

# Models

# TSS Removal in a Coupled DyRF and HSSFCW Treating WSP Effluents

## **Abstract**

A mathematical model was developed to simulate the retention and removal of Total Suspended Solids (TSS) in the coupled Dynamic Roughing Filter (DRF) and Subsurface Horizontal Flow Constructed Wetland (HSSFCW) treating effluents from Waste Stabilization Ponds (WSP) system. The model was based on the deep – bed filtration models with an extension term that incorporates biological activities (biodegradation). This was necessitated by the fact that the latter models are based on suspension with a low organic solid content. This is not the case with the wastewater effluent. The filtration and sedimentation processes were simulated by simple equations of first order kinetics, while biodegradation process was simulated by Monod's equation. The model was calibrated using the experimental data that were obtained from the experimental rigs constructed at the outlet of the facultative WSP and was validated by data obtained from the experimental rigs placed after the maturation WSP.

The mathematical model simulation of the behaviour of DRF – HSSFCW treatment process allowed the evaluation of the most important process variables for the optimisation of the treatment processes. The simulations were performed using STELLA™ II software. From the model simulation, it was found that the sedimentation process was the major removal route of the TSS in the DRF accounting for 65% of the total removal followed by the filtration process (25%). However, the filtration process was the major route of removal of the TSS in the HSSFCW accounting for 75% removal followed by biodegradation, which accounted for 15%.

## **Introduction**

### ***Conceptual Model for Removal of Total Suspended Solids (TSS)***

This model was based on the deep–bed filtration models, and incorporates an extension term that considers biological activity (biodegradation). This was necessary because the latter models are based on suspension with a low organic solid content, which is not the case with the wastewater effluent (Bader, 1970). The filtration and sedimentation processes were simulated by simple 1<sup>st</sup>-order kinetic equations, while the biodegradation process was simulated by Monod's equation. Conservation of mass equations were developed for interactive physical and biological species

reacting to environmental factors affecting process mechanisms. Figure 1 provides a conceptual diagram of a DRF – HSSFC system, including the state variables. The mass balance for this system includes the following parameters: VSS and FSS in the DRF and VSS and FSS in the HSSFCW.

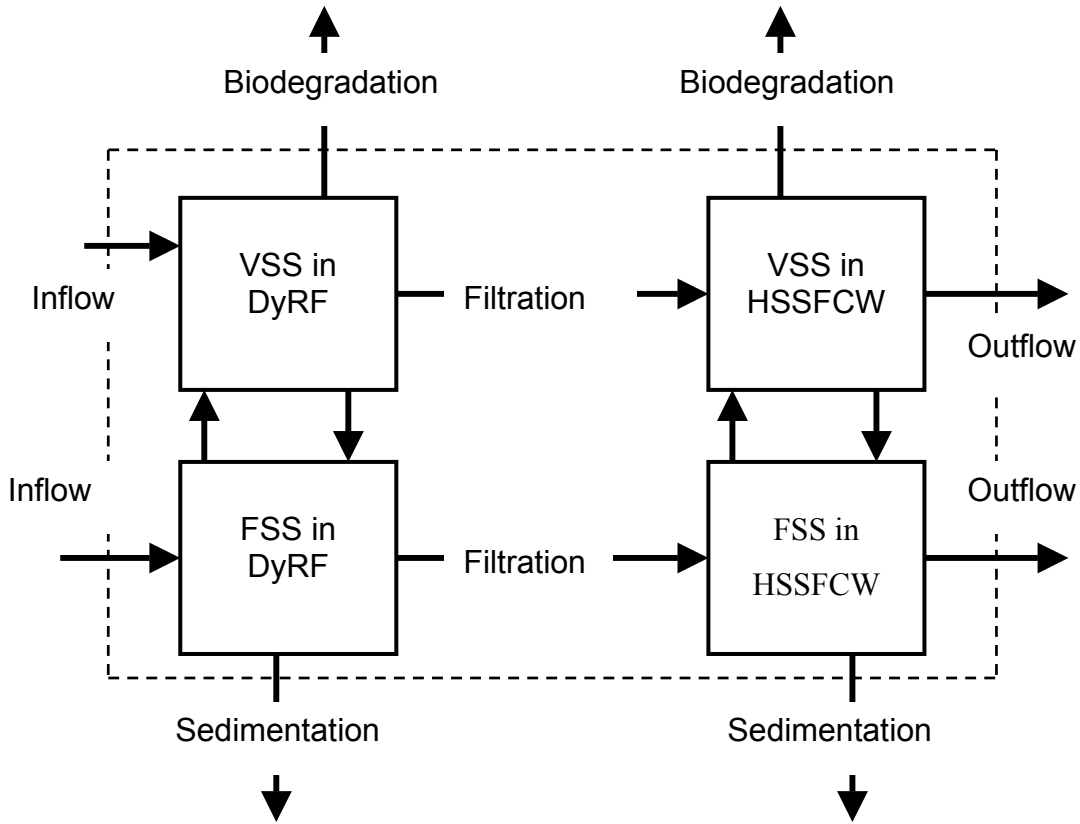


Fig. 1. Conceptual Diagram for Model Development of DyRF - HSSFCW

### Mass Balance Equations for Removal of Total Suspended Solids (TSS)

The mass balance equations for the above conceptual diagram are outlined below in Equations 1-4, as follows:

$$\frac{d(FSS_{CW})}{dt} = FSS_{CW} + F_{CW} - O_{CW} - S_{CW} \quad (1)$$

Where  $FSS_{CW}$  = FSS in HSSFCW (mg/l) (from field data),  $F_{CW}$  = Filtration process in HSSFCW (mg/l. d) (from mathematical expression),  $O_{CW}$  = Outflow from the HSSFCW (mg/l. d), and  $S_{CW}$  = sedimentation process in HSSFCW (mg/l. d) (from mathematical expression).

$$\frac{d(FSS_{RF})}{dt} = FSS_{RF} + (I_{RF} - F_{RF} - S_{SF} - B_{WSP}) \quad (2)$$

Where  $FSS_{RF}$  = FSS in DyRF (mg/l) (from field data),  $F_{RF}$  = Filtration process in DyRF (mg/l. d) (from mathematical expression),  $I_{RF}$  = Inflow to the DyRF (mg/l. d),  $S_{RF}$  = sedimentation process in DyRF (mg/l. d) (from mathematical expression), and  $B_{WSP}$  = Water overflowing over DyRF going back to WSP.

$$\frac{d(VSS_{CW})}{dt} = VSS_{CW} + (F_{CW} - O_{CW} - B_{CW}) \quad (3)$$

Where  $VSS_{CW}$  = VSS in HSSFCW (mg/l) (from field data),  $B_{CW}$  = Biodegradation process in HSSFCW (mg/l. d) (from mathematical expression), and other terms as defined in above equations.

$$\frac{d(VSS_{RF})}{dt} = VSS_{RF} + (I_{RF} - B_{WSP} - F_{RF} - B_{RF}) \quad (4)$$

Where  $VSS_{RF}$  = VSS in DyRF (mg/l) (from field data),  $B_{RF}$  = Biodegradation process in DyRF (mg/l. d) (from mathematical expression), and other terms as defined in above equations.

However, mathematical expressions for the different processes also can be written. For the case of the inorganic part of TSS (the Fixed Suspended Solids, FSS), the equations for different processes for different components are as discussed below.

For filtration in HSSFCW:

$$F_{CW} = \frac{FSS_{CW} \times f \times 0.15 \times 0.95}{V_{CW}} \quad (5)$$

Where:  $f$  = filtration rate (m/d),  $V_{CW}$  = volume of the HSSFCW ( $m^3$ ), and the factors 0.15 and 0.95 (Jørgensen, 2001) take the efficiency of the system into account. A similar mathematical expression applies in DyRF.

For the outflow from the system (HSSFCW):

$$Q_{CW} = \frac{FSS_{CW} \times Q_o}{V_{CW}} \quad (6)$$

Where  $Q_o$  = outflow rate ( $m^3/d$ ).

For the sedimentation process in HSSFCW:

$$S_{CW} = \frac{FSS_{CW} \times S_R}{d} \quad (7)$$

Where,  $S_R$  sedimentation rate (m/d), and  $d$  = depth of the HSSFCW (m).

For the inflow process to the DyRF:

$$I_{RF} = \frac{Q_i \times FSS_{in}}{V_{RF}} \quad (8)$$

Where  $Q_i$  = Inflow rate ( $m^3/d$ ),  $V_{RF}$  = volume of DyRF ( $m^3$ ), and  $FSS_{in}$  incoming FSS (mg/l).

For the filtration process in DyRF:

$$F_{RF} = \frac{FSS_{RF} \times f \times 0.15 \times 0.95}{V_{RF}} \quad (9)$$

For the sedimentation process in DyRF,

$$S_{RF} = \frac{FSS_{RF} \times S_R}{d_d} \quad (10)$$

Where  $d_d$  is the depth of DyRF.

There also are mathematical expressions for the organic part of TSS (the Volatile Suspended Solids, VSS).

For filtration in HSSFCW:

$$F_{CW} = \frac{VSS_{CW} \times f \times 0.15 \times 0.95}{V_{CW}} \quad (11)$$

For the outflow from HSSFCW:

$$Q_{CW} = \frac{VSS_{CW} \times Q_o}{V_{CW}} \quad (12)$$

For the biodegradation in HSSFCW:

$$B_{CW} = VSS_{CW} \times k_{20}^{\theta-20} \times \frac{DO}{(k_2 + DO)} \quad (13)$$

Where  $k_2$  is biodegradation rate constant,  $k_{20}$  is the temperature dependent factor, DO is the dissolved oxygen (mg/l), and  $\theta$  is the temperature of the system.

For the incoming flow in DyRF:

$$I_{RF} = \frac{Q_i \times VSS_{in}}{V_{RF}} \quad (14)$$

Where  $VSS_{in}$  is the incoming VSS (mg/l).

For filtration in DyRF:

$$F_{RF} = \frac{VSS_{RF} \times f \times 0.15 \times 0.95}{V_{RF}} \quad (15)$$

For biodegradation in DyRF:

$$B_{RF} = VSS_{RF} \times k_{20}^{\theta-20} \times \frac{DO}{(k_2 + DO)} \quad (16)$$

A summary of the parameters used in this study is provided in Table 1 in the next page.

**Table 1. Parameters used in this study**

Name	Values (units)	Source
$k_1$	0.3 (d <sup>-1</sup> )	Jørgensen (2001)
$k_2$	0.5 (d <sup>-1</sup> )	Jorgensen (2001)
VSS	mg VSS/l	Obtained from the study
FSS	mg FSS/l	Obtained from the study
Q	d <sup>-1</sup>	Obtained from the study
DO and temp	mg/l and °C	Obtained from the study
Sed. rate	m/d	Calibrated
Filt. rate	m/d	Obtained from the study
Vol. DyRF	m <sup>3</sup>	Obtained from the study
Vol. SSF	m <sup>3</sup>	Calculated from the study
$K_{20}$	1.04	Metcalf and Eddy (1997)

## Methodology

### *Experimental Setup*

Pilot field-scale plots configured in one train of two in series were constructed at the immediate outlet of a UDSM WSPs system. The system consists of DRF and HSSFCW. The DRF had a length of 1.5 m, a width of 0.5 m and a depth of 0.7 m. It comprised of three layers of graded gravel, including a 0.2 m bottom layer with gravel of 19 – 25 mm and a drainage system, a 0.2 m middle layer with gravel of 13 – 19 mm, and a 0.2 m top layer with gravel of 6 – 13 mm. The experiments were run with filtration rates of 2.0 m/hr. An influent value ( $Q_i$ ) was chosen on the basis of DRF guidelines for surface flow velocity given by Galvis *et al.* (1993). Facultative WSP effluent is applied first to the DRF, while the effluent from the DRF is discharged to the HSSFCW on a continuous basis. For the purposes of this study, only a small amount of effluent was diverting to the DRF before it entered the HSSFCW cell. The diverted WSP effluent flowed to a 0.8 x 0.8 m distribution chamber, from which wastewater samples were taken to evaluate the processes. To simplify the latter terminology, the WSP effluent to the DRF was henceforth termed influent, in relation to filter operation. The HSSFCW cell was 1.75 x 0.6 - m in plane and 0.6 - m deep. Both the DRF and HSSFCW were constructed of ferro-cement materials because of cost considerations. The underdrains consisted of 50-mm diameter PVC pipe containing drain holes overlaid with 0.3 m of gravel arranged in three layers according to size. The underdrain system supported 0.8 m of sand media. The specifications of the medium used in each pair of filters are presented in Table 2. The open channel built at the inlet was used to measure the flow rate to the DRF.

Table 2. Media characteristics used in DRF

Type of media	Average diameter (mm)	Void (%)	Media surface area (m <sup>2</sup> /m <sup>3</sup> )
Fine gravel (4 – 8)	6	28	327
Medium (8 – 12)	10	40	150
Coarse (12 – 16)	14	41	25
Coarse (16 – 25)	20.5	49	17

Figures 2 and 3 are schematic illustrations of the pilot filters layout and cross – section, respectively.

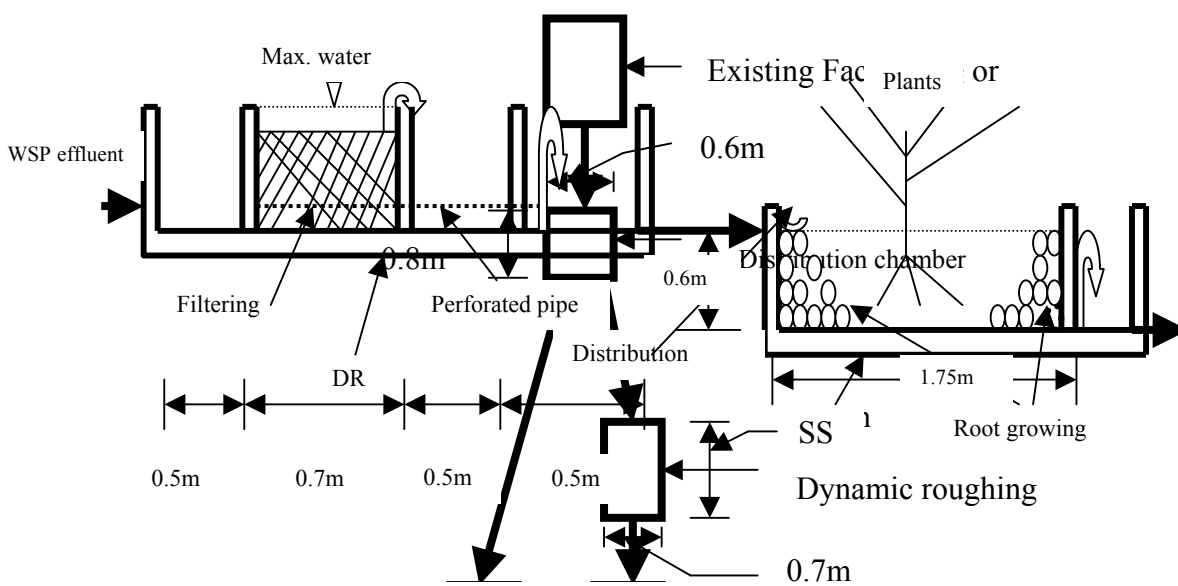


Figure 3. Cross section of DRF and HSSFCW structured in stages

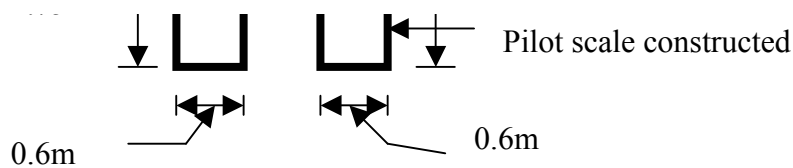


Figure 2. Schematic representation of WSP, DRF and HSSFCW

### Sampling and Analysis

Samples were taken simultaneously at different sampling points. All tests were carried out in accordance with the methods outlined in APHA (1992). Daily samples were collected from the inlet, inside of, and at the outlet of the DRF, and from the inlet, inside of, and at the outlet of HSSFCW. For the purpose of this modeling effort, samples were analyzed for Total Suspended



Solids (TSS), Volatile Suspended Solids (VSS), Fixed Suspended Solids (FSS). Also measured were the water temperature (T), pH and Dissolved Oxygen (DO).

### Model Calibration

The model was evaluated by comparing model-computed values with the observed data for the pilot scales of DyRF – HSSFCW receiving WSP effluents. The computed and observed effluent TSS values are shown in Figures 4 and 5. Because fixed time integration steps were used because of the highly non-linear dependencies, the model predictions were considered as trends, rather than accurate numeric values. Nevertheless, these simulations generated pertinent results consistent with the experimental results associated with this study. Accordingly, the reduction in the Total Suspended Solids (TSS) was judged to have been satisfactorily modeled.

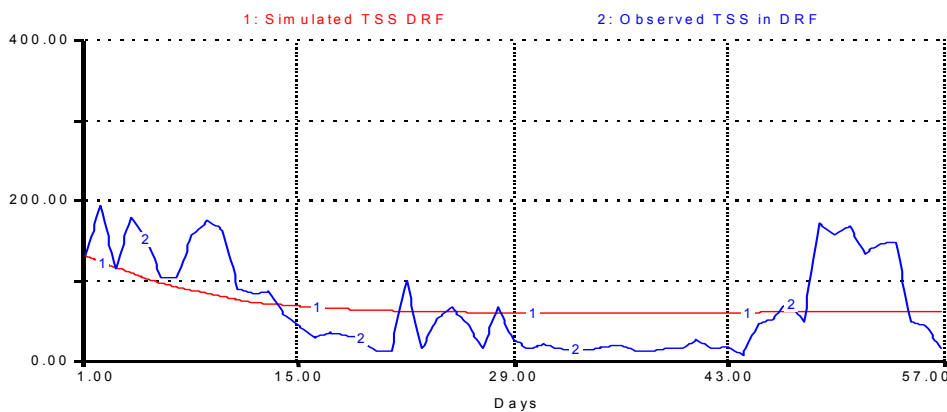


Figure 4. The observed and simulated TSS values in the DyRF

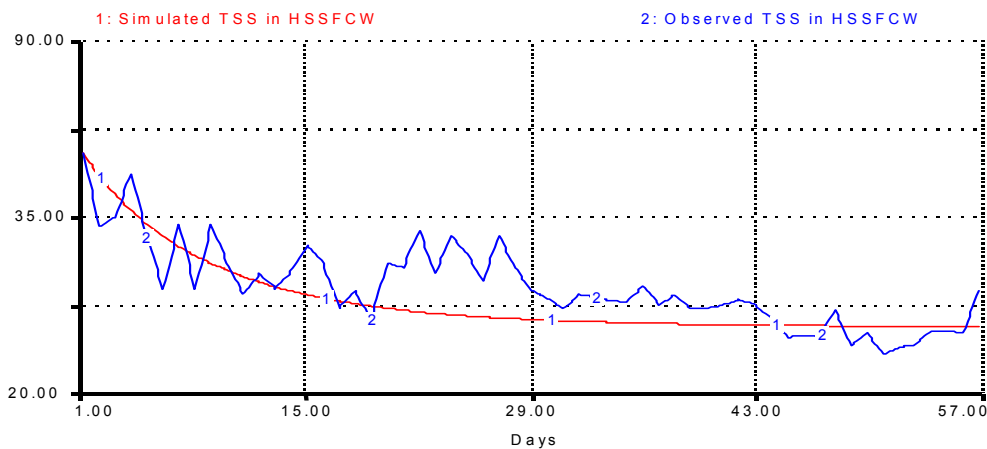


Figure 5. The observed and simulated TSS values in the HSSFCW

## Discussion

The model developed in this study predicted the decreases in the Total Suspended Solids (TSS) in both the DyRF and HSSFCW systems. From the model simulations, it was found that the sedimentation process was the major TSS removal route in the DyRF, accounting for a mean of 63.7% (26.67 g TSS/m<sup>2</sup>.d) of the total removal, followed by the filtration process mean removal rate of 22.1% (9.25 g TSS/m<sup>2</sup>.d). In contrast, the filtration process was the main TSS removal route in the HSSFCW, accounting for a mean removal of 77.4% (7.23 g TSS/m<sup>2</sup>.d), followed by biodegradation, which accounted for a mean removal of only 16.2% (1.52 g TSS/m<sup>2</sup>.d). The sedimentation on the exposed surface of the gravel bed of DyRF also can be explained. The area over the gravel surface is considered as a plain sedimentation tank, where the removal of TSS is dependent on two factors: (1) the settling velocities of the suspended particles, and (2) the overflow rate. The higher efficiency at the start of the filter run was favored by the cleanliness of the filter, and the low flow rate ( $Q_0$ ).

