to be between 0.1 and 0.3 (Pavlostathis and Girlado-Gomez, 1991). Based on literature data some researchers adopted D_f as some percentage of D_w.

$$\beta = \frac{\tanh(\phi) K_{fa} L_f}{\phi} \tag{13}$$

in which ϕ is characteristic biofilm parameter, K_{fa} is first-order reaction rate constant of biofilm in d^{-1}, L_f is biofilm thickness in m and L_s is liquid sublayer thickness in m is 1.19×10^{-4}–2.26×10^{-4} m. The thickness of biofilm (L_f) growing on plant roots and aggregate surfaces was optimised based on the range reported in the literature. The first-order rate constant of biofilm biomass (K_{fa}), which increases as temperature increases, was obtained through field and laboratory experiments. Parameters needed for calculation of K_{fa} are the volatile suspended solids (VSS) concentration and the biofilm density in the wetland unit. The biofilm characteristic parameter, ϕ, was evaluated using Eq. (14).

$$\phi = \sqrt{\left(\frac{K_{fa} L_f^2}{D_f}\right)} \tag{14}$$

The specific surface area is the sum of the wetland bottom, walls of the wetland unit and the biofilm covering the aggregate media. It was evaluated using Eq. (15).

$$a_{s1} = \frac{1}{H} + \frac{2}{W} + \frac{2}{L} + \frac{A_S}{H} \tag{15}$$

where H is water depth in the pond in m, W is pond width in m, L is length of the bed in m, A_s is effective aggregate surface area per unit pond aerial surface area (m^2/m^3). The biofilm growing on aggregates, on sidewalls and at the bottom of the wetland was assumed to be an ideal biofilm of constant thickness and density. Within the biofilm, diffusion and consumption of nitrogen are assumed to occur simultaneously. Advective transport in the biofilm is considered negligible. In addition, the diffusion and kinetic coefficients were assumed to be constant throughout the wetland unit. The role of biofilm attached on plant roots on nitrification was modelled using Eq. (16).

$$rb_2 = a_{s2} \frac{\alpha\beta}{(\alpha + \beta)} \tag{16}$$

$$a_{s2} = \frac{R_S(1 - \lambda_t)}{H} \tag{17}$$

where rb_2 is rate of reaction of plant-biofilm biomass (d^{-1}), a_{s2} is specific surface area of plants, R_S is effective root surface area per unit areal surface area of a pond at full coverage by *Phragmites*, λ_t is fraction of area of a wetland unit uncovered by plant roots per total wetland unit surface area (ranged from 1.0 to 0.0). The sticking coefficient α and β values were calculated by using Eqs. (12) and (13) as discussed earlier. Since D_w, L_s, and L_f were assumed constant, the terms α and β will not vary along the wetland unit length for a particular set of climatic conditions.

The biofilm biomass activities were assumed to affect denitrification process in the same manner as it affected nitrification process. The rate of denitrification (r_{dn}) was modelled by a combination of denitrifying bacteria activities both in suspended and attached (biofilm) phases. In case of suspended biomass, Dawson and Murphy (1972) theory, which describes the denitrification process to follow the Arrhenius kinetics within a temperature range between 3 and 28 °C, was considered. Therefore, in order to model denitrification the first order Arrhenius kinetic and the biofilm equations described earlier were used. The resulting expression is shown by Eq. (18).

$$r_{dn} = \left[(D_{r,20} + rb_1 + rb_2) \times \theta_1^{(T-20)}\right] \times NO_3 \tag{18}$$

where $D_{r,20}$ is Denitrification rate constant at 20 °C (d^{-1}) is 0–1.0 (Bacca and Arnett, 1976), θ_1 is Arrhenius constant, ranges from 1.02 to 1.09 (Bacca and Arnett, 1976).