On the other hand, sedimentation in the gravel bed contributed to the removal of TSS in DyRF. By way of explanation, the sedimentation efficiency in the gravel bed depends on the surface loading,  $S_1 = Q_e (A_1)^{-1}$ . Reducing  $Q_e$  during the filter run causes  $S_1$  to become smaller, thereby increasing the removal efficiency. This observation is similar to that reported by Galvis *et al.* (1993), Latorre *et al.* (1994), Wegelin *et al.* (1991) and Boller (1993).



# Nitrogen Removal from Domestic Wastewater by Indigenous Macrophytes in Horizontal Sub-surface Flow Constructed Wetlands in Tanzania

## Introduction

The overall objective of this study was to develop a model for identifying the most suitable indigenous emergent macrophytes species of the six tested for wastewater treatment in HSSFCW in Tanzania, based on nitrogen removal. The main nitrogen removal mechanisms studied were plant uptake and denitrification.

## Conceptual Model

Figure 1 shows the conceptual model for nitrogen removal in HSSFCW. STELLA<sup>®</sup> (Version 6.0 of 1998) programming language has been used for model simulation and programming, based on the principle of conservation of mass (Jørgensen, 1994). It is assumed that ammonia and nitrate nitrogen removal from wetlands by macrophytes depended on the biomass of the roots. Thus, the removal rate increased with the increasing plant root biomass (PLRB).

## Mathematical Descriptions of Model Interactions

The change in the amount of ammonia nitrogen through nitrification and plant uptake was as shown in equation 1:

$$\left(\frac{\partial Q}{\partial t}\right)_{ammoni} = Q_i + Q_{min} - Q_{nitrif} - Q_{out} - Q_{upt} \dots \dots \dots (1)$$

where  $Q_i$ ,  $Q_{min}$ ,  $Q_{nitrif}$ ,  $Q_{out}$  and  $Q_{upt}$  are inflow rate, mineralisation rate, nitrification rate, outflow rate, and uptake rate ( $\text{mg}/\text{m}^3/\text{day}$ ), respectively.

Loss of ammonia through evaporation or infiltration was neglected, due to the fact that the maximum water flow level was below the substrate, and the walls were lined. Thus, the general equation of the biochemical processes in the state variable  $[C_{\text{NH}_3\text{-N}}]$  can be represented by Equation 2, as follows:

$$\left(\frac{\partial C}{\partial t}\right) = \left(\frac{Q_i C}{V_i V_p}\right)_{in} - \left(\frac{Q C}{V_i V_p}\right)_{eff} + \left(\frac{\partial C}{\partial t} X_A\right)_{min} - \left(\frac{\partial C}{\partial t} X_B\right)_{nitrif} - \left(\frac{\partial V}{\partial t} C\right)_{upt} - \left(\frac{\partial C}{\partial t} V\right)_{oxd} \dots \dots \dots (2)$$

where  $Q_i$ ,  $Q$  = inflow and outflow of wastewater to and from the wetland [ $m^3/d$ ],  $C$  = concentration of ammonia N in the constructed wetland [ $mg/l$ ],  $V_t$  = total volume of the constructed wetland [ $m^3$ ],  $V_p$  = Pore volume - fraction of the wetland volume occupied by the wastewater [ $m^3$ ],  $X_A$  and  $X_B$  = biomass decrease and increase of mineralised and nitrifying bacteria [ $mg/l$ ],  $in$  and  $eff$  = inflow and effluent;  $min$ ,  $nitrif$ ,  $upt$  and  $oxd$  = mineralisation of organic biomass, nitrification, uptake and oxidation.

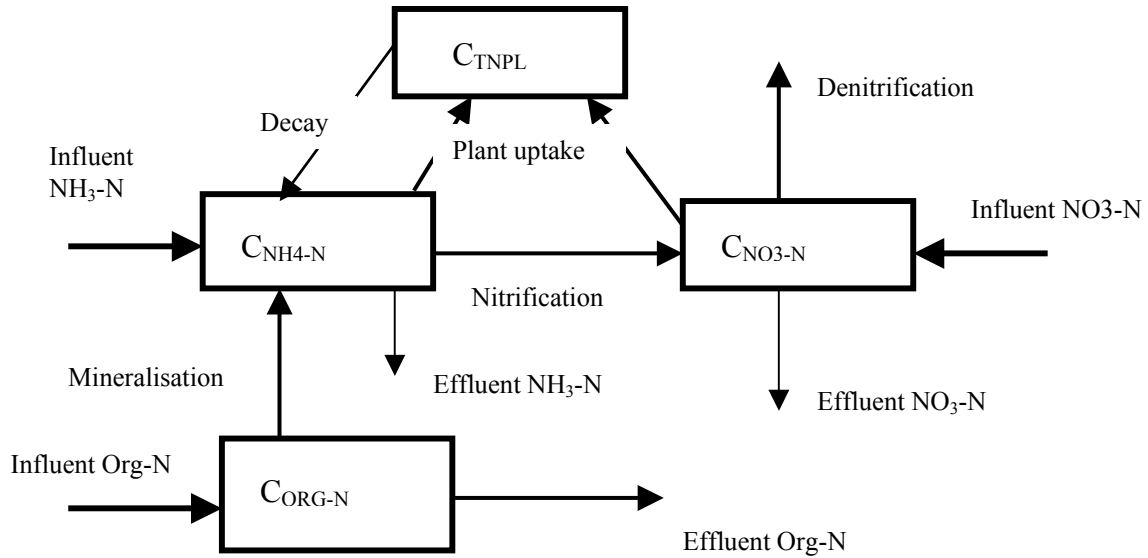


Fig.1. A Simplified Conceptual Wetland N Model

A fraction of N entering the constructed wetland in dead organic matter through mineralisation is influenced by temperature, as shown in Equation 3.

$$k_T = k_{\min(20)} \theta^{(T-20)} \dots\dots\dots (3)$$

where  $k_T$  = oxidation rate at field temperature,  $k_{\min(20)}$  is oxidation rate at standard temperature of the wetland, and  $\theta$  is temperature coefficient.

**Nitrification**

The change in the quantity of ammonia-N in the wetland through nitrification is defined by the Monod Equation 3. Nitrification is a first-order kinetics process. Thus, it can be presented as shown in Equation 4:

$$r_N X_B = [\mu_{\max(XB)} f(S)] X_B \dots\dots\dots (4)$$

where  $r_v X_B$  is the volumetric biological growth (mg/l);  $\mu_{\max(XB)}$  is the bacterial growth rate (per day);  $f(S)$  is the function of substrate quality on growth kinetics of the Monod type; and  $X_B$  is the concentration of bacterial biomass (mg/l).

Temperature, pH, and substrate concentration affect the growth rate of nitrifying bacteria. Thus, Equation 4 can be rewritten to reflect the direct effects of the forcing functions, as follows:

$$r_v X_B = [\mu_{\max(XB)} f(S, pH, DO, T)] X_{PB} \dots \dots \dots (5)$$

where  $f[S, pH, T]$  is the limitation due to substrate, pH, and temperature of wastewater.

Equation 5 is based on the limitation due to the substrate, as follows:

$$f(S) = \mu_{\max(XB)} \left( \frac{S_{NH_3-N}}{K_{SNH_3-N} + S_{NH_3-N}} \right) \left( \frac{S_{NO_3-N}}{K_{NO_3-N} + S_{NO_3-N}} \right) \dots \dots \dots (6)$$

where  $K_{SNH_3-N}$  is the half saturation constant for ammonia nitrogen (mgNH<sub>4</sub>N/l),  $\mu_{\max}$  is the bacterial growth rate (day<sup>-1</sup>),  $S_{NH_3-N}$  is the concentration of organic matter,  $K_{NO_3-N}$  is the half saturation constant for nitrate nitrogen, and  $S_{NO_3-N}$  is the concentration of nitrate nitrogen in the constructed wetland.

The influence of pH on the growth rate of microorganisms is presented in Equation 8 (Kayombo, 2001):

$$f(pH) = \mu_{\max(XB)} \left( \frac{K_{pH}}{K_{pH} + Y} \right) \dots \dots \dots (8)$$

Where;  $\mu_{\max}$  = the maximum growth rate of nitrifying bacteria [day<sup>-1</sup>],  $K_{pH}$  = the pH constant, and

$$Y = 10^{(OptpH - pH)} - 1 \dots \dots \dots (9)$$

where OptpH = optimum pH at which the growth of bacteria is maximum.

The function of dissolved oxygen on the update process is formulated as a Monod's equation, thereby being represented as shown in Equation 10:

$$f(DO) = \mu_{\max(XB)} \left( \frac{S_{DO}}{K_{SDO} + S_{DO}} \right) \dots \dots \dots (10)$$

where  $S_{DO}$  is the dissolved oxygen concentration in the constructed wetland (mg/l), and  $K_{SDO}$  is the saturation constant for the dissolved oxygen (mg/l).

Nitrifiers prefer moderate temperatures, ranging between 20 - 30° C. The function of temperature in the nitrification equation follows the first-order kinetic process, as shown in Equation 11:

$$f(T) = \mu_{\max(XB)} \exp(\kappa[T - 20]) \dots \dots \dots (11)$$

where  $\kappa$ = temperature dependent rate constant for nitrification (° C<sup>-1</sup>), and T = temperature of the pore water in the wetland (° C).

These processes are described by the multiplication of the Michaelis-Menten equations of these restrictive factors (Asaeda *et al.*, 2001), and can be represented by Equation 12:

$$Photo = k_{co} * P_m * \frac{NH_3 - N}{K_N + NH_3 - N} * \frac{NO_3 - N}{K_N + NO_3 - N} * \frac{PAR}{K_{par} + PAR} * \frac{K_{age}}{K_{age} + Age} * X_{PB} \dots \dots \dots (12)$$

where Photo is the photosynthesis of carbohydrates by macrophytes,  $k_{co}$  is the conversion constant from oxygen to the oven dry weight (gg<sup>-1</sup> O<sub>2</sub>),  $P_m$  is the maximum gross photosynthesis (g O<sub>2</sub> g<sup>-1</sup>h<sup>-1</sup>), NH<sub>3</sub>.N is the ammonia-nitrogen concentration (mg/m<sup>2</sup>), NO<sub>3</sub>-N is the nitrate-nitrogen concentration (mg/m<sup>2</sup>),  $K_N$  is the half saturation nitrogen (mg N/m<sup>3</sup>), PAR the insolation of photosynthetically-active radiation (PAR) averaged for a day (μEm<sup>-2</sup>/day),  $K_{age}$  is the half saturation constant for the age [mg/day],  $K_{par}$  is the half-saturation constant of light (PAR) for gross photosynthesis and Age is the age of the plant (day). PB is the annual plant biomass (g/m<sup>2</sup>/yr).

Transforming the organic matter to oxygen demand (2.67g O<sub>2</sub> g<sup>-1</sup> C (Pereira *et al.*, 1994):

$$P_m = 0.408T + 10.12 \dots \dots \dots (13)$$

$$K_{par} = 349 - 4.99T \dots \dots \dots (14)$$

$$R_r = 0.033T + 0.108 \dots \dots \dots (15)$$

where  $R_r$  is the respiration rate of plant irrespective of plant parts (per day)

$$Mortality = PB * K_{mort} \dots \dots \dots (16)$$

where  $K_{mort}$  = the mortality rate of plant biomass (per day).

and

$$Harvesting = PB * fr \dots \dots \dots (17)$$

where fr = fraction of biomass that is harvested (per day).

## Denitrification

The quantity of nitrate-nitrogen in the wetlands required for the growth of denitrifying bacteria is shown in Equation 18:

$$\left(\frac{\partial Q}{\partial t}\right)_{NO_3-N} = Q_i + Q_{nitrif} - Q_{denitr} - Q_{NO_3-Nupt} - Q_{NO_3-Nout} \dots \dots \dots (18)$$

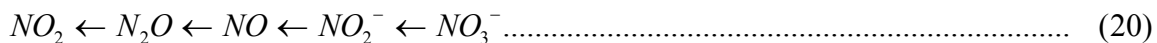
where  $Q_i$ ,  $Q_{nitrif}$ ,  $Q_{denitr}$ ,  $Q_{NO_3-Nout}$  and  $Q_{NO_3-Nupt}$  is inflow rate, nitrification rate, denitrification rate, uptake rate and outflow rate ( $mg/m^3/day$ ), respectively.

The general equation of the biochemical processes is shown in Equation 19:

$$\left(\frac{\partial C}{\partial t}\right) = \left(\frac{QC}{V_{cp}}\right)_{in} - \left(\frac{QC}{V_{cp}}\right)_{eff} + \left(\frac{\partial C}{\partial t} X_B\right)_{nitrif} - \left(\frac{\partial C}{\partial t} X_C\right)_{denitrif} - \left(\frac{\partial V}{\partial t} C\right)_{upt} \dots \dots \dots (19)$$

where  $Q_i$ ,  $Q$  = inflow and outflow of wastewater to and from the wetland [ $m^3/d$ ],  $C$  = concentration of nitrate-N in the wetland [ $mg/l$ ],  $V_{cp}$  = corrected pore volume - fraction of the constructed wetland volume occupied by the wastewater [ $m^3$ ],  $X_B$  and  $X_C$  = biomass decrease and increase of mineralised and nitrifying bacteria [ $mg/l$ ],  $in$  and  $eff$  = inflow and effluent;  $nitrif$ ,  $denitrif$ , and  $upt$  = nitrification, denitrification, and uptake

The change in the quantity of nitrate-N concentration in the constructed wetland through the denitrification process reduces these nitrogen compounds through a series of reactions, finally producing nitrogen gas, as shown in Equation 20 (Ward, 2000):



This can be rewritten as Equation 21, to reflect the direct effects of the forcing functions:

$$r_v X_B = [\mu_{\max(XB)} f(S_{nitr}, T)] X_B \dots \dots \dots (21)$$

The Michaelis-Menten equation can be used to represent this equation as a function of temperature, nitrate concentration and maximum growth rate of denitrifying bacteria, as shown in Equation 22:

$$r_v X_B = \mu_{\max 2} * K_d * \frac{S_{NO_3-N}}{(K_{dm} + S_{NO_3-N})} * X_B \dots \dots \dots (22)$$



Where:  $\mu_{\max 2}$  = the maximum growth rate of denitrifying bacteria [1/d],  $K_d$  = half saturation constant for nitrate concentration in wetlands [mg/l],  $[NO_3N]$  = the concentration of nitrate-nitrogen in the wetlands [mg/l],  $K_{dm}$  = maximum half saturation constant of nitrate nitrogen [mg/l], and  $X_B$  = the biomass of the denitrifying bacteria.

The total nitrogen absorbed by the macrophyte is the sum of the nitrogen absorbed as ammonia and nitrate. Equation 23 gives the sum of the two forms of nitrogen taken up by plants:

$$TN = NH_3-N_{upt} + NO_3-N_{upt} \dots \dots \dots (23)$$

where  $NH_4-N$  is the quantity of ammonia nitrogen absorbed by macrophytes [mg/day],  $NO_3-N_{upt}$  is the quantity of nitrate-nitrogen absorbed by macrophytes [mg/day], and  $NH_3-N_{upt}$  is the quantity of ammonia-nitrogen absorbed by macrophytes [mg/day].

Mineralisation and outflow are the major factors that deplete organic nitrogen in the constructed wetlands, as shown in Equation 24:

$$\left(\frac{\partial Q}{\partial t}\right)_{OrgN} = Q_i + Q_{dec} - Q_{min} - Q_{out} \dots \dots \dots (24)$$

where  $Q_i$ ,  $Q_{dec}$ ,  $Q_{min}$  and  $Q_{out}$  is inflow rate, decay rate, mineralisation rate, and outflow rate ( $mg/m^3/day$ ), respectively, and  $OrgN_{inconc}$  is the concentration of organic-N in the influent wastewater [ $mg/m^3/d$ ].

The decay rate of macrophytes above the ground is influenced by the ambient temperature, and follows the first-order kinetic process, as shown in Equation 25:

$$k_{dm} = k_{d(20)} \beta^{(T_a - 20)} \dots \dots \dots (25)$$

where  $k_{dm}$  = macrophyte maximum decay rate [ $day^{-1}$ ] at ambient (field) temperature,  $k_{d(20)}$  is the decay rate at 20°C ( $day^{-1}$ ),  $\beta$  is the exponential temperature coefficient, and  $T_a$  is the ambient or field temperature.

### The Mass Loading Rate

The mass loading rate for all nitrogenous forms was calculated on the basis of Equation 26:

$$MLR_{vol} = \frac{CoQ}{V} = \frac{Co}{HRT} \dots\dots\dots (26)$$

where  $MLR_{vol}$  = volume based loading rate ( $g/m^3 \cdot d$ ),  $Co$  = influent concentration ( $mg/L$ ),  $Q$  = flow rate ( $m^3/d$ ),  $V$  = water volume ( $m^3$ ), and  $HRT$  = hydraulic retention time.

The parameters, variables and constants used in developing the model are summarized in Table 1.

Table 1. The parameters, variables and constants in the model

Symbol	Description	Value	Unit	Source
Ta	Average air temperature during study	27	°C	Field
Fr	Fraction of biomass harvested	0.001	$g/m^2/day$	Estimate
Kage	Half saturation constant of age of macrophytes. (annual N biomass produced)	500	$g N/yr$	Field
Sun	Solar radiation falling on a specified surface area	200	$E/m^2/day$	Calibrated
Kmort	Fraction of biomass mortality from daily biomass produced	0.001	per day	Asaeda <i>et al.</i> (2000)
T <sub>2</sub>	Surface soil temperature	25-30	° C	Field
kt <sub>2</sub>	temperature coefficient for mortality	1.04		Jorgensen (1983)
Vwet	Volume of wetland	0.35	$M^3$	Field
PoreV	Pore volume	0.4	$M^3$	Field
OptpH	pH favorable for nitrifying bacterial growth,	6.7		Kayombo (2000)
KpH	Half saturation constant for pH	220		Calibrated
$\mu_{max}$	maximum growth rate of nitrifying bacteria ( <i>Nitrosomonas</i> )	1.2	per day	Calibrated
K <sub>T</sub>	Temperature coefficient for nitrification and denitrification	1.07		Jorgensen (1989)
RNmax	Maximum root N-concentration	144.582	$mg/m^2$	Hootsmans (1994)
RNmin	Minimum root N-concentration	71.106	$mg/m^2$	Hootsmans (1994)
Rb	Root biomass per unit volume	15237	$mg/m^3$	Hootsmans (1994)
K <sub>o</sub>	Half saturation constant for N bioaccumulated by macrophytes	0.0000489	$g/m^3$	Estimate

## Model Results

After its development, the model was calibrated and validated, using the observed and simulated data. The results for  $NH_3-N$  and  $NO_3-N$  in the wetlands, and TPLN from the plants, have been graphically presented in Figs. 2 - 4. The simulated and observed results for wetland ammonia, and nitrate concentration in this model are in good agreement with those found using graphical methods. Ammonia and nitrate increase after 35 days of planting, meaning there is an increase in root surface area for microbiological activity, where organic N is mineralised into ammonia-N, which is later nitrified into nitrate N.