Biomass uptake by autotrophic bacteria involves NH_3-N or nitrates although ammonia is preferred (Shin and Polprasert, 1988). In modelling the uptake rate of ammonia (r_{g1}) it was assumed that ammonia would be taken as long as is available in the system. Microorganisms in suspended and biofilm carry out the overall uptake. The Monod kinetic equation for suspended and the biofilm equation discussed earlier were combined to give Eq. (19) used to model the ammonia uptake by microorganisms.

$$r_{g1} = \left[(\mu_{max,20} + rb_1 + rb_2) \times \theta^{T-20} \times \left(\frac{NH_3_N}{K_1 + NH_3_N}\right)\right] \times ON \times P_1 \tag{19}$$

where $\mu_{max,20}$ is maximum growth rate of bacteria at 20 °C (d^{-1}), θ is microorganisms growth temperature coefficient is 1.08–1.10 (Metcalf and Eddy, Inc., 1995), P_1 is ammonia uptake preference factor, K_1 is ammonia uptake half saturation constant.

As it was for ammonia, autotrophic bacteria carry out the nitrate uptake. However, in this model, it was assumed that nitrate would be consumed if all ammonia has been depleted in the system. Eq. (20) was used to model the rate of nitrate uptake by microorganisms (r_{g2}).

$$r_{g2} = \left[(\mu_{max,20} + rb_1 + rb_2) \times \theta^{T-20} \times \left(\frac{NO_3_N}{K_1 + NO_3_N}\right)\right] \times ON \times P_2 \tag{20}$$

where K_2 is nitrate uptake half saturation constant, P_2 is nitrate uptake preference factor.

The rate of ammonium uptake by plants (r_{u1}) was formulated by the first order kinetics. The uptake is proportional to the concentration of inorganic-nitrogen. Eq. (21) was used to model the ammonium uptake by plants.

$$r_{u1} = N_{dem}\left[\frac{NH_4_N}{K_m + NH_4_N}\right]\left[\frac{NH_4_N}{NH_4_N + NO_3_N}\right] \quad (21)$$

where K_m is ammonium uptake by plants half rate saturation constant, N_{dem} is inorganic-nitrogen demand. The product of biomass productivity multiplied by nitrogen biomass ratio gives N_{dem}.

The nitrate uptake by plants is similar to ammonium uptake by plants. Eq. (22) was used to model the rate of nitrate uptake by plants (r_{u2}).

$$r_{u2} = N_{dem}\left[\frac{NO_3_N}{K_m + NO_3_N}\right]\left[\frac{NO_3_N}{NH_4 - N + NO_3_N}\right] \quad (22)$$

The decay rate of plants (r_{dc}) was modelled using first order kinetics in accordance with Eq. (23).

$$r_{dc} = R_{decay} \times N_{plants} \quad (23)$$

where R_{decay} is decaying rate first order constant (d^{-1}), assumed to be 0.006/d (Martin and Reddy, 1997) and N_{plants} is nitrogen uptake by plants.

The nitrogen accumulated in the soil (aggregates) due to sedimentation process taking place in the system, ultimately is regenerated back to ammonia. The rate of regeneration (r_r) is assumed to follow first order kinetics, which is described by Eq. (24).

$$r_r = R_{reg} \times N_{aggr} \quad (24)$$

where R_{reg} is regeneration rate constant of ammonia (d^{-1}).

The aggregates and plants in wetland unit influence the rate of sedimentation (r_s) by reducing the settling time of organic-nitrogen. However, the influence of plants on sedimentation rate was ignored because the effective root depth of plants is only about one-fifth of the depth available for sedimentation. For example, the effective depth of roots was 12 cm while the depth of flow was 60 cm. Therefore; the influence of aggregates on sedimentation was modelled using Eq. (25). The gravels, which are collectors of sediments, were assumed spherical.