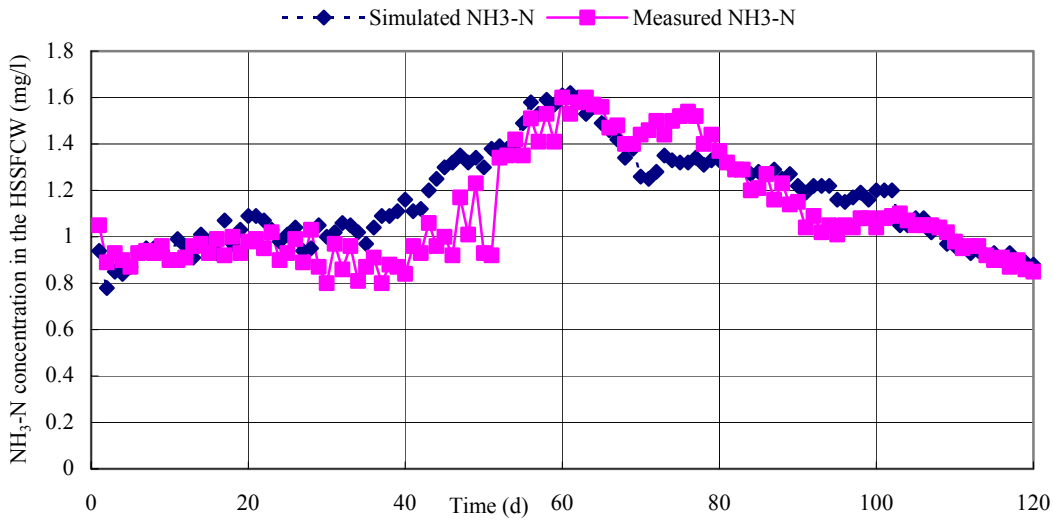


Fig. 2. Model Calibration: Simulated and Observed NH<sub>3</sub>-N Concentration in HSSFCW Planted with Indigenous Macrophytes

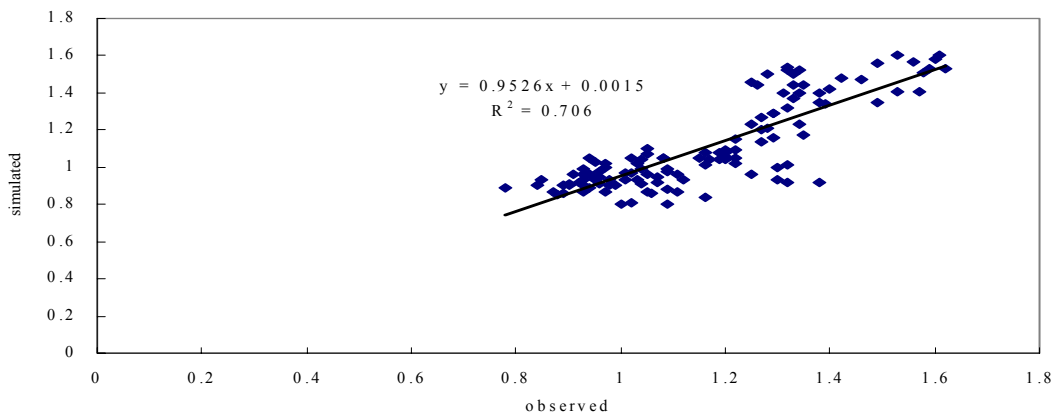


Fig. 3. Regression of Ammonia Concentration in HSSFCW Planted with Indigenous Macrophytes

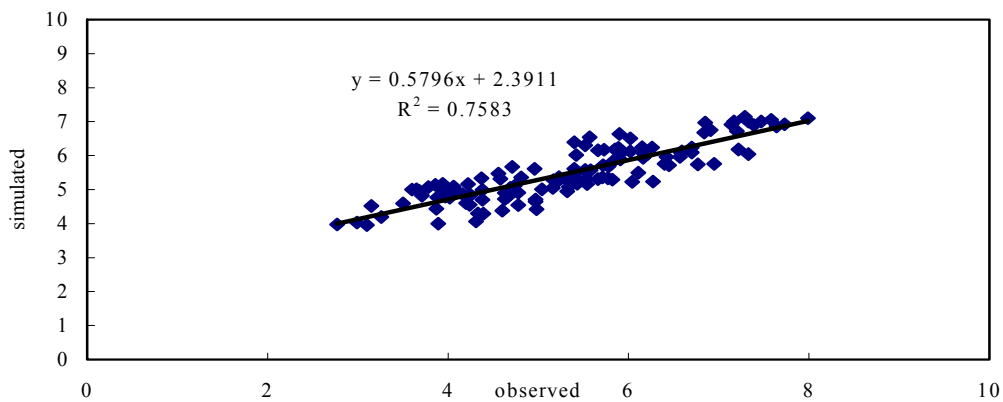


Fig. 4. Validation of Nitrate Concentration in HSSFCW Planted with indigenous Macrophytes

This is also the period of exponential growth. Thus, there is a possibility of reduced nitrification activity, due to low oxygen concentrations in the wetland. Both ammonia and nitrate concentrations decrease after 60 days, due to increased nitrification of ammonia into nitrate, and denitrification of nitrate. About 80 days after planting, ammonia and nitrate concentrations gradually decrease to almost constant level (Fig. 2). The nitrogen bioaccumulation in the plant biomass increases gradually as the plant grows.

Model validation and regression curves gave similar trends to the model calibration. The high regression coefficients between the simulated and measured data indicate that they are of reasonable quality. However the  $\text{NO}_3\text{-N}$  regression is a bit lower than for  $\text{NH}_3\text{-N}$  and plant-N, indicating there is a need to increase the size of the wetlands to allow sufficient surface area for nitrification and denitrification to occur. Moreover, there is a need to improve data collection techniques, since  $\text{NH}_3\text{-N}$  volatilizes if not properly handled in the laboratory. The model is capable of simulating the  $\text{NH}_3\text{-N}$ ,  $\text{NO}_3\text{-N}$  and Plant-N cycle in the wetlands receiving WSP effluent.

## Conclusions

The results obtained in the present work, and taking into consideration data from literature, it is concluded that the model can be used to select indigenous aquatic macrophytes for the treatment of wastewater polluted with domestic sewage and industrial effluent, provided certain parameters are known, an example being the plant root biomass.

# **Transformation in horizontal sub-surfaceflow constructed wetlands planted with *Phragmites Mauritanus***

## **Introduction**

The use of constructed wetlands is now recognised as an acceptable, low-cost eco-technology, especially beneficial to small communities that cannot afford expensive conventional treatment systems (White, 1995; Billore *et al.*, 1999). During the last three decades, the multiple functions and values of wetlands have been recognised not only by scientists, but also the public (Brix, 1994). Wetlands are among the most important ecosystems on Earth because of their unique hydrologic conditions, and their role as ecotones between terrestrial and aquatic systems (Mitsch and Gosselink, 1993). The potential applications of wetlands range from the secondary treatment of municipal and various types of industrial wastewaters to the polishing of tertiary-treated water and control of diffuse pollution. Successful case studies indicate that wetlands can significantly reduce suspended solids, biological oxygen demand (BOD), pathogens, heavy metals and excessive nutrients from wastewater (Gersberg *et al.*, 1984; Rogers *et al.*, 1991; Ojo and Mashauri, 1996). This section presents a mathematical model that permits dynamic simulations of nitrogen interactions in horizontal, sub-surface flow constructed wetlands receiving effluents from primary facultative ponds. Nitrogen transformation processes considered in this model include nitrification, denitrification, plant uptake, decomposition and accretion of organic nitrogen. Volatilisation was not included because it only plays a negligible role in reducing nitrogen at the typically neutral pH levels found in sub-surface wetland systems. The mechanistic approach, which is mathematically complex, but also more rational than empirical and semi-empirical models, was applied. This approach also was found suitable by other researchers (Billore *et al.*, 1999; Martin and Reddy, 1997; Cooper *et al.*, 1996; Kadlec and Knight, 1996; Vymazal *et al.*, 1998). The research was conducted in the University of Dar es Salaam pond system. The modelling process was carried out with Stella II software, following the structural procedure for model development (Jorgensen, 1994).

Most wetland processes are presented as first-order kinetics, except for plant uptake and nitrification, which are presented with Michaelis-Menten kinetics. Stella II software (STELLA ® 6.0.1) was used to simulate these processes. The system being modeled was planted with *Phragmites mauritianus*. The denitrification process, which ensures permanent nitrogen removal, accounts for 0.219 g/m<sup>2</sup>.d (only 15.0% of the incoming nitrogen load of 1.458 g N/m<sup>2</sup>.d). Harvesting of the plants removed 0.195 g N/m<sup>2</sup>.d (13.4% of the total) from the wetland system. Accretion of organic nitrogen was a major pathway, accounting for 0.279 g/m<sup>2</sup>.d (19.2% of all the influent nitrogen). The accumulation of ammonia-nitrogen was found to be high, compared to other water phase state variables (organic nitrogen and nitrate nitrogen). This was due to relatively low ammonia uptake (0.285 g/m<sup>2</sup>.d) and nitrification (0.200 g/m<sup>2</sup>.d), compared to combined incoming ammonia from the pond (0.893 g/m<sup>2</sup>.d), mineralisation (0.048 g/m<sup>2</sup>.d) and regeneration of NH<sub>3</sub>-N from the sediments (0.230 g/m<sup>2</sup>.d).

## Methods and Materials

### *Site Description*

Four field-scale units of sub-surface flow constructed wetlands, with horizontal flow characteristics, were built to receive effluent from primary facultative ponds at the University of Dar es Salaam waste stabilization pond system (Fig. 2, Annex 4-A). The system is located at latitude 6° 48' S and longitude 39° 13' E. The area has monthly mean air temperatures between 23 – 28° C. The primary facultative pond receives wastewater of largely domestic characteristics emanating from the campus. The quality of the water flowing to the constructed wetlands is highly dependent on the university's academic timetable. During the long vacation, the pond loading will be very low, compared to the time period the university is open, during which the wastewater flow rates change significantly.

### **System Design, Planting and Monitoring**

The system size was based on its organic and hydraulic loading rates. Darcy's equation was used to provide the slope of the system, with the retention time being calculated on the basis of the slope. Based on BOD<sub>5</sub> and hydraulic loading rates, four cells of rectangular shape (length of 11.0 m; width of 3.7 m; depth of 1.0 m), covering a surface area of 40.7m<sup>2</sup>, were built after the primary pond. The gravel beds were 0.75 m thick, with the gravel ranging from 6 to 25 mm in equal proportions. The wastewater was allowed to flow 15 cm below the gravel surface. Two cells were planted with *Phragmites mauritianus*; one with *Typha domingensis*, and the remaining cell was unplanted

(control). Stem and rhizomes from nearby river were used as plant seeds. The planting density was 2.9 plants/m<sup>2</sup> in each planted bed, with an initial plant nitrogen content of 8 g/m<sup>2</sup>. A monitoring program was begun in February 2000, four months after planting, in order to give sufficient time for the establishment of vegetation and bio-film, as well as development of litter and standing dead compartments.

## **Measurement of Flow and Physical-chemical Parameters**

The flow rate was controlled, using a 12-mm diameter gate valve, and being measured at the inlet and outlet, using a beaker and stopwatch. All the wetland cells were fed influent from a primary facultative pond at a constant flow rate of 2 m<sup>3</sup>/d. An overflow pipe was provided in the distribution chambers before the cells in order to maintain constant head.

The pH, DO, and temperature were measured *in situ*. Ammonia-nitrogen (NH<sub>3</sub>-N), total Kjeldahl-nitrogen (TKN), nitrate-nitrogen (NO<sub>3</sub>-N) and nitrite-nitrogen (NO<sub>2</sub>-N) were analysed in the laboratory, in accordance with the procedures in Standard Methods (1992). The temperature and pH were measured with a Metrohm pH meter (model 704). The DO was measured with a DO meter (YSI model 50B). The TKN was determined with the semi-micro Kjeldahl method, while the NH<sub>3</sub>-N concentration was determined by direct distillation. Organic nitrogen (Org-N) was calculated by difference between TKN and NH<sub>3</sub>-N. Cadmium reduction and diazotization methods were used to determine NO<sub>3</sub>-N and NO<sub>2</sub>-N concentrations, respectively. Water sampling was done at the influent and effluent, as well as along the length of the system. The sampling time during the day did not have any significant influence on the results.

## **Conceptual Model of Nitrogen Transformation**

The conceptual model for nitrogen transformation and removal in a horizontal, sub-surface constructed wetland is shown in Fig. 1. The model shows the material flow in the influent and effluent of each state variable. Nitrification and denitrification were simplified to avoid the complexity of having many state variables. The model includes mineralisation, nitrification, denitrification, and plant uptake. Other processes are decaying/decomposition of plants, and accretion of organic nitrogen. This conceptual diagram shows that state variables lay on three sectors; namely, water, plants and gravel, as shown by dotted lines. Volatilisation was assumed to be negligible, due to low pH values. Studies of hydraulic characteristics in wetlands have shown

that sub-surface flow constructed wetlands are neither plug flow nor completely mixed, but rather dispersed flow (Reed *et al.*, 1995). For mathematical simplicity, however, it is assumed the wetlands operate near plug flow, than as a completely-mixed flow regime.

### Mathematical equations

Based on the schematic outline in Fig. 1, the mathematical equations for the mass balance of organic nitrogen (Org-N), ammonia nitrogen (NH<sub>3</sub>-N), nitrate nitrogen (NO<sub>3</sub>-N), nitrogen in plant (Plant-N) and nitrogen in gravel bed (gravel-N) are shown in Equations 1 – 5, respectively. The units of g N/m<sup>2</sup>.day were selected for transformations and transport (processes), and g N/m<sup>2</sup> for storage. Such units are common in modelling

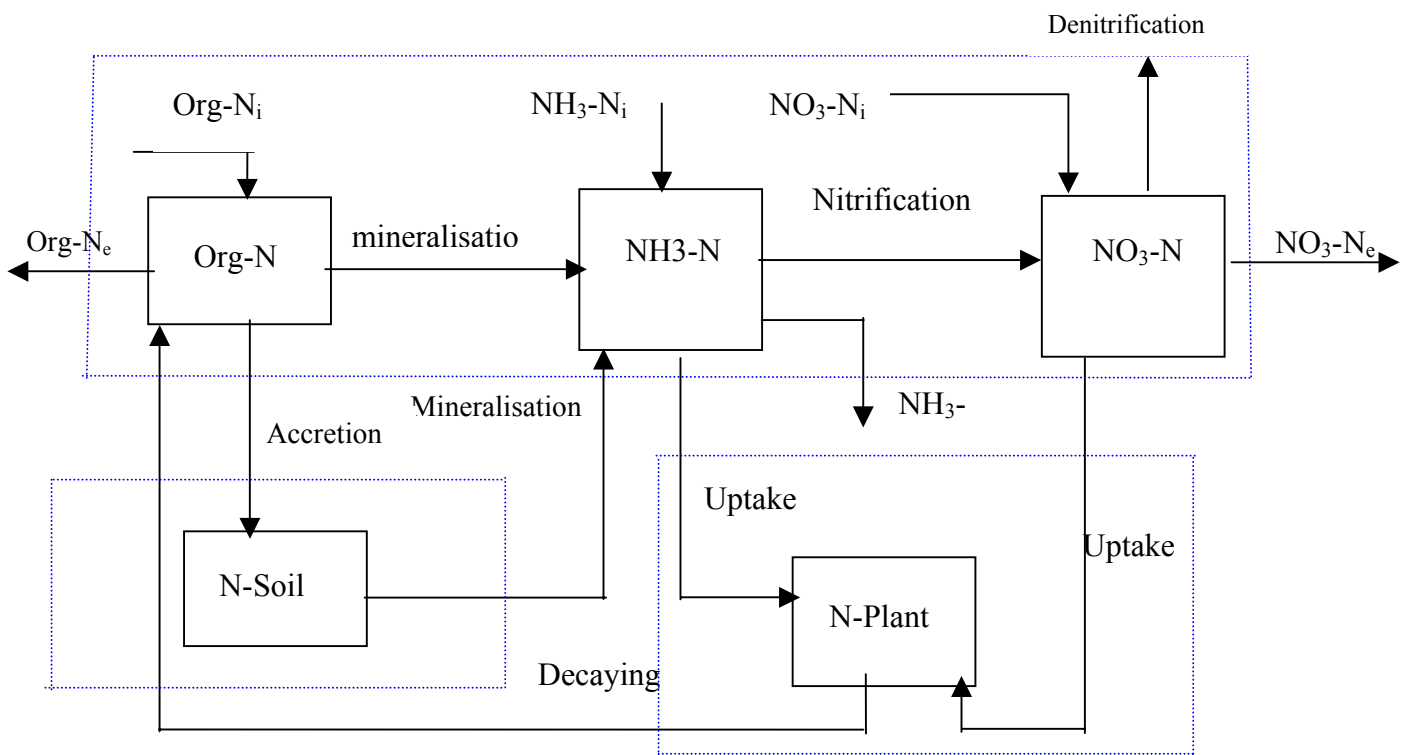


Fig. 1: Nitrogen Transformation and Removal in SSF CW

wetland treatment systems (Martin and Reddy, 1997). The modelling processes were carried out using Stella II software (STELLA ® 6.0.1), following the structural procedure for model development (Jorgensen, 1994). The best values of unknown coefficients were found by calibration. Data were processed using 4th-order Runge-Kutta approximations incorporated in the software. The inputs of NH<sub>3</sub>-N, NO<sub>3</sub>-N and Org-N were daily mean concentration (mg/l) values taken from the field, along with pH, temperature and DO.