$$r_s = 1.3\eta\alpha\frac{u(1-p)}{d_c} \quad (25)$$

$$\eta = \frac{(\rho_s - \rho)gd_p^2}{18\mu u_o} \quad (26)$$

where α is sticking coefficient, u is flow velocity in m/d, p is media porosity is 44% in the wetland, d_c is diameter of collector ≈0.02 m for aggregate, η is single collector removal efficiency, ρ_s is density of settling particle in kg/m^3, ρ is density of water in kg/m^3, μ is dynamic viscosity of fluid N s/m^2, u is flow velocity in m/s^1, and d_p is diameter of colloidal particles that settle is 0.4–10 μm. The dynamic viscosity of water is the function of temperature. For temperature above 20 °C, the dynamic viscosity of water varies with temperature in accordance with Eq. (27).

$$\log\left[\frac{\mu}{\mu_{20}}\right] = \frac{1.3272(20-T) - 0.001053(T-20)^2}{T+105} \quad (27)$$

4. Results and analysis

4.1. Model calibration and parameter optimisation

The modelling process was carried out using Stella II software (STELLA 6.0.1) and following the structural procedure for model development (Jorgensen, 1994). The aforementioned mathematical equations for mass balance of organic-nitrogen, ammonia-nitrogen, nitrate-nitrogen, nitrogen in plants, and nitrogen in gravel bed along with forcing functions were entered in Stella II software. The data collected by Senzia (2003) were used as inputs to the model during model calibration. The inputs were the daily mean concentration of NH_3-N, NO_3-N, organic-nitrogen as well as the daily mean temperatures, dissolved oxygen and pH values. The best values of unknown coefficients were obtained through calibration. The model efficiency (R^2) was calculated from Nash and Sutcliffe (1970), which is given by Eq. (28).

$$R^2 = \frac{F_0 - F}{F} \quad (28)$$

where F_0 is the sum of the difference of squares between the observed and the mean of observed values while F is the sum of the difference of squares between the observed and computed values. The efficiency of the model was found to be 78%, which indicates that the observed data fits well with the simulated values. The values of optimised coefficients and constants used in the model during calibration are given in Table 1.

Figs. 3–5 show the model predicted well the concentration of ammonia-nitrogen, nitrate-nitrogen and organic-nitrogen, respectively. The mass balance of nitrogen load in the effluent of the wetlands indicates a good agreement between the observed and simulated nitrogen loads (Table 2). Nitrate-nitrogen simulation was reasonably good ($R^2 = 0.56$) although the model failed to predict the low peaks of nitrate-nitrogen observed in the wetland unit probably because of optimization of some kinetic biofilm parameters. It is worth mentioning that measurement of biofilm parameters in the field will disturb operation of wetland and consequently the effluent quality.

Fig. 6 shows nitrogen mass balance for all state variables as simulated by the model. One of the major nitrogen transformation routes was through settling of particulate organic-nitrogen on aggregates. About 0.872 gN/m^2 d of organic-nitrogen was removed through sedimentation, but 0.752 gN/m^2 d was returned to water phase through regeneration. Therefore only 0.12 gN/m^2 d of nitrogen accumulated in the gravel media. High regeneration of