Mineralisation of organic nitrogen, which is the biological transformation of organically-combined nitrogen to ammonia through degradation, was modelled using 1<sup>st</sup>-order kinetics with respect to the organic nitrogen concentration (Martin and Reddy, 1997). The mineralisation process depends on the anaerobic mineralisation rate per day ( $A_m$ ) and the concentration of organic nitrogen. The rate of mineralisation,  $r_m$  ( $g/m^2.d$ ), may be computed with Equation 6.

$$\frac{d(\text{org} - N)}{dt} = \left(\frac{Q_i}{A} \text{org} - N_i\right) - \left(\frac{K_s \times S}{L} \text{org} - N\right) - r_m - r_a + r_{dc} \quad (1)$$

$$\frac{d(\text{NH}_3 - N)}{dt} = \left(\frac{Q_i}{A} \text{NH}_3 - N_i\right) - \left(\frac{K_s \times S}{L} \text{NH}_3 - N\right) - r_n - r_1 + r_m + r_r \quad (2)$$

$$\frac{d(\text{NO}_3 - N)}{dt} = \left(\frac{Q_i}{A} \text{NO}_3 - N_i\right) - \left(\frac{K_s \times S}{L} \text{NO}_3 - N\right) + r_n - r_2 - r_{dn} \quad (3)$$

$$\frac{d(N - \text{Plant})}{dt} = r_1 + r_2 - r_{dc} \quad (4)$$

$$\frac{d(\text{gravel} - N)}{dt} = r_a - r_r \quad (5)$$

where  $Q_i$  = influent flow rate ( $m^3/d$ ),  $L$  = length of the bed ( $m$ ),  $K_s$  = hydraulic conductivity ( $m/d$ ) and  $S$  is the slope of the bed (%); the processes are  $r_n$  = nitrification rate ( $g/m^2.d$ ),  $r_{dn}$  = denitrification rate ( $g/m^2.d$ ),  $r_m$  = mineralisation rate ( $g/m^2.d$ ),  $r_{dc}$  = decaying rate ( $g/m^2.d$ ),  $r_r$  = regeneration rate of  $\text{NH}_3\text{-N}$  from the aggregate ( $g/m^2.d$ ),  $r_1$  = uptake rate of  $\text{NH}_3\text{-N}$  by plants ( $g/m^2.d$ ),  $r_2$  = uptake rate of  $\text{NO}_3\text{-N}$  by plants ( $g/m^2.d$ ), and  $r_a$  = accretion rate of organic nitrogen in the sediments ( $g/m^2.d$ ).

$$r_m = A_m \times \text{org} - N \quad (6)$$

where  $A_m = 0.08 d^{-1}$  was adopted (Martin and Reddy, 1997).

The rate of nitrification ( $r_n$ ), which is governed by the growth of chemoautotrophic nitrifying bacteria, depends on the pH, temperature, and ammonia and dissolved oxygen concentrations, in accordance with Equation 7.

$$r_n = \frac{\mu_n}{Y_n} \left( \frac{NH_4 - N}{K_N + NH_4 - N} \right) \times \left( \frac{DO}{K_{nO_2} + DO} \right) \times C_T \times C_{pH} \quad (7)$$

Where  $C_{pH}$  is the *Nitrosomonas* growth-limiting factor for a given pH. Downing (1966) reported that for a  $pH \geq 7.2$ , no significant inhibition occurs; thus,  $C_{pH} = 1.0$ . When the pH falls below 7.2, the existence of free ammonia inhibits the growth of nitrifying bacteria. Thus, the nitrification rate is corrected by introducing  $C_{pH}$ , in accordance with Equation 8.

$$\text{If } pH < 7.2, C_{pH} = 1 - 0.833(7.2 - pH) \text{ Else } C_{pH} = 1 \quad (8)$$

The term  $K_N$  is the half-saturation constant for *Nitrosomonas*. The literature values range from 0.32 to 56  $g/m^3$ . The half-rate saturation constant value of 6.8  $g/m^3$  was adopted, following the recommendation of Nielsen *et al.* (1999).

The nitrification rate is also temperature dependent. An exponential function, illustrated in Equation 9, describes the temperature correction factor.

$$C_T = e^{\alpha(T - T_0)} \quad (9)$$

where  $T_0$  is the reference temperature, and  $\alpha$  is an empirical constant. The values of  $T_0$  and  $\alpha$  were 15°C and 0.098/°C, respectively.

The maximum *Nitrosomonas* growth rate  $\mu_n$  of 0.05  $d^{-1}$  was found by calibration. This was relatively lower than values in the literature (0.33-2.21  $d^{-1}$ ). High  $\mu_n$  values will deplete all  $NH_3-N$ , which is not practical from the measured data. Very low  $\mu_n$  values will accumulate much  $NH_3-N$ , and the system will not properly denitrify  $NO_3-N$ . The yield coefficient ( $Y_n$ ) of *Nitrosomonas* was assumed to be 0.13 (Charley *et al.*, 1980). The oxygen *Nitrosomonas* half-saturation  $K_{nO_2}$  was assumed to be 1.3 mg/l, in accordance with Charley *et al.*, (1980). This value is within the literature values (0.3-1.3 mg/l), as given in (Hallingson-Sorensen and Jorgensen, 1993).

Dawson and Murphy (1972) showed that denitrification followed the Arrhenius kinetics in the temperature range between 3 - 28°C. Because the temperature in the constructed wetlands in this study was within this range ( $26.7 \pm 1.34^\circ C$ ), denitrification was modelled using 1<sup>st</sup>-order Arrhenius kinetics, in accordance with Equation 10.

$$r_d = R2_{20} \theta^{(T-20)} \text{NO}_3 - \text{N} \quad (10)$$

The Arrhenius constant ( $\theta$ ) varies from 1.02 to 1.09, and the denitrification constant ( $R2_{20}$ ) may vary from 0 to 1 (Bacca and Arnett, 1976). The rate coefficient optimised from the model calibration provided the values of  $\theta = 1.09$  and  $R2_{20} = 0.30$ .

The decay process was modeled, using 1<sup>st</sup>-order kinetics, according to Equation 11.

$$r_{dc} = D_{rate}(\text{N} - \text{Plant}) \quad (11)$$

where  $D_{rate}$  is the plant nitrogen-decaying rate ( $\text{d}^{-1}$ ), assumed to be  $0.006 \text{ d}^{-1}$ .

The decomposition of N-soil ( $r_r$ ), which is the liberation of  $\text{NH}_3\text{-N}$  from organic nitrogen accumulated in aggregate, also was modelled using 1<sup>st</sup>-order kinetic with respect to N-gravel, in accordance with Equation 12.

$$r_r = \text{reg.rate}(\text{N} - \text{gravel}) \quad (12)$$

where the reg. rate was assumed to be  $0.015 \text{ d}^{-1}$

The accretion of organic nitrogen to the sediments depends on the concentration of organic nitrogen, according to 1<sup>st</sup>-order kinetics, in accordance with Equation 13.

$$r_a = \text{AC\_R}(\text{org} - \text{N}) \quad (13)$$

The coefficient  $\text{AC\_R}$  was obtained from model calibration, with a value of  $0.85 \text{ d}^{-1}$  giving the best results.

$\text{NH}_3\text{-N}$  and  $\text{NO}_3\text{-N}$  are converted to biomass (vegetative uptake), in accordance with Equations 14 and 15.

$$\text{NH}_4 - \text{N}_{\text{uptake}} = \text{N}_{\text{demand}} \left[ \frac{\text{NH}_4 - \text{N}}{K_m + \text{NH}_4 - \text{N}} \right] \left[ \frac{\text{NH}_4 - \text{N}}{\text{NH}_4 - \text{N} + \text{NO}_3 - \text{N}} \right] \quad (14)$$

$$\text{NO}_3 - \text{N}_{\text{uptake}} = \text{N}_{\text{demand}} \left[ \frac{\text{NO}_3 - \text{N}}{K_m + \text{NO}_3 - \text{N}} \right] \left[ \frac{\text{NO}_3 - \text{N}}{\text{NH}_4 - \text{N} + \text{NO}_3 - \text{N}} \right] \quad (15)$$

The last term in the above equations address vegetative uptake. The species in the greatest concentrations will be preferentially assimilated. Most aquatic macrophytes prefer  $\text{NH}_4\text{-N}$  over

NO<sub>3</sub>-N, which also was observed in this study.  $K_m$  (nitrogen half- saturation constant) was found by calibration to 0.1g N/m<sup>2</sup>.d

## Model Simulations

Simulations were performed with the parameters identified in the previous section to determine the general relationships and interactions affecting the fate and transport of nitrogen in sub-surface flow constructed wetlands. The simulated and measured values for, ammonia-nitrogen, nitrate-nitrogen and organic-nitrogen are shown in Figures 2, 3 and 4, respectively.

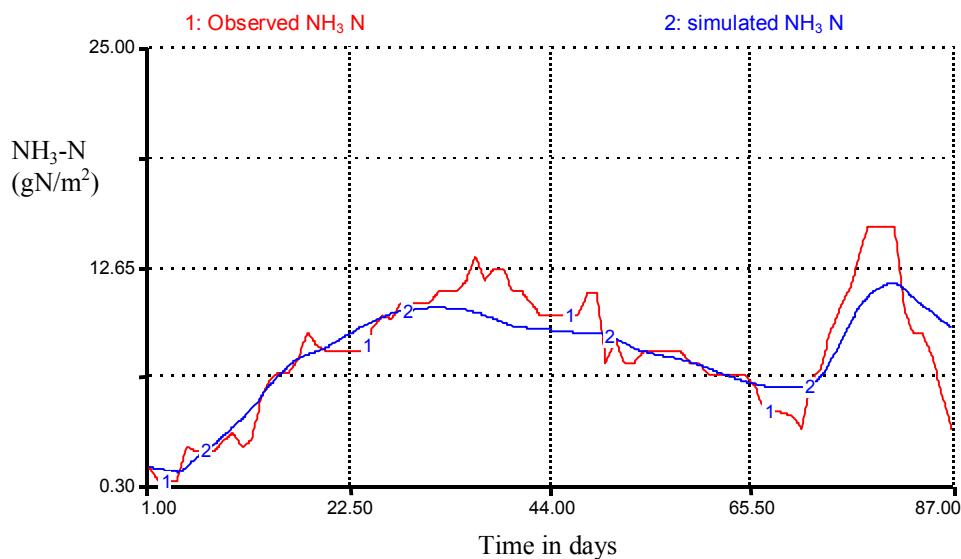


Fig. 2: Simulations and Observed Values of NH<sub>3</sub>-N

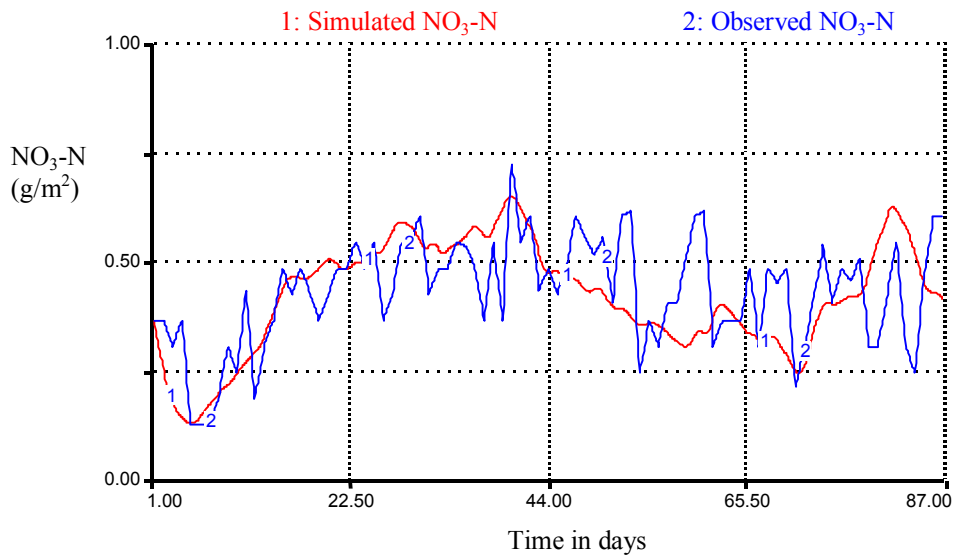


Fig. 3: Simulated and Observed Values of  $\text{NO}_3\text{-N}$

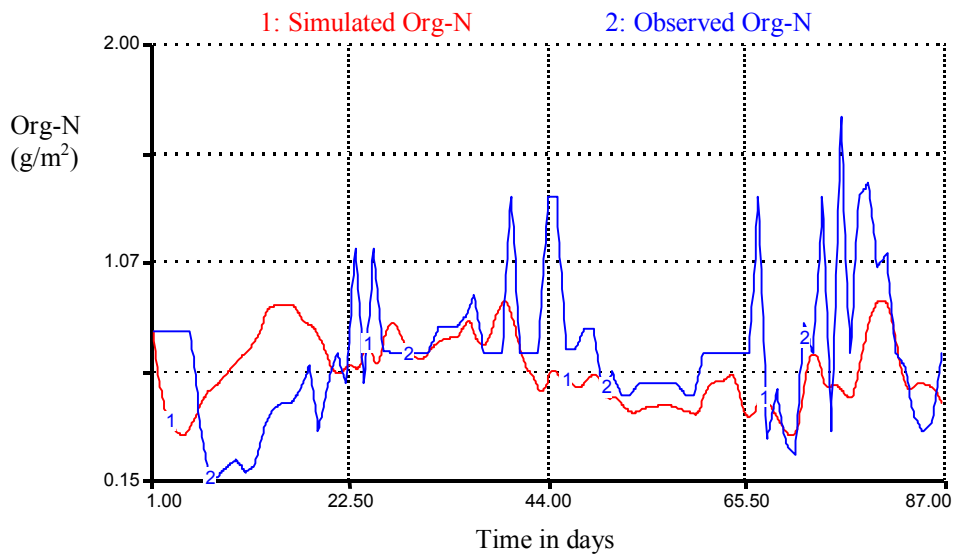


Fig. 4: Simulated and Observed Values of Org-N

There is good agreement between the simulated and measured nitrate-nitrogen, ammonia-nitrogen and organic-nitrogen concentrations, particularly in view of the fact that this work was carried in the field, where physico-chemical and environmental factors are not controlled. This demonstrates the chosen model structure (Fig 1) is capable of simulating the behaviour of horizontal sub-surface flow constructed wetlands.

## Nitrogen Mass Balance

Figure 5 summarises the nitrogen flows for the entire compartments (state variables), expressed in  $\text{g}/\text{m}^2\cdot\text{d}$ , as simulated by the model. It was found out that  $0.509 \text{ g N}/\text{m}^2\cdot\text{d}$  of organic nitrogen in water will be transported to the gravel phase. However,  $0.230 \text{ g N}/\text{m}^2\cdot\text{d}$  of this quantity can be returned to  $\text{NH}_3\text{-N}$  in the water phase, leaving  $0.279 \text{ gN}/\text{m}^2\cdot\text{d}$  accumulated in the gravel phase. Macrophytes can take  $0.297$  ( $\text{NH}_3\text{-N}$  &  $\text{NO}_3\text{-N}$ ) for their growth, although there is a possibility of  $0.102 \text{ g N}/\text{m}^2\cdot\text{d}$  being decomposed and returned to organic nitrogen of the water phase. Thus, the quantity of nitrogen that can be removed from the system permanently by harvesting the CW plants is  $0.195 \text{ g N}/\text{m}^2\cdot\text{d}$ .

While denitrification will remove  $0.219 \text{ g N}/\text{m}^2\cdot\text{d}$  completely from the system, mineralisation and nitrification transform  $0.048$  and  $0.200 \text{ g N}/\text{m}^2\cdot\text{d}$ , respectively.

Based on the mass balance presented in Fig. 5, the accretion of organic nitrogen, nitrification/denitrification and plant uptake were identified as the major pathways accounting for nitrogen removal from sub-surface wetlands. Cumulatively, these processes account for about 47.6% removal ( $0.693 \text{ g N}/\text{m}^2\cdot\text{d}$ ) of the influent nitrogen from the pond ( $1.458 \text{ g N}/\text{m}^2\cdot\text{d}$ ). A similar study demonstrated a simulation removal of 38%. A removal of 45-70% also was reported by Gale *et al.* (1993). While accretion is responsible for 19.2%, denitrification is responsible for 15.03% removal. If plant harvesting is done, the quantity of the nitrogen accumulated in the plants (which will be removed from the system) accounts for 13.4% ( $0.195 \text{ g N}/\text{m}^2\cdot\text{d}$ ) of the entire influent nitrogen load from the primary facultative pond. A study in Uganda with similar macrophytes reported 29% plant uptake (Sekiranda and Kiwanuka, 1998). However, Meuleman (1999) reported  $0.214 \text{ g N}/\text{m}^2\cdot\text{d}$  uptake for *Phragmites australis*

When mass balance is worked out, high accumulation of ammonia-N is taking place. This is due to relative low ammonia uptake ( $0.285 \text{ g N}/\text{m}^2\cdot\text{d}$ ) and nitrification ( $0.219 \text{ g N}/\text{m}^2\cdot\text{d}$ ) compared to combined incoming ammonia from the pond ( $0.893 \text{ g N}/\text{m}^2\cdot\text{d}$ ), mineralisation ( $0.048 \text{ g}/\text{m}^2\cdot\text{d}$ ) and regeneration of ammonia from the media ( $0.230 \text{ g N}/\text{m}^2\cdot\text{d}$ ). Reed and Brown (1995) reported that additional  $\text{NH}_3\text{-N}$  in HSSFCW effluent frequently occurs when a preliminary treatment is undertaken prior to CW in the facultative pond.

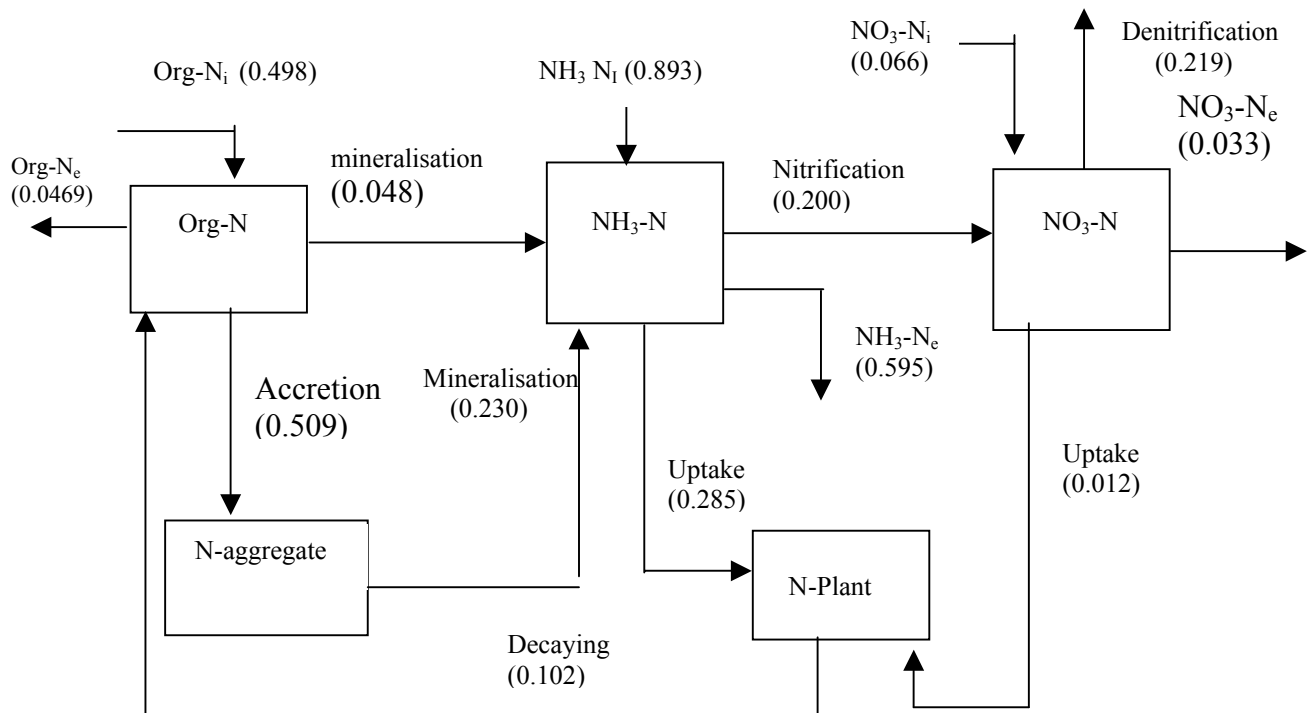


Fig. 5: Nitrogen Transformation and Removal in HSSFCW (g N/m<sup>2</sup>.d).