Table 1
Model calibration values

Parameter	Description	Literature range	Source	Calibration
μ_n	Maximum *Nitrosomonas* growth rate (d^{-1})	(0.33–2.21)	Jorgensen et al. (1991)	0.01
μ_{max_20}	Maximum growth rate of algae and bacteria at 20 °C	0.18	Ferrara and Hermann (1980)	0.18
D_r	Denitrification rate (d^{-1})	0–1.0	Bacca and Arnett (1976)	0.195
K_{fa}	First order reaction constant (d^{-1})	336.6	Polprasert and Agarwalla (1994)	336.6
Y_n	*Nitrosomonas* yield coefficient (mg VSS/mg N)	0.03–0.13	Charley et al. (1980)	0.15
α	Sticking coefficient	0.0008–0.012	Polprasert and Khatiwada (1998)	0.0072
a_{s1}	Biofilm specific area/volume ratio (m^2/m^3) of aggregate	5.76–20.83	Polprasert and Agarwalla (1994)	1.5
D_w	Diffusion coefficient in liquid layer	5.26×10^{-3}	Polprasert and Agarwalla (1994)	5.26×10^{-3}
ρ	Water density (kg/m^3)	995.69	Metcalf and Eddy, Inc. (1995)	995.7
L_s	Liquid layer thickness (m)	$(1.19–2.21) \times 10^{-4}$	Rittman and McCarty (1980)	1.19×10^{-4}
L_f	Biofilm thickness (m)	$(1.46–1.62) \times 10^{-3}$	Polprasert and Agarwalla (1994)	1.615×10^{-3}
a_{s2}	Biofilm specific area/volume ratio (m^2/m^3) of plants	–	–	1.67–1.93
d_s	Density of settling particle (kg/m^3)	1050–1500	Metcalf and Eddy, Inc. (1995)	1050
R_{reg}	Ammonia regeneration rate constant	–	–	0.085
d_p	Settling particle diameter	30–1000 nm	O'Melia et al. (1997)	5 μm
R_{decay}	Plant decay rate constant (d^{-1})	0.006	Martin and Reddy (1997)	0.009
R_{min}	Mineralization rate (d^{-1})	0.0005–0.143	Martin and Reddy (1997)	0.01
D_w	Diffusion coefficient in liquid layer	5.26×10^{-3}	Polprasert and Agarwalla (1994)	5.26×10^{-3}
D_f	Diffusion coefficient in biofilm layer (m^2/d)	5.26×10^{-5}	Rittman and McCarty (1980)	23.4×10^{-6}
d_c	Diameter of collector (m)	0.020	–	0.025
p	Porosity (%)	–	–	0.44

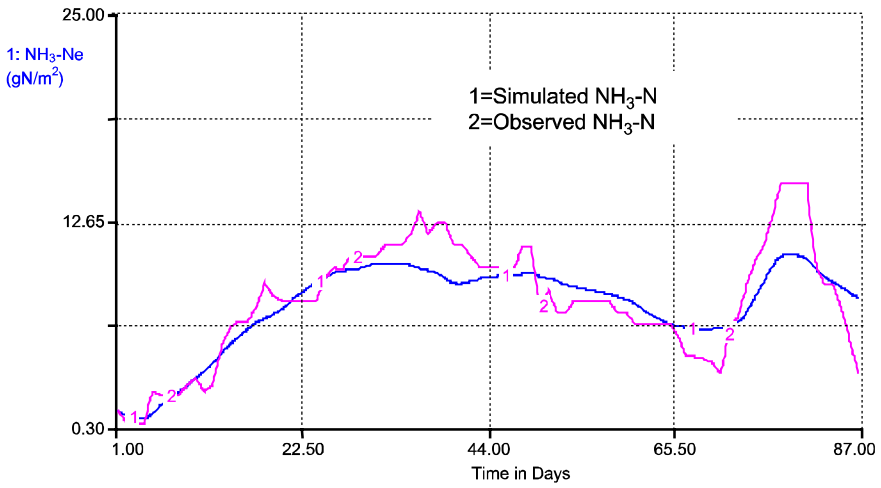


Fig. 3. Simulated NH_3-N against observed NH_3-N.

ammonia from the gravel bed was a result of anaerobic decomposition of organic-nitrogen trapped in the bed as particulate matter. These results significantly differ with those of Senzia (2003) who reported accumulation of organic-nitrogen in gravel media of 0.279 gN/m^2 d, because the author did not take into account the effect of biofilm in his work.