An attempt was made to compare the model simulation outputs from this study to the results of other researchers. Table 1 clearly demonstrates that the model values simulated in this study were comparable to the findings of other researchers.

**Table 1: Comparison of Nitrogen Transport in This and Other Studies**

Mechanism	This study	Other literature values and source
Plant uptake (g N/m <sup>2</sup> .d)	0.195	0.214 ( <i>Phragmites australis</i> , infiltration wetland Meuleman (1999), 0.283 (Uganda Papyrus swamp; Gaudet, 1977)
Nitrification (g N/m <sup>2</sup> .d)	0.200	> 0.014 (Danish <i>Phragmites australis</i> ; Meulieman, 1999)
Denitrification (g N/m <sup>2</sup> .d)	0.219	0.24-0.25 (Glumso Reed-swamp; Jorgensen, 1994), 0.017-1.02 (European survey bogs and hardwood swamp (Muller <i>et al.</i> , 1980))
Mineralisation/regeneration (g N/m <sup>2</sup> .d)	0.278 (0.048 - 0.230)	0.1123-0.3424 (organic soils in Florida; 0.0118-0.0162 (Minnesota bog (Urban and Eisenreich, 1982); 0.0603 (Messer and Brezonik, 1977))
Decomposition/decay (d <sup>-1</sup> )	0.006	0.0004-0.005 (Common Reed (Hietz, 1992)
Biomass productivity (kg-dw/ha.y)	43800	10,000-60,000 ( <i>Phragmites</i> ; Reddy and Smith, 1987)
Accretion (g N/m <sup>2</sup> .d)	0.279	0.027-0.493 (Richardson, 1989)
Standing stock (g N/m <sup>2</sup> )	17.042	14.0-43.0 ( <i>Phragmites</i> ); 8.8-31.5 (Theresa marsh, Wisconsin (Klopatek, 1978), 61.61 (Uganda Papyrus swamp (Gaudet, 1977)

## Model Validation

The model was validated using independent data collected from the second cell of *Phragmites*. As shown in Figures 6, 7 and 8, there was a good agreement between the predicted (simulated) and observed (measured) data.

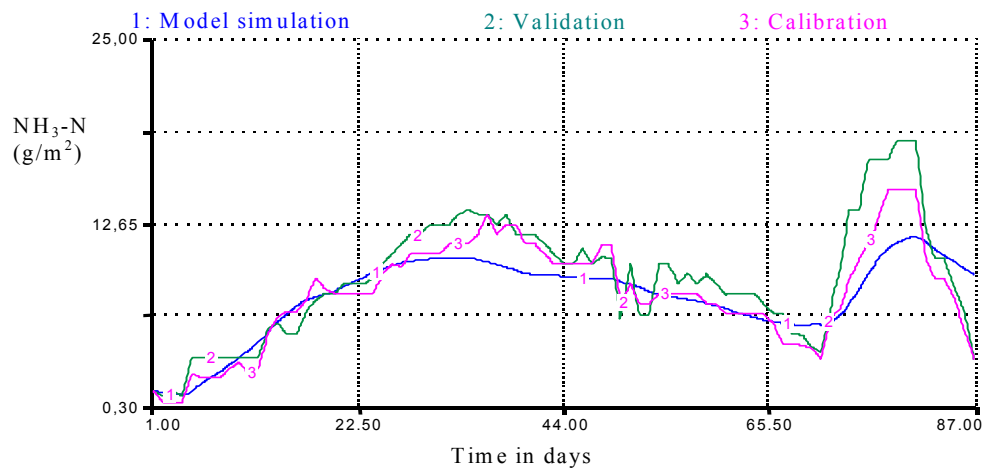


Fig. 6: Model Validation for  $\text{NH}_3\text{-N}$

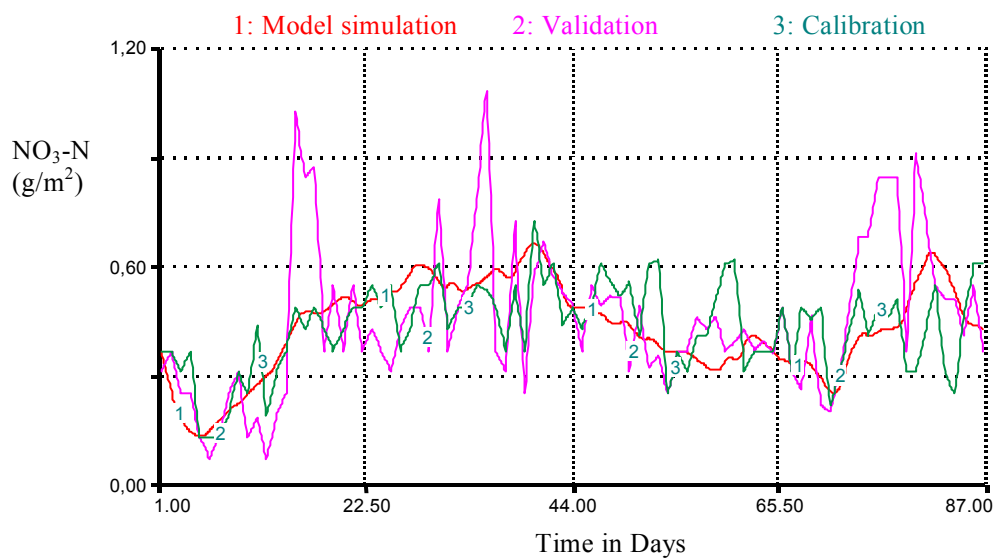


Fig. 7: Model Validation for  $\text{NO}_3\text{-N}$



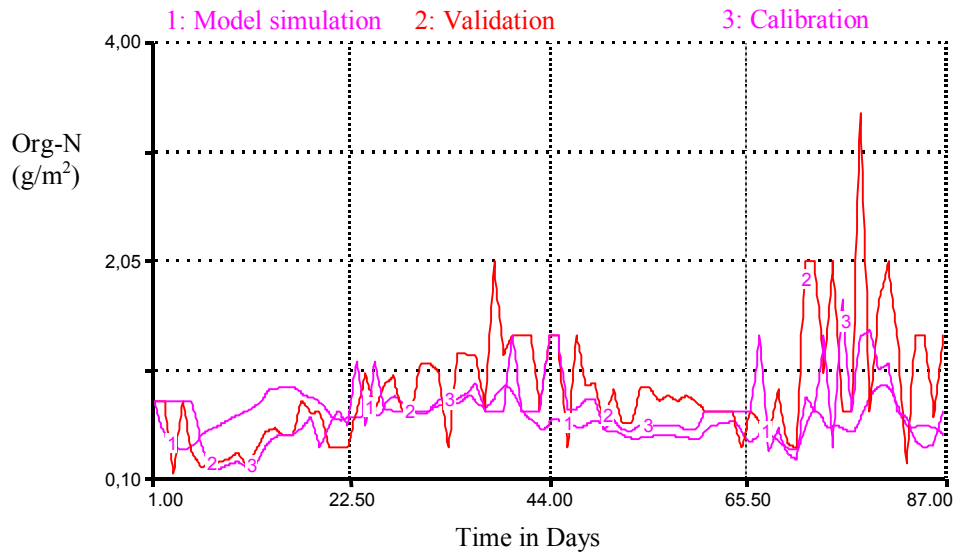


Fig. 8: Model Validation for Org-N

### Model Applications and Limitations

The model developed herein is suitable for horizontal sub-surface constructed wetlands receiving wastewaters of largely domestic characteristics for secondary treatment. Its application requires knowledge of the inflow concentrations (mg/l) of  $\text{NH}_3\text{-N}$ ,  $\text{NO}_3\text{-N}$  and total organic nitrogen, and the pH, temperature and dissolved oxygen concentration of the water in the wetland. The surface area of the sub-surface flow constructed wetlands, the depth of the water in the wetland, the inflow water flow rates, and the hydraulic conductivity of the gravel media also are important needed parameters for the model. The initial nitrogen values in the macrophytes and aggregates also are necessary. The selection of estimation methods for integrating the differential equations is provided in the Stella software. A 4<sup>th</sup>-order Runge-Kutta equation was selected, due to its low truncation error and fast convergence on given initial values.

### Conclusions

Based on the findings of this study, it was concluded that the accretion of organic nitrogen, nitrification/denitrification and plant uptake are the major mechanisms for nitrogen removal in sub-surface constructed wetlands. On average, accretion, denitrification and plant uptake account for 19.15% ( $0.279 \text{ g N/m}^2\cdot\text{d}$ ), 15.0% ( $0.219 \text{ g N/m}^2\cdot\text{d}$ ) and 13.4% ( $0.198 \text{ g N/m}^2\cdot\text{d}$ ), respectively, of the removal of total nitrogen flowing to the pond. Volatilisation processes were not included in the

model because they play a negligible role in reducing nitrogen, because of low pH values in the wetlands.

Nitrification is a main route for facilitating the denitrification processes. Nitrification was relatively high, although dissolved oxygen in the system was relatively low, transporting  $0.20 \text{ g N/m}^2\cdot\text{d}$ . Decaying and mineralisation processes, however, account for  $0.102 \text{ g N/m}^2$  and  $0.048 \text{ g N/m}^2\cdot\text{d}$ , respectively. Regeneration of ammonia from the media was responsible for  $0.23 \text{ g N/m}^2\cdot\text{d}$ . Denitrification, which ensures permanent removal of nitrogen, also was limited by the small quantity of  $\text{NO}_3\text{-N}$  coming from the pond.

# Removal of Heavy Metals

## Introduction

Heavy metals are used in large quantities in many industries. Wastewater from these industries naturally contains heavy metals and, if no legislation exists on this issue, heavy metals are discharged with the wastewater to the surrounding waterbodies. Heavy metals are toxic to humans and all other living organisms, thereby being undesirable in the environment. Constructed wetlands can be a solution to preventing the pollution of lakes and streams from heavy metals. To this end, the following material focuses on lead (Pb), copper (Cu) and zinc (Zn) removal from wastewater by a constructed wetland.

## Methods and Materials

The flow rate was adjusted twice daily to secure the correct flow. Samples were collected twice daily from the inlet and outlet, once in the morning and in the late afternoon. Sampling pots along the basin made it possible to extract water from inside the wetland. Once each week, 3 water samples were taken along the wetland from these samplings pots, and all were analysed by flame atomic adsorption spectrometry (FAAS).

## Conceptual Model of Heavy Metal Removal

The models synthesized for removal of lead (Pb), copper (CU) and zinc (Zn) all have the same composition. Thus, the conceptual model shown in figure 1 applies to all 3 metals. Me is used as a short name for metal (Pb, Cu and Zn, respectively).

The wetland is divided into compartments 1, 2, and 3. Each compartment denotes 1/3 of the wetland, including the first, middle and last third. Each compartment contains three state variables, including metals in plants, metals in pore water, and metals in gravel. The compartments are connected by a flow of water. The reason for this division is that plants have a higher growth rate in the first part of the wetland, since they are more exposed to nutrients in this part than in the last part of the area.

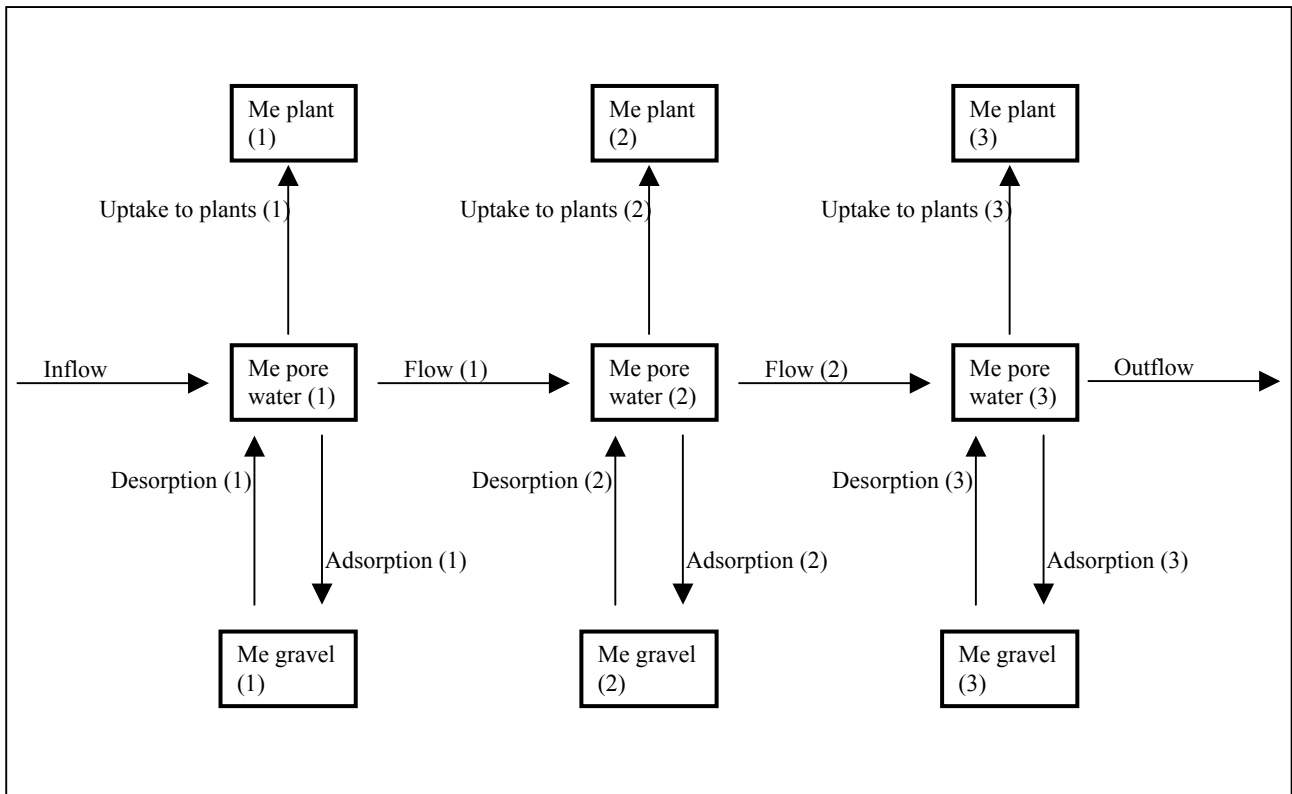


Fig. 1. General Conceptual Model of Heavy Metal Removal

### Description of the Processes

The initial values of the heavy metals in the gravel compartments are the values measured in the three compartments, respectively. These values are multiplied by the quantity of gravel in one-third of the wetland, to produce the results in milligrams (mg). The same is true for the heavy metal concentrations in plants and pore water.

### Equations that Apply to All Three Models

An initial plant biomass of  $3,6 \text{ kg dw/m}^2$  is assumed. Thus, each third of the wetland will have an initial plant biomass of  $39,96 \text{ kg dw}$ . The growth rate of the *Phragmites* in the wetland is determined by Senzia *et al.*(2001) to be  $33 \text{ t dw/ha.yr}$ , equal to  $0,09035 \text{ kg dw/m}^2.\text{d}$ . The growth rate of  $0,09035 \text{ kg dw/m}^2.\text{d}$  is assumed to be valid for the inlet section of the wetland. The plants are growing  $20 \text{ mm/d}$  in the inlet section,  $16 \text{ mm/d}$  in the central section, and only  $15 \text{ mm/d}$  in the outlet section (Senzia, 2003). The central section is assumed to have a growth rate of:

$$\frac{16}{20} \times 0,09035 \text{ kg dw/m}^2 \cdot \text{d} = 0,07228 \text{ kg dw/m}^2 \cdot \text{d}$$

The outlet section is assumed to have a growth rate of:

$$\frac{15}{20} \times 0,09035 \text{ kg dw/m}^2 \cdot \text{d} = 0,06776 \text{ kg dw/m}^2 \cdot \text{d}$$

A linear growth is assumed. These growth rate values are added to the mass of plants each day, with the resulting values inserted into the model as three graphs.

Table 1 identifies other parameters used in all three models.

Table 1. General Parameters for the Three Models

Parameter	Value
Bulk density of gravel <sup>a</sup>	1.520 kg dw/m <sup>3</sup>
Gravel volume	19,8 m <sup>3</sup>
Dry weight of gravel per one-third of wetland	10.032 kg dw
V <sub>water</sub> per one third of wetland	2.833 L

For these parameters, the suffix 1 is used for the first compartment, 2 for the second compartment and 3 for the third compartment of the wetland. The suffix S is used when a species is measured in the gravel, while pw is used for the pore water.

### Equations specific to the lead (Pb) model:

The simplified Freundlich equation is:

$$Me_s = K \times Me_{pw}$$

Pb (mg/kg dw) and Pb<sub>pw</sub> (mg/L) considered together give the following expression:

$$Pb_s = -120,98 \times Pb_{pw} + 725,92 \quad r^2 = 0,0396$$

Because the simplified Freundlich equation has a better correlation than both the Freundlich and Langmuir isotherms, this equation is chosen to describe the adsorption process. The correlation is

still very poor, however, with the following parameters only used as a fundamental for calibration.

The full equation is:

$$Pb_s(\text{mg}) = \frac{-120,98(\text{L/kgdw}) \times M_s(\text{kgdw})}{V_{\text{water}}(\text{L})} \times Pb_{pw}(\text{mg}) + \frac{725,92(\text{mg/kgdw}) \times M_s(\text{kgdw})}{3}$$

$$\text{Slope2} = \frac{-120,98(\text{L/kgdw}) \times M_s(\text{kgdw})}{V_{\text{water}}(\text{L})} \quad \text{Intercept2} = \frac{725,92(\text{mg/kgdw}) \times M_s(\text{kgdw})}{3}$$

The adsorption is in equilibrium with the desorption; thus, the above expression can be used to describe both processes. Assuming each process excludes the other, the adsorption is described by the following expression:

$$\text{IF}(Pb_s < \text{slope2} \times Pb_{pw} + \text{intercept2}) \text{THEN}((\text{slope2} \times Pb_{pw} + \text{intercept2} - Pb_s) \times 0,0141) \text{ELSE}(0)$$

$Pb_s$  is subtracted because a difference is being added to the gravel compartment, and the multiplication by 0,0141 is due to calibration. The expression states that if the concentration in gravel is less than the predicted concentration, adsorption will occur. Using the same expression, desorption is described as:

$$\text{IF}(Pb_s > \text{slope2} \times Pb_{pw} + \text{intercept2}) \text{THEN}(((Pb_s - \text{intercept2})/\text{slope2} - Pb_{pw}) \times 0,1) \text{ELSE}(0)$$

$Pb_{pw}$  is subtracted here, as a difference is being added to the pore water compartment. The concentration in gravel has to be larger than the predicted concentration for desorption to happen.