Uptake of nitrogen by plants was 0.280 gN/m^2 d, which was entirely from ammonia because of preference of plant for ammonia rather than nitrate. Mineralization of organic-nitrogen to ammonia was 0.007 gN/m^2 d, while nitrification of ammonia was 0.425 gN/m^2 d. By comparing the ammonia inflow and outflow of the system, there was accumulation of ammonia nitrogen of 0.360 gN/m^2 d, which is largely caused by regeneration of ammonia from the gravel bed. Denitrification process removed 0.436 gN/m^2 d, while uptake of ammonia by plants removed 0.297 gN/m^2 d. However, decaying of plants to organic-nitrogen was 0.140 gN/m^2 d, which means that nitrogen that can be removed permanently from the system by plant harvesting is 0.157 gN/m^2 d. This figure is close to 0.146 gN/m^2 d, which was reported by Senzia (2003).

In accordance with mass balance presented in Fig. 6, the major nitrogen transformation mechanisms and permanent removal of nitrogen from the system in descending order are denitrification, plant uptake and sedimentation. Denitrification process removed 29.9%, plant uptake (harvesting) account for 10.8% while sedimentation account for 8.2% of the total influent nitrogen. The model simulation on plant harvesting agrees well with the result reported

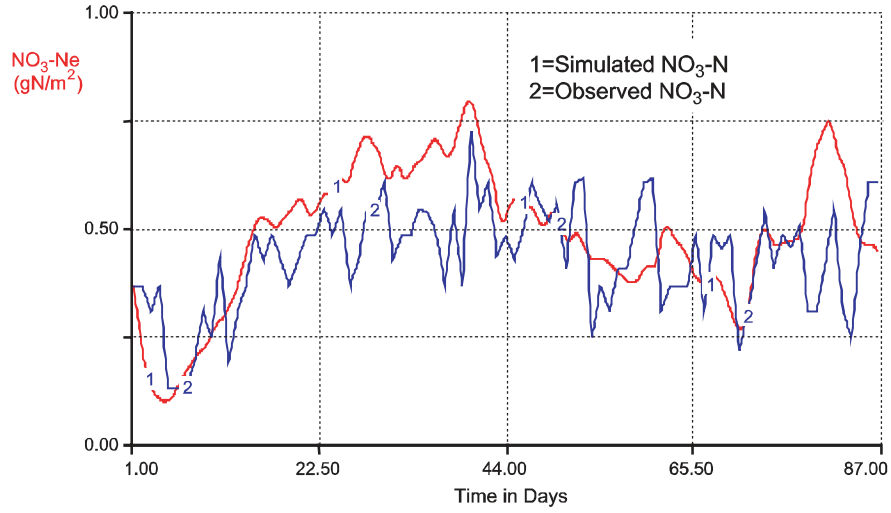


Fig. 4. Simulated NO_3-N against observed NO_3-N.

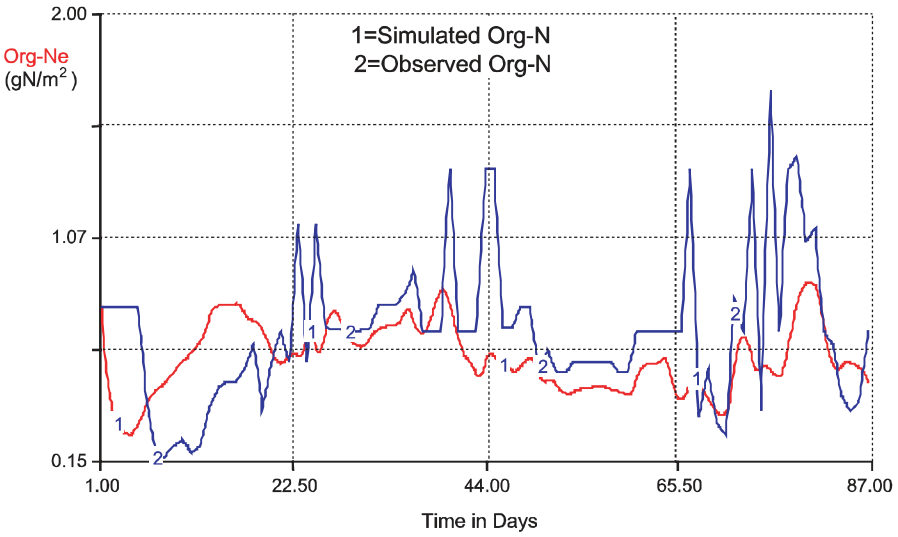


Fig. 5. Simulated organic-nitrogen against observed organic-nitrogen.