The uptake to plants is described by the following equation:

$$Pb_{\text{plant1-3}} = Pb_{pw} \times m_{\text{plant1-3}} \times r_{1-3}$$

Coherent values of  $Pb_{\text{plant}}$  (mg/kg dw) and  $(Pb_{pw} \times m_{\text{plant}})$  (mg\*kg dw/L) are considered together to determine 'r'. The following expression is obtained:

$$Pb_{\text{plant1-3}} = 11,374 \times Pb_{pw} \times m_{\text{plant1-3}} + 878,3 \quad r^2 = 0,211$$

The full equation is as follows:

$$Pb_{\text{plant1-3}}(\text{mg}) = \frac{11,374(\text{L}/\text{kgdw}^2) \times (m_{\text{plant1-3}}(\text{kgdw}))^2}{V_{\text{water}}(\text{L})} \times Pb_{\text{pw}}(\text{mg}) + 878,3(\text{mg}/\text{kgdw}) \times m_{\text{plant1-3}}(\text{kgdw})$$

$$r = \frac{11,374(\text{L}/\text{kgdw}^2)}{V_{\text{water}}(\text{L})} \quad r_{1-3} = r \times m_{\text{plant1-3}}((\text{kgdw})^{-1})$$

$$\text{intercept}_{1-3} = 878,3(\text{mg}/\text{kgdw}) \times m_{\text{plant1-3}}(\text{kgdw})$$

Because lead (Pb) is added to the plant compartments,  $Pb_{\text{plant1-3}}$  is subtracted. The modelling equation is as follows:

$$Pb_{\text{plant1-3}} = (r_{1-3} \times Pb_{\text{pw}} \times m_{\text{plant1-3}} + \text{intercept}_{1-3} - Pb_{\text{plant1-3}}) \times 0,005$$

The multiplication by 0,005 is due to calibration.

The inflow to the pore water compartment 1 is the concentration of Pb in the inlet (mg/L) times the inflow (L/d).

### Equations specific to the copper (Cu) model:

The Langmuir equation has a better correlation than the two Freundlich equations. Thus, the Langmuir equation is chosen to describe the adsorption process. This correlation is poor, however, and the following parameters are only used as a fundament for calibration.

Langmuir equation:  $(Cu_s)^{-1}$  in mg/kg and  $(Cu_{\text{pw}})^{-1}$  in mg/L considered together give the following expression:

$$(Cu_s)^{-1} = 0,000092 \times (Cu_{\text{pw}})^{-1} + 0,0124 \quad r^2 = 0,272$$

The constants in this equation are:

$$\frac{Km}{D} = 0,000092 \text{kgdw}/\text{L}$$

$$D^{-1} = 0,0124 \text{kgdw}/\text{mg} \Leftrightarrow D = 80,645 \text{mg}/\text{kgdw}$$

$$Km = 80,645 \text{mg}/\text{kgdw} \times 0,000092 \text{kgdw}/\text{L} = 0,00726 \text{mg}/\text{L}$$

The full equation is as follows:

$$C_{us}(mg) = \frac{80,645(mg/kgdw) \times M_s(kgdw) \times C_{upw}(mg)}{(0,00726(mg/L) \times V_{water}(L) + C_{upw}(mg))}$$

Adsorption is in equilibrium with desorption. Thus, the above expression can be used to describe both processes. Assuming that each process excludes the other, adsorption is described by the following expression:

$$IF(C_{us} < D2 \times C_{upw} / (Km2 + C_{upw})) THEN ((D2 \times C_{upw} / (Km2 + C_{upw}) - C_{us}) \times 0,014) ELSE (0)$$

$C_{us}$  is subtracted because a difference is being added to the gravel compartment, and the multiplication by 0,014 is due to calibration. The expression states that if the concentration in gravel is less than the predicted concentration, adsorption occurs. Using the same expression, desorption is described as follows:

$$IF(C_{us} > D2 \times C_{upw} / (Km2 + C_{upw})) THEN ((C_{us} \times Km2 / (D2 - C_{us}) - C_{upw}) \times 0,1) ELSE (0)$$

$C_{upw}$  is subtracted here, as a difference is being added to the pore water compartment. The concentration in gravel has to be larger than the predicted concentration for desorption to occur. The initial values of Cu in the plant compartments ( $C_{uplant1-3}$ ) are the weighted averages of Cu in the plants from the three parts of the wetland, multiplied by the mass of plants in the corresponding third of the wetland (e.g.,  $C_{uplant1} = 27,33 (mg/kg dw) \times m_{plants1} (kg dw)$ ).

The uptake in plants is described by the following equation:

$$C_{uplant1-3} = C_{upw} \times m_{plant1-3} \times r_{1-3}$$

Coherent values of  $C_{uplant}$  in mg/kg dw and ( $C_{uplant} \times m_{plant}$ ) in mg\*kg dw/L are considered together to determine 'r'. The following expression is obtained:

$$C_{uplant1-3} = -6,4478 \times C_{upw} \times m_{plant1-3} + 66,841 \quad r^2 = 0,0042$$

The full equation is as follows:

$$C_{uplant1-3} = \frac{-6,4478(L/kgdw^2) \times (m_{plant1-3}(kgdw))^2}{V_{water}(L)} \times C_{upw}(mg) + 66,841(mg/kgdw) \times m_{plant1-3}(kgdw)$$



Because Cu is added to the plant compartments,  $Cu_{plant1-3}$  is subtracted, with the modelling equation giving:

$$Cu_{plant1-3} = (r_{1-3} \times Cu_{pw} \times m_{plant1-3} + intercept_{1-3} - Cu_{plant1-3}) \times 0,15$$

The multiplication by 0,15 is due to calibration.

The initial values for Cu in the pore water compartments ( $Cu_{pw1-3}$ ) are the measured values from the three potholes in the wetland, multiplied by the amount of water in one-third of the wetland.

### Equations special for the zinc (Zn) model:

As the simplified Freundlich has a better correlation than the Langmuir isotherm and the Freundlich isotherm, this equation is chosen to describe the adsorption process. However, the correlation is still not optimal, and the following parameters are only used as a fundament for calibration. The full equation is as follows:

Simplified Freundlich:

$Zn_s$  in mg/kg dw and  $Zn_{pw}$  in mg/L considered together give the following expression:

$$Zn_s = 492,71 \times Zn_{pw} + 80,32 \quad r^2 = 0,193$$

$$Zn_s(\text{mg}) = \frac{492,71(\text{L/kgdw}) \times M_s(\text{kgdw})}{V_{\text{water}}(\text{L})} \times Zn_{pw}(\text{mg}) + \frac{80,32(\text{mg/kgdw}) \times M_s(\text{kgdw})}{3}$$

$$\text{Slope2} = \frac{492,71(\text{L/kgdw}) \times M_s(\text{kgdw})}{V_{\text{water}}(\text{L})} \quad \text{Intercept2} = \frac{80,32(\text{mg/kgdw}) \times M_s(\text{kgdw})}{3}$$

The adsorption is in equilibrium with desorption. Thus, the above expression can be used to describe both processes. Assuming that each process excludes the other, adsorption is described by the following expression:

$$\text{IF}(Zn_s < \text{slope2} \times Zn_{pw} + \text{intercept2})\text{THEN}((\text{slope2} \times Zn_{pw} + \text{intercept2} - Zn_s) \times 0,002)\text{ELSE}(0)$$

$Zn_s$  is subtracted because a difference is being added to the gravel compartment, and the multiplication by 0,002 is due to calibration. The expression states that if the concentration in

gravel is less than the predicted concentration, adsorption occurs. Using the same expression, desorption is described as follows:

$Zn_{pw}$  is subtracted here, as a difference is being added to the pore water compartment. The concentration in gravel has to be larger than the predicted concentration for desorption to happen.

The uptake in plants is described by the following equation:

$$Zn_{plant1-3} = Zn_{pw} \times m_{plant1-3} \times r_{1-3}$$

Coherent values of  $Zn_{plant}$  in mg/kg dw and  $(Zn_{pw} \times m_{plant})$  in mg\*kg dw/L are considered together to determine 'r'. The following expression is obtained:

$$Zn_{plant1-3} = 5,9987 \times Zn_{pw} \times m_{plant1-3} + 83,365 \quad r^2 = 0,0984$$

The full equation is as follows:

$$Zn_{plant1-3}(mg) = \frac{5,9987(L/kgdw^2) \times (m_{plant1-3}(kgdw))^2}{V_{water}(L)} \times Zn_{pw} + 83,365(mg/kgdw) \times m_{plant1-3}(kgdw)$$

Because Zn is added to the plant compartments,  $Zn_{plant1-3}$  are subtracted, with the modelling equation as follows:

$$Zn_{plant1-3} = (r_{1-3} \times Zn_{pw} \times m_{plant1-3} + intercept_{1-3} - Zn_{plant1-3}) \times 0,05$$

The multiplication by 0,05 is due to calibration.

## Model Simulations

The simulations of the three models are presented below. In all graphs, the simulation is illustrated by the blue line (noted by the number 1), while the red line (noted by the number 2) gives the measured (and the extrapolated) outlet values.

### *Lead*

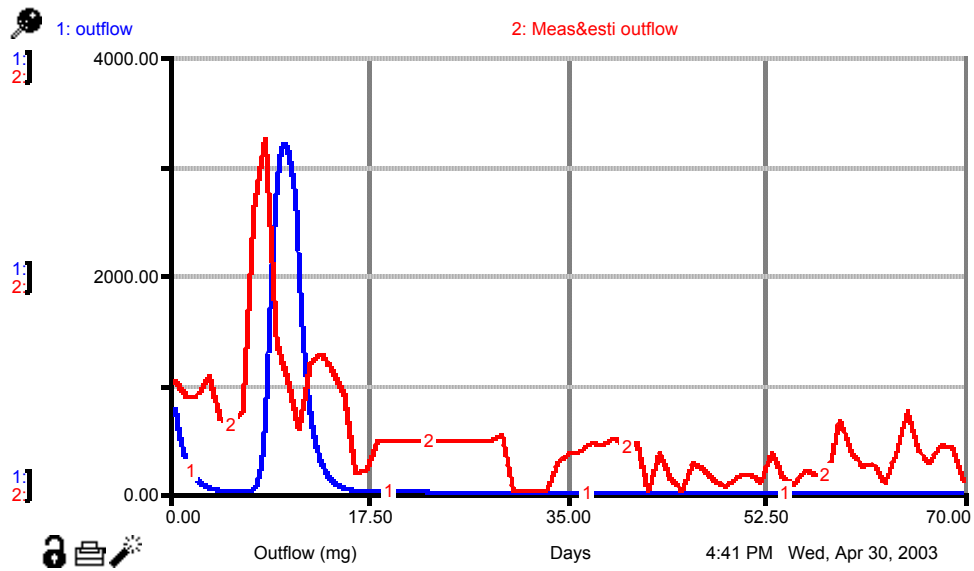


Fig. 2. Outlet of lead, mg/day.

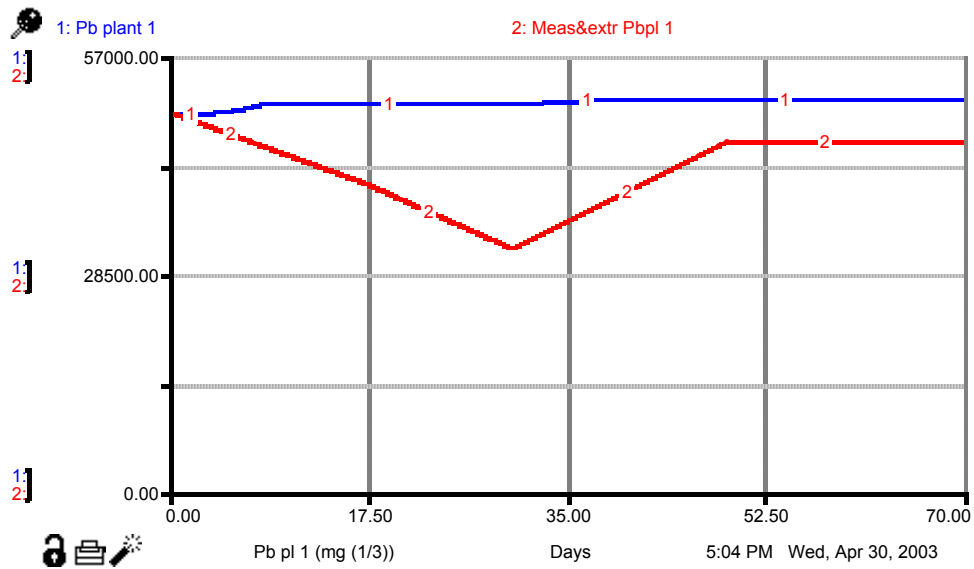


Fig. 3. Uptake of Lead by Plants in the First Compartment of the Wetland (mg/day).

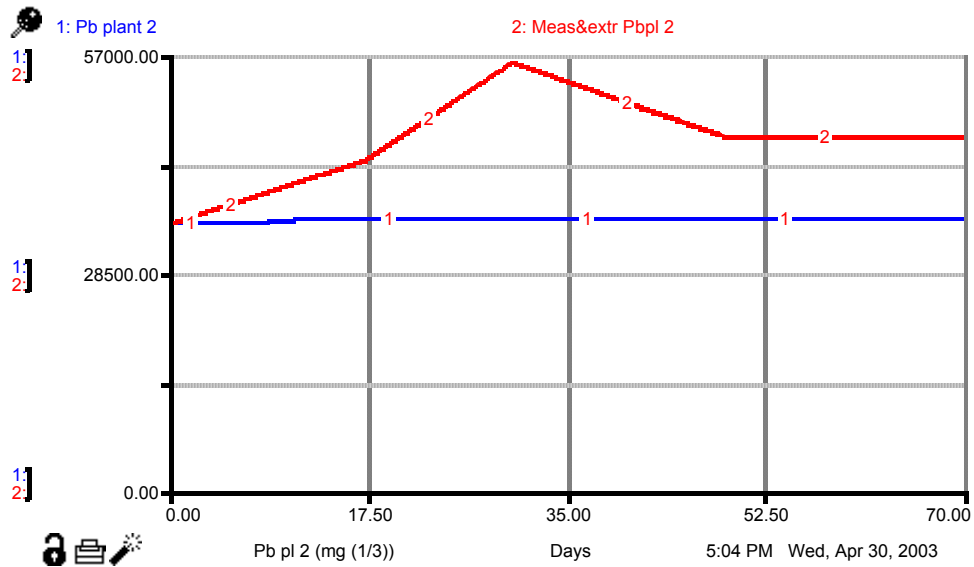


Fig. 4. Uptake of Lead by Plants in the Second Compartment of the Wetland (mg/day).

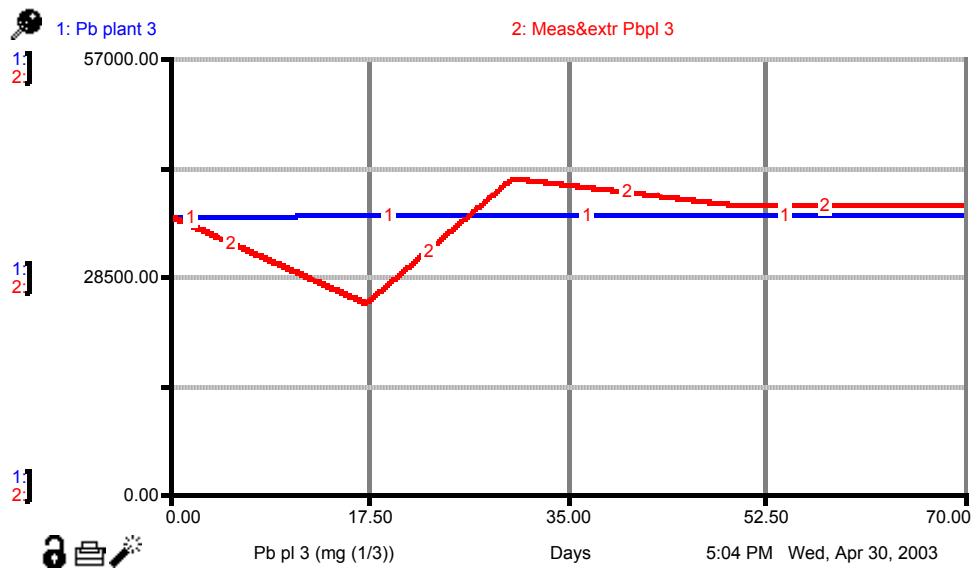


Fig. 5. Uptake of Lead by Plants in the Third Compartment of the Wetland (mg/day).

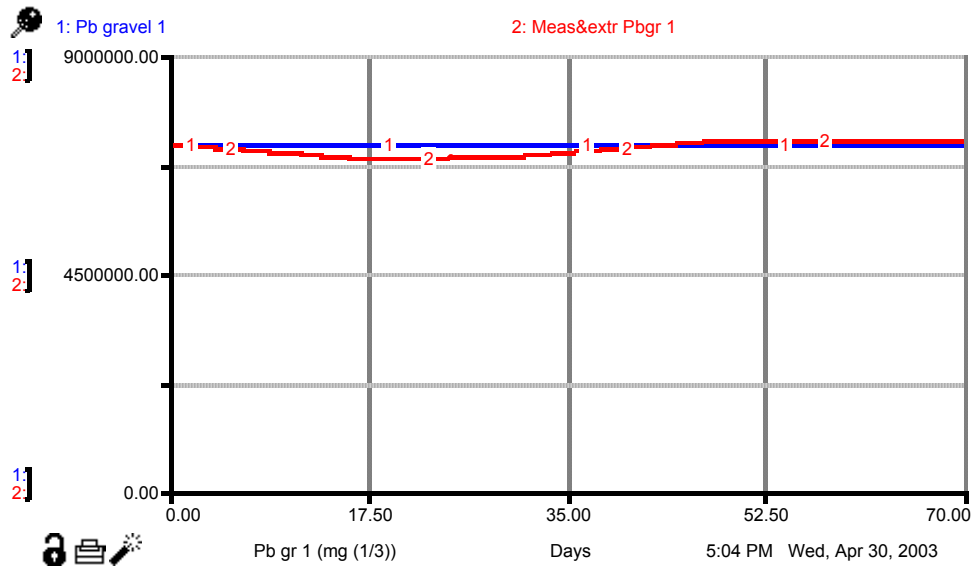


Fig. 6. Adsorption of Lead to Gravel in the First Compartment of the Wetland (mg/day).

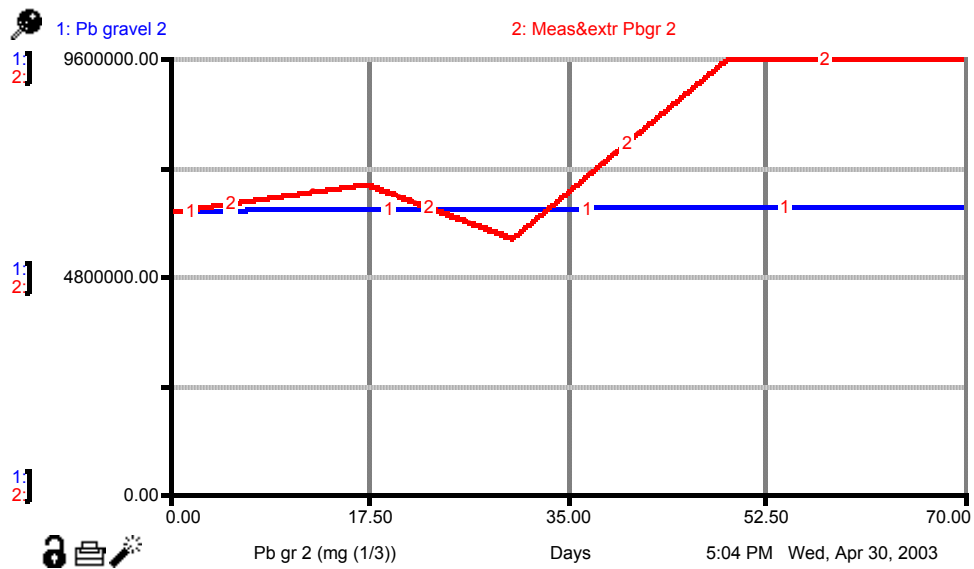


Fig. 7. Adsorption of Lead to Gravel in the Second Compartment of the Wetland (mg/day).

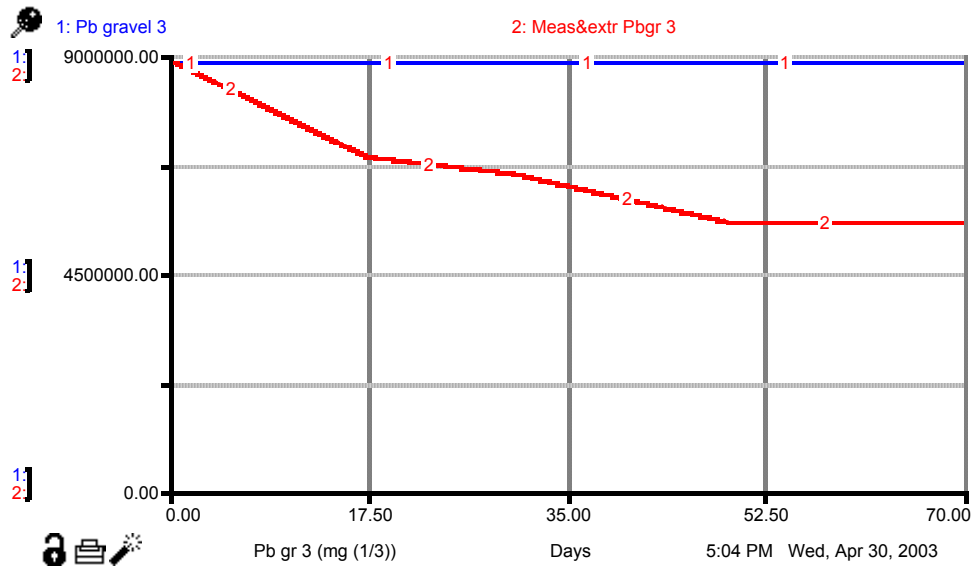


Fig. 8. Adsorption of Lead to Gravel in the Third Compartment of the Wetland (mg/day).

## Copper

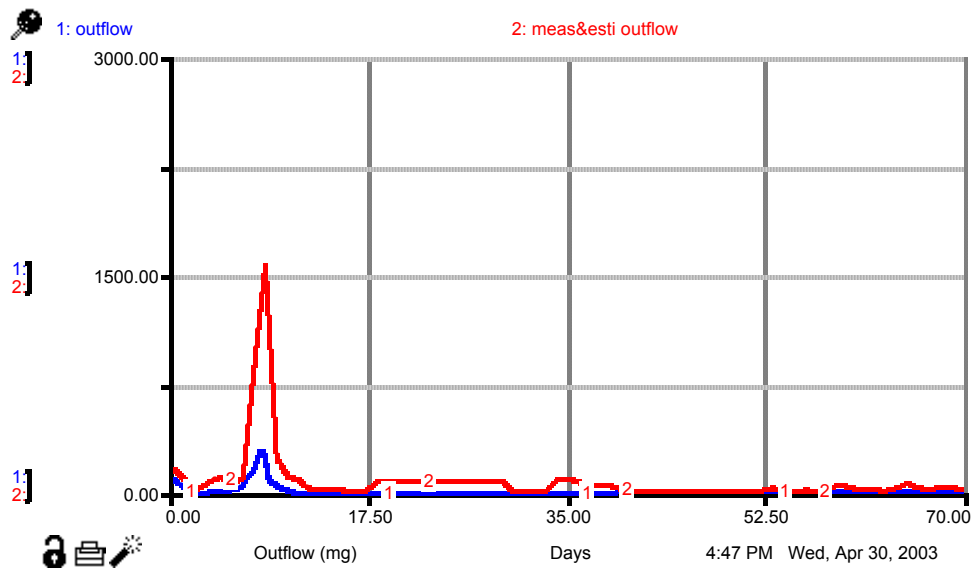


Fig. 9. Outlet of Copper (mg/day)

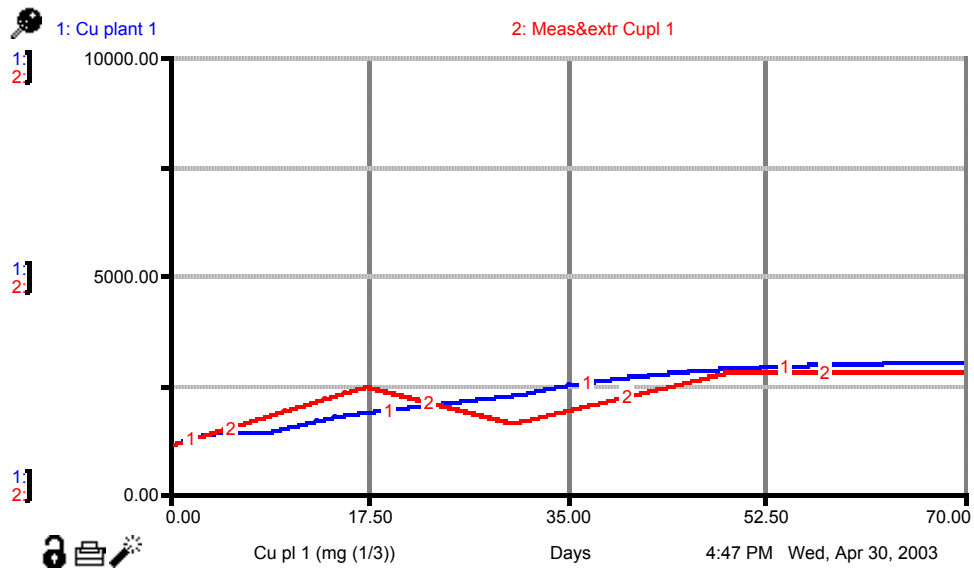


Fig. 10. Uptake of Copper by Plants in the First Compartment of the Wetland (mg/day).

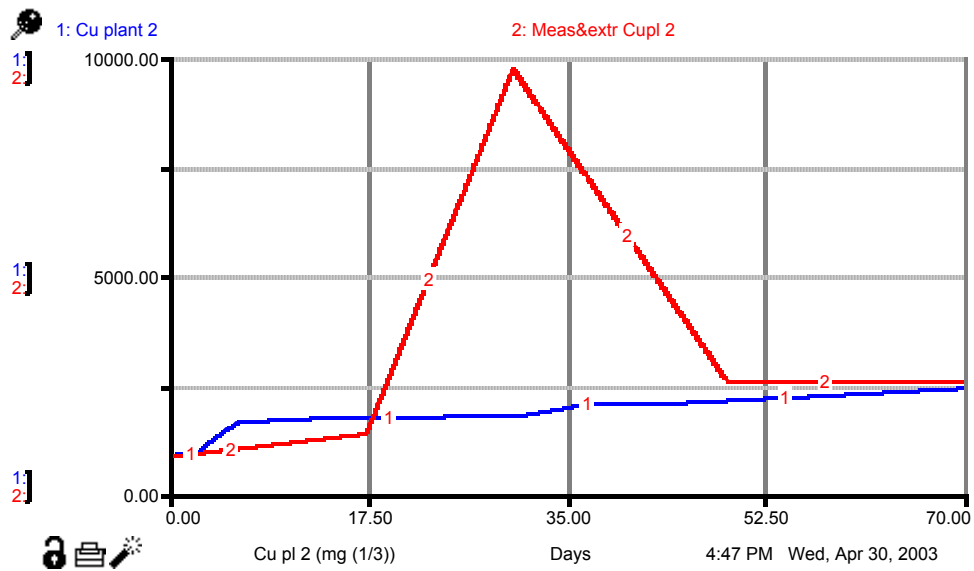


Fig. 11. Uptake of Copper by Plants in the Second Compartment of the Wetland (mg/day).

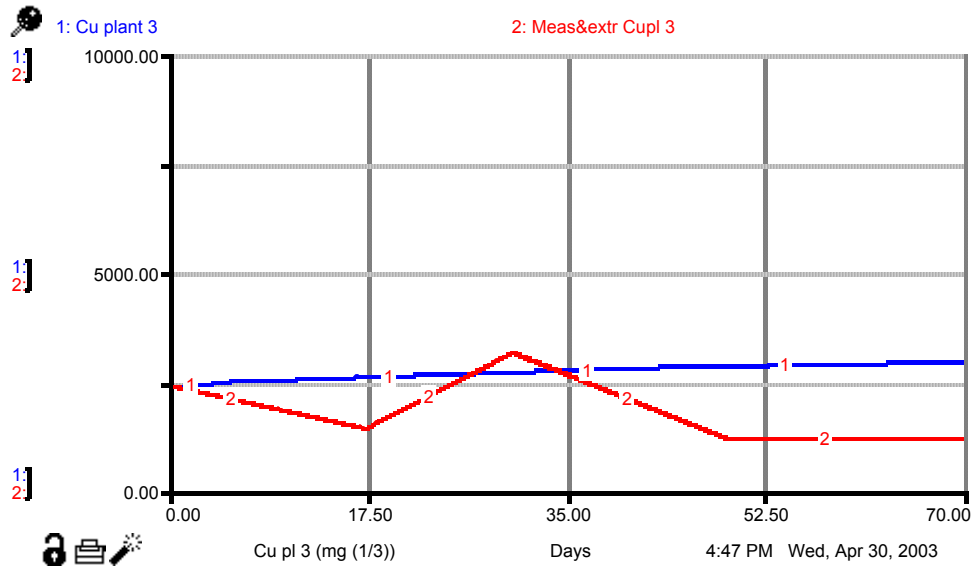


Fig. 12. Uptake of Copper by Plants in the Third Compartment of the Wetland (mg/day).

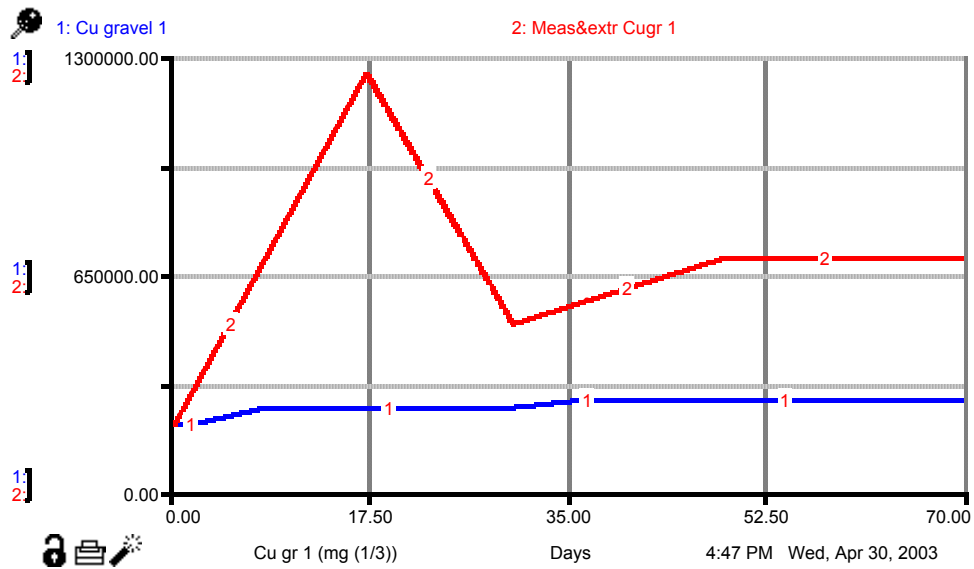


Fig. 13. Adsorption of Copper to Gravel in the First Compartment of the Wetland (mg/day).



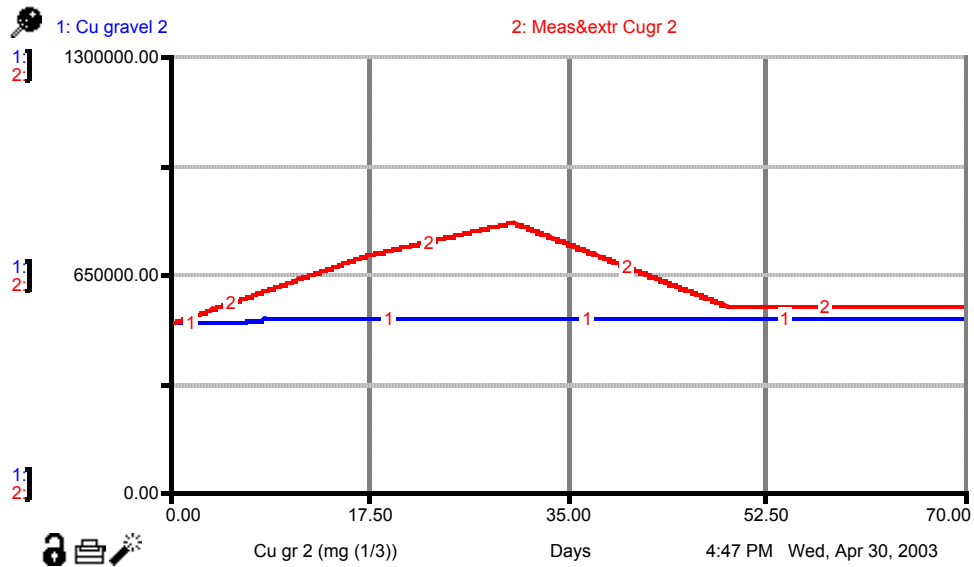


Fig. 14. Adsorption of Copper to Gravel in the Second Compartment of the Wetland (mg/day).

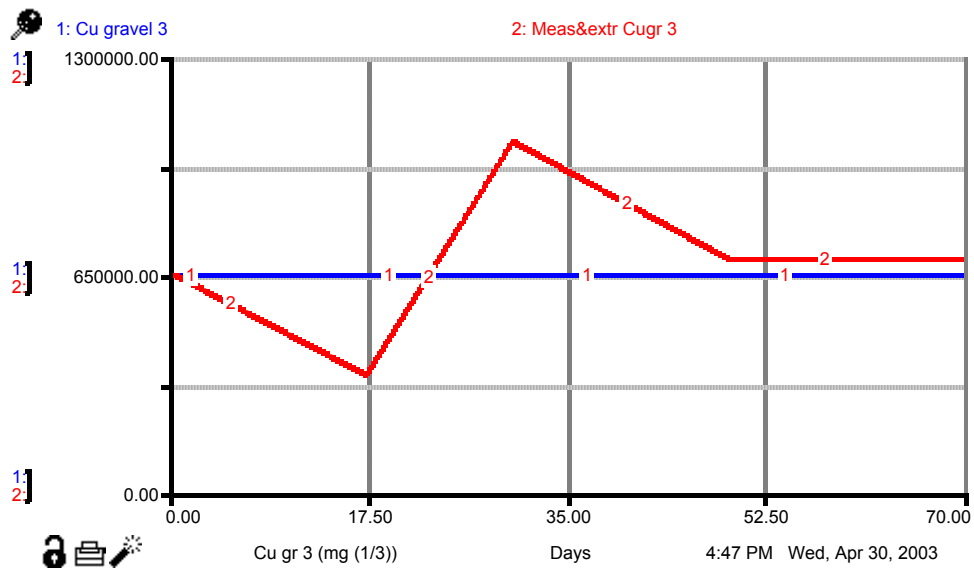


Fig. 15. Adsorption of Copper to Gravel in the Third Compartment of the Wetland (mg/day).

# Zinc

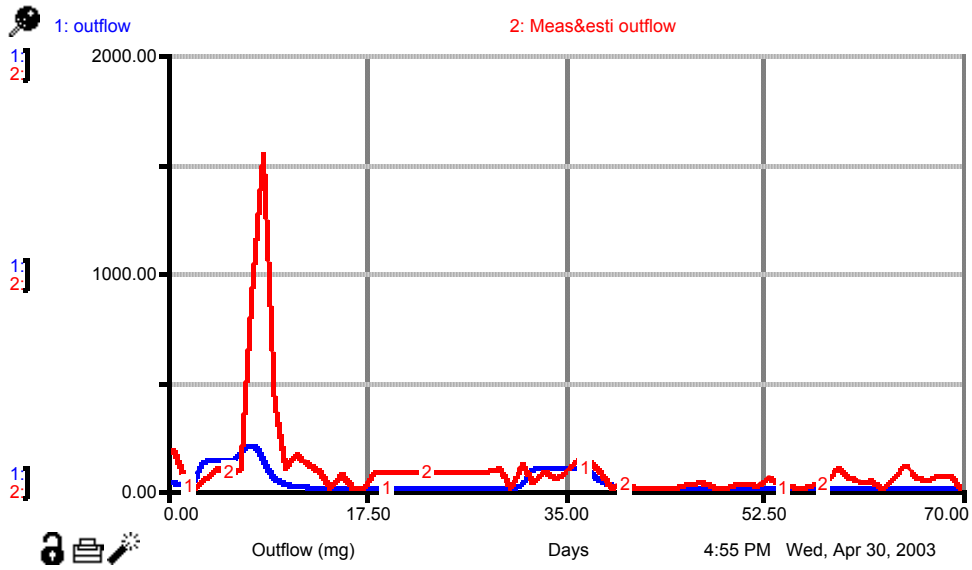


Fig. 16. Outlet of Zinc (mg/day)

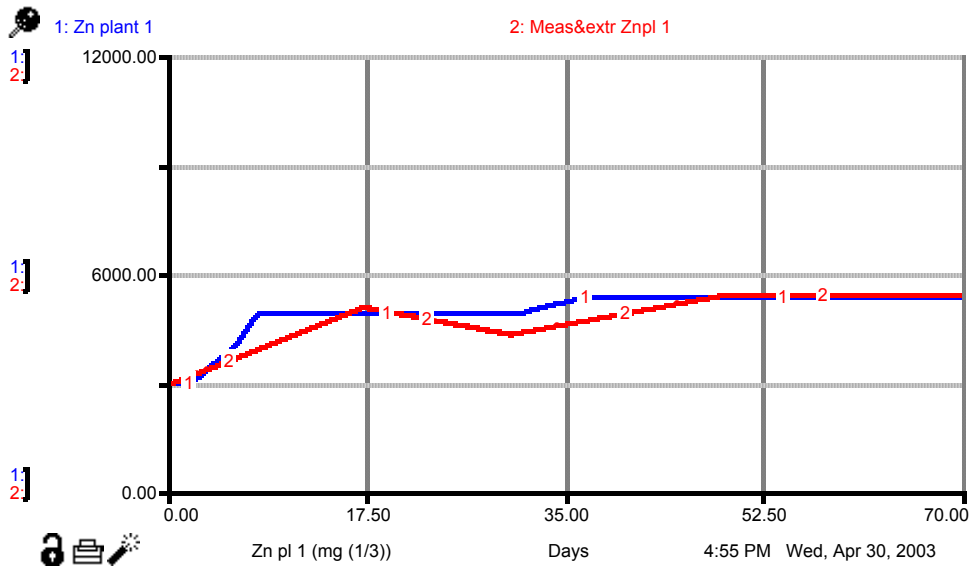


Fig. 17. Uptake of Zinc by Plants in the First Compartment of the Wetland (mg/day).