Table 2
Observed, simulated and validated nitrogen load in the effluent of wetlands

	Influent load (g/m^2 d)	First wetland unit used for simulation				Second wetland unit used for validation			
		Observed effluent load (g/m^2 d)	Observed removal efficiency (%)	Simulated effluent load (g/m^2 d)	Simulated removal efficiency (%)	Observed effluent load (g/m^2 d)	Observed removal efficiency (%)	Validated effluent load (g/m^2 d)	Validated removal efficiency (%)
Organic-nitrogen	6.07	0.67	89.0	0.56	90.8	0.85	86.0	0.56	90.8
Ammonia-nitrogen	10.90	7.82	28.3	7.50	31.2	7.93	27.2	7.50	31.2
Nitrate-nitrogen	0.81	0.42	48.1	0.48	40.7	0.44	45.7	0.48	40.7
Total nitrogen	17.78	8.91	50.1	8.54	48.0	9.22	48.1	8.54	48.0

by US EPA (1988) that plant tissue analysis at several location indicate that single annual harvest of the plant material might account for 10% or less of the nitrogen removal by the system. The total nitrogen removal in this study was 48.9%, which compares well with similar studies by Martin and Reddy (1997) who observed 38% removal and Gale et al. (1993) who reported 45–70% removal efficiency. In a similar study, Senzia (2003) reported the major pathways accounting for nitrogen removal from subsurface wetland to be accretion of organic-nitrogen (19.2%),

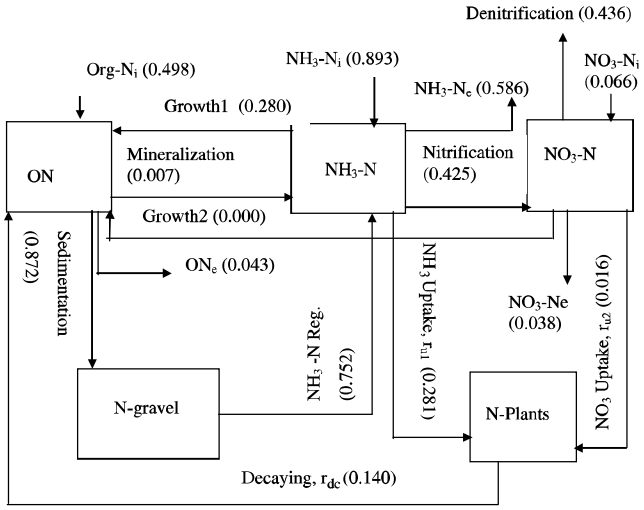


Fig. 6. Mass balances for nitrogen transformation and removal.

denitrification process (15.03%), and plant harvesting 13.4%, respectively with a total removal of nitrogen of 47.6%.

4.2. Model validation

The model was validated by using a set of independent data collected from the second wetland unit planted with *P. mauritianus*. Figs. 7–9 show the model validation for ammonia, nitrate and organic-nitrogen state variables, respectively. In general the simulated data fits reasonably well with the observed data with the overall efficiency (R^2) of 61%, suggesting that the developed model can be applied in other wetlands. Table 2 further shows a good agreement between the observed and validated data for ammonia, nitrate and organic-nitrogen effluent loads and removal efficiencies.

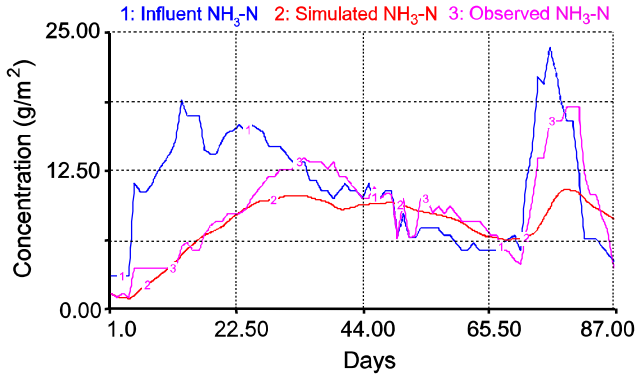


Fig. 7. Simulated NH_3-N against observed NH_3-N effluents during model validation.

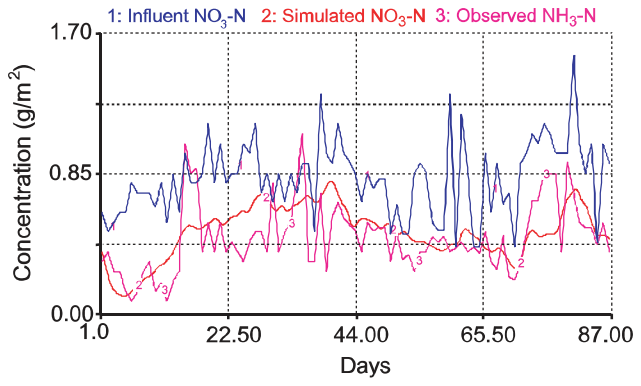


Fig. 8. Simulated NO_3-N against observed NO_3-N effluents during model validation.

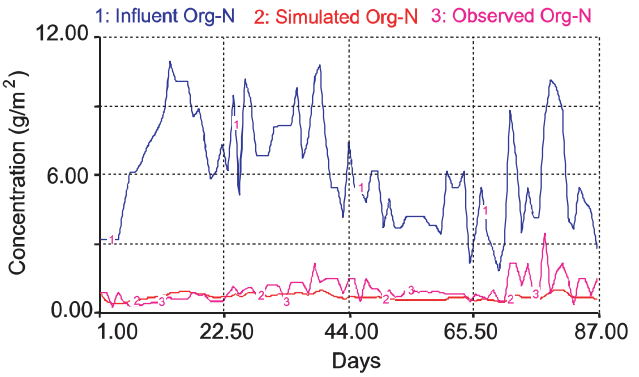


Fig. 9. Simulated versus observed effluent organic-nitrogen during model validation.

4.3. Application of the model

The developed model can be used to estimate the removal of nitrogen in horizontal subsurface flow constructed wetlands for wastewater with domestic characteristics. The important parameters needed in this model include temperature, porosity, dissolved oxygen, depth of water, pH, aggregate surface area; roots surface area, the wastewater flow rates, density and size of settling particles and biofilm parameters. The model also requires the knowledge of plant density and influent concentrations (mg/l) of NH_3-N, NO_3-N and organic-nitrogen. With all input data given, the model can be used to simulate any state variable or process.

5. Conclusions

The mathematical model developed in this work demonstrated that the model can predict the nitrogen transformation mechanisms in constructed wetlands with a reasonable accuracy. From the output of the model the following conclusions are made:

1. The major nitrogen transformation routes are sedimentation and regeneration mechanisms, which accounted for 0.872 gN/m^2 d and 0.752 gN/m^2 d, respectively. Significant transformation was also observed through denitrification and nitrification, which were responsible for transformation of 0.436 gN/m^2 d and 0.425 gN/m^2 d, respectively. Other contributing routes are uptake of nitrogen by plants (0.297 gN/m^2 d), plant decay (0.140 gN/m^2 d) and mineralization (0.007 gN/m^2 d).

2. The total nitrogen removal in the wetland was 48.9% of the total influent nitrogen, which was contributed by denitrification (29.9%), uptake of nitrogen by plants (10.8%) and net sedimentation (8.2%). However, nitrogen removal through plant uptake requires plant harvesting from the wetlands.

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