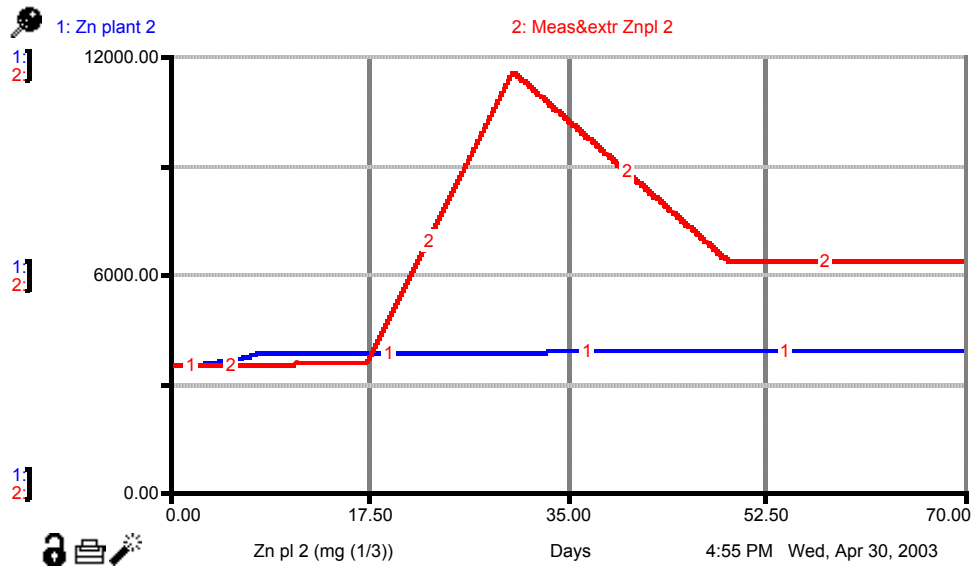


Fig. 18. Uptake of Zinc by Plants in the Second Compartment of the Wetland (mg/day).

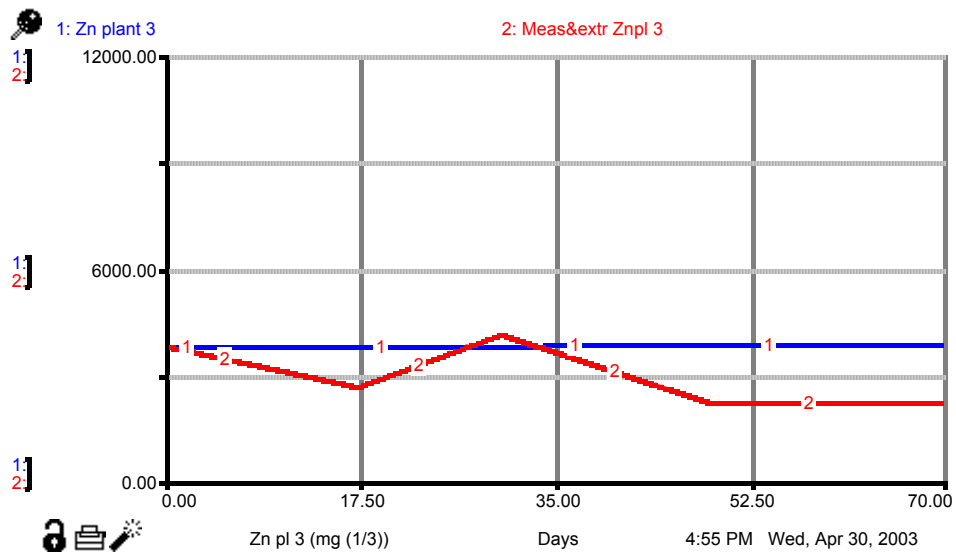


Fig. 19. Uptake of Zinc by Plants in the Third Compartment of the Wetland (mg/day).

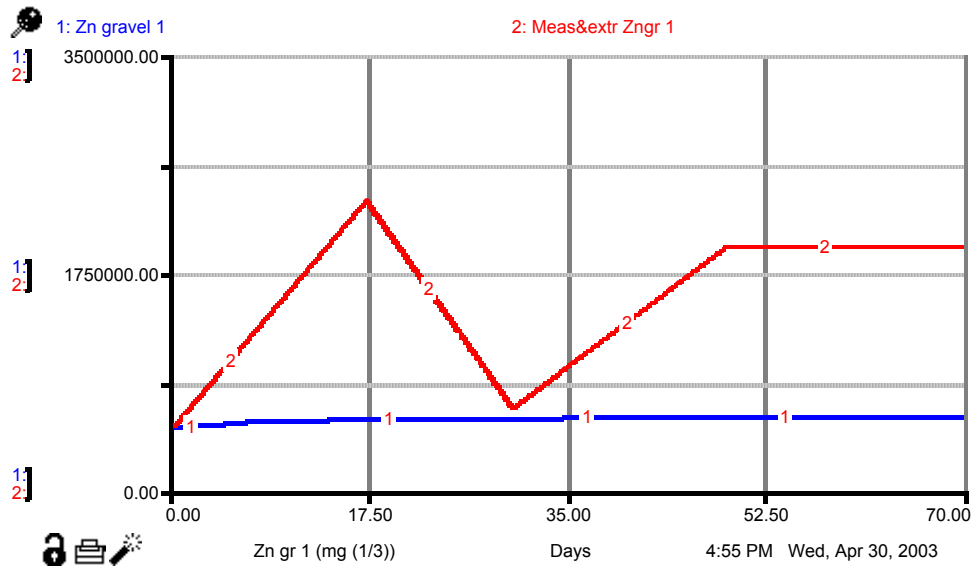


Fig. 20. Adsorption of Zinc to Gravel in the First Compartment of the Wetland (mg/day).

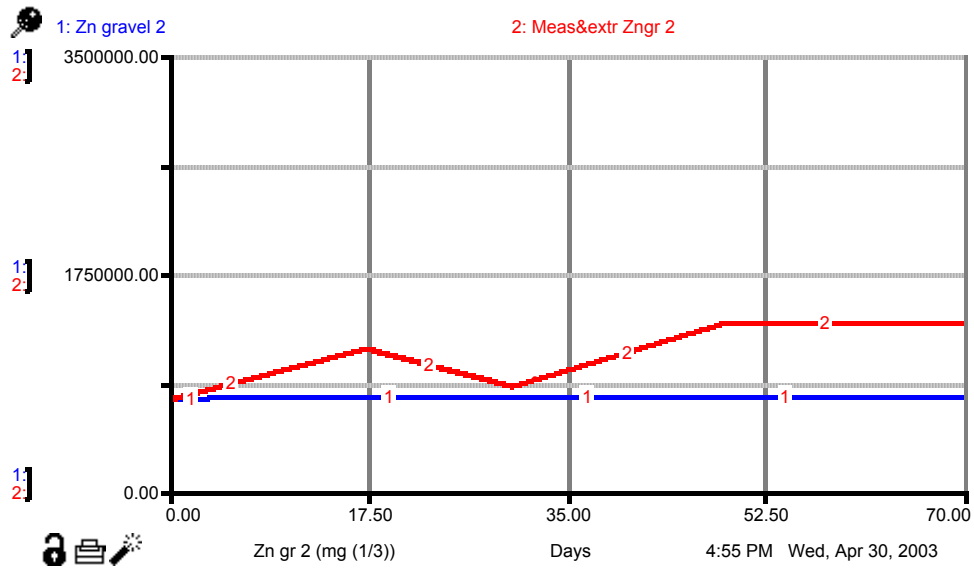


Fig. 21. Adsorption of Zinc to Gravel in the Second Compartment of the Wetland (mg/day)

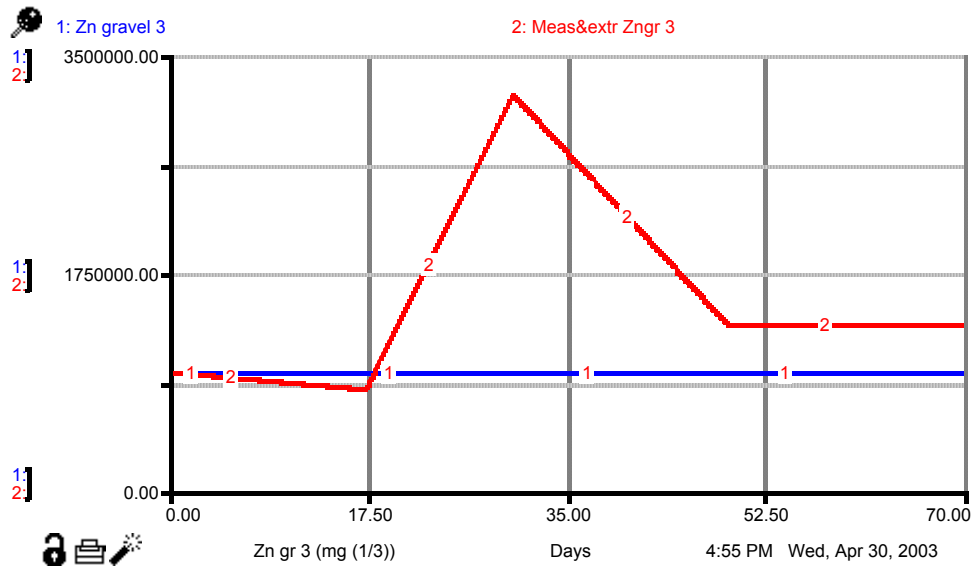


Fig. 22. Adsorption of Zinc to Gravel in the Third Compartment of the Wetland (mg/day)

## Mass Balances

The mass balances calculated from the analysis of water, plants, and gravel are very poor, being very unrealistic. However, mass balances obtained from the models are as noted in the following tables 2-4.

Outflow (%)	17,38
Plants (%)	2,97
Gravel (%)	79,65
Total removal (%)	<b>82,62</b>

Table 2. Mass Balance of Lead Obtained from Model Simulations.

Outflow (%)	2,05
Plants (%)	2,53
Gravel (%)	95,42
Total removal (%)	<b>97,95</b>

Table 3. Mass Balance of Copper Obtained from Model Simulations.

Outflow (%)	4,53
Plants (%)	2,76
Gravel (%)	92,71
Total removal (%)	<b>95,47</b>

Table 4. Mass Balance of Zinc Obtained from Model Simulations.

Simulated removal rates of all three metals are similar to those calculated from the water analyses, with only the total uptake to plants and gravel being different. The reason the measurements of absorption to gravel are false is because of the tendency of the wetlands to form water channels. The water runs in channels through the wetland, therefore making it impossible to get a gravel sample representative of the entire wetland.

### **Validation**

Because of a lack of relevant data, it has unfortunately not been possible thus far to validate any of the three models.

### **Conclusions**

Except for the inability to perform model validation, the models have presented results. The removal rates are in agreement with reality. Further, the models predict mass balances that were not possible to calculate.

# Phosphorus Removal

## Introduction

Phosphorus removal is, and will always be a, major topic in wastewater treatment because municipal wastewater contains significant quantities of phosphorus compounds. Phosphorus often is the limiting factor for phytoplankton growth in lakes and coastal areas. Thus, it often is necessary to remove phosphorus from wastewater.

## Methods and Materials

The water flow was adjusted every day to approximately 2 m<sup>3</sup>/day. Samples from the inlet and outlet were collected twice daily -- once in the morning and once in the late afternoon. The average concentration of these two samples was chosen to represent the inlet and the outlet concentrations on the sampling day.

The model simulates the removal of two species of phosphorus; namely, suspended phosphorus (organic P) and reactive phosphorus (mostly orthophosphate). Reactive phosphorus was measured by directly treating the sample, using the ascorbic acid method. Suspended phosphorus was measured by filtering the sample, drying the Whatman GFC 55Ø, 45 µm filter containing the deposited suspended material, digesting the filter by the sulphuric acid-nitric acid method, and diluting and treating the sample by the ascorbic acid method to determine the suspended phosphorus concentration in the original sample.

## Conceptual Model of Phosphorus Removal

The conceptual model for phosphorus removal in a horizontal, sub-surface flow constructed wetland planted with *Phragmites Mauritanus*, and with limestone as substrate, is shown at Figure 1. The figure illustrates 4 state variables, including reactive phosphorus in the water phase, organic phosphorus in the water phase, phosphorus in plants, and phosphorus in the substrate (soil). To simplify the model, it is assumed that there is no flow from reactive P to organic P, no flow from reactive P to gravel, and no flow from substrate to suspended P. Instead, only a flow from gravel to reactive P was chosen.

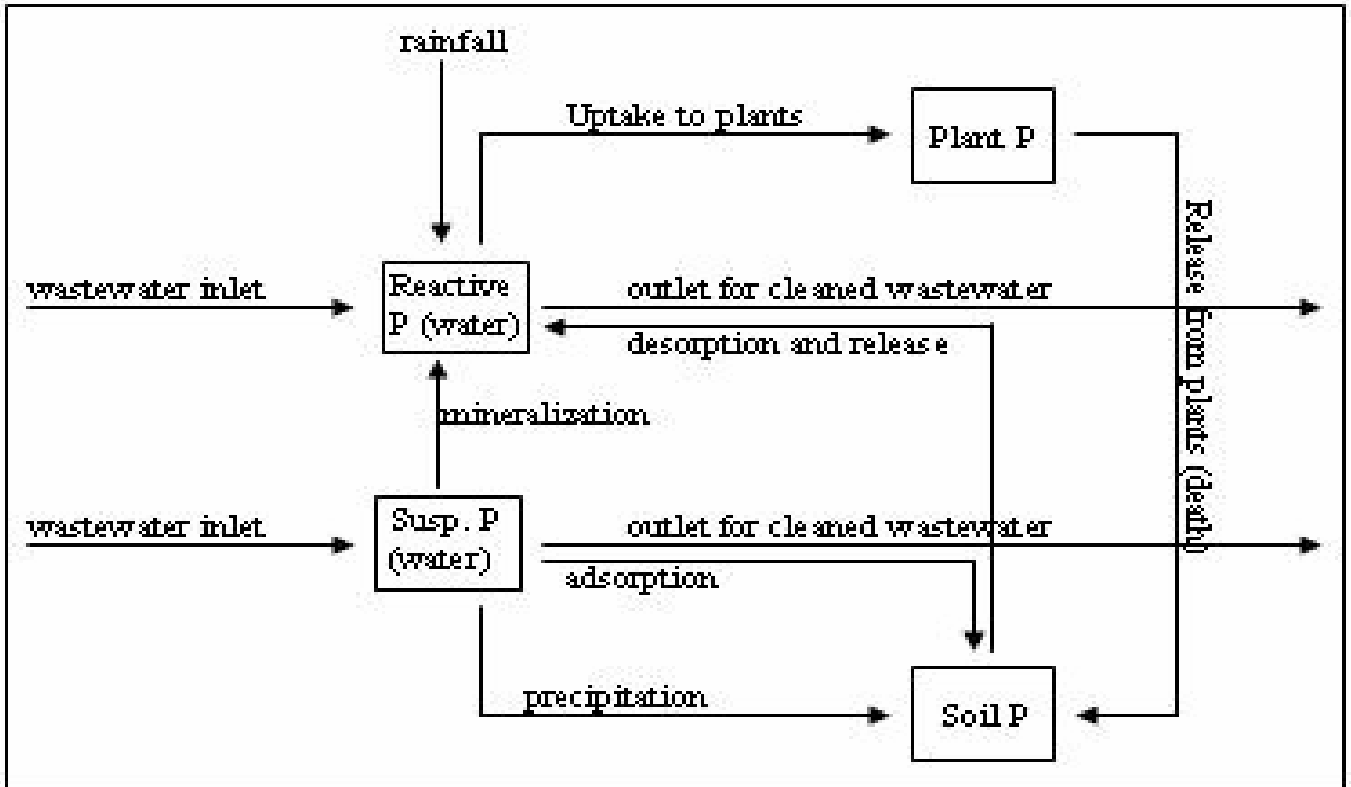


Fig. 1. Conceptual Model of Phosphorus Removal

## Description of the Model Processes

The selected model forcing functions were rain, phosphorus inlet, wastewater flow rate, inlet water temperature, plant growth rate, and plant death rate, as illustrated in Table 1.

Table 1. Forcing Functions and Parameters Used in Model.

Forcing functions	Unit	Parameters	Units
Average t of water	Celcius	Rain P	g/day
Inflow reactive P	g/m <sup>3</sup>	Inlet of reactive P	g/day
Inflow of susp P	g/m <sup>3</sup>	Inlet of organic P	g/day
Flow	m <sup>3</sup> /day	Rate of plant uptake	1/day
V(rain)	m <sup>3</sup> /day	Plant uptake	g/day
C (P in rain)	g/(m <sup>3</sup> .day)	Desorption and release	g/day
		Adsorption	g/day
		Precipitation	g/day
		Outlet of reactive P	g/day
		Outlet of organic P	g/day
		Rate of plant death	1/day
		Loss of biomass P	g/day

The data used in the model is presented in the following section.



Inflow of orthophosphate and suspended phosphorus – The initial phosphorus concentrations used in the model were the average of the phosphorus measurements: 2.0 g reactive P/m<sup>3</sup> and 1.2 g suspended P/m<sup>3</sup>. A set of data were subsequently inserted.

Rain data -- 7.4 x 10<sup>-3</sup> m is the average daily rain volume over a period of two-and-one-half months (February to April). It can be calculated that 0.30 m<sup>3</sup>/day is the total volume of rain that enters the wetland each day. The average quantity of orthophosphate in the rain is 0.07 g/m<sup>3</sup>.day, calculated from the measurements of the analysed rain samples. In all, this gives a loading of 0.371 g phosphorus per day from rainwater.

Adsorption and Desorption -- The initial value of adsorbed P was set to 802 g, as calculated from knowledge of the quantity of gravel in the wetland (24168 kg), and from analysis of the gravel that gave a P content of 0.0332 mg/g.

The Langmuir adsorption isotherm ( $1/C(\text{ads}) = K_m / C(\text{water}) + 1 / C(\text{max})$ ) is used in the model to describe the adsorption of suspended phosphorus. The correlation coefficient ( $r^2$ ) is not ideal and the standard deviation is large:

$$1/C(\text{ads}) = 0,0052/C(\text{water}) + 0,0002 \quad (r^2 = 0,2888)$$

The Langmuir adsorption coefficient, however, is selected because it has been purposed several times in the literature, including by Kadlec and Knight (1996) and Reddy *et al.* (1998).

It is assumed that desorption takes place only when no adsorption occurs, and that phosphate is the only species desorbed. Desorption is described as the opposite of the Langmuir adsorption isotherm. In addition to the desorption, a release of adsorbed phosphorus is added to the equation because of mineralization. By calibration, this release is found to be 8 x 10<sup>-4</sup> times the adsorbed gravel. Dead biomass adds to adsorbed gravel. Although it is likely that the litter should add to the pool of suspended phosphorus, because the litter is very large parts of the suspended material, it is defined to be a part of the gravel.

Precipitation -- The precipitation of suspended solids is due to the filtrating effect possessed by the gravel. By calibration, the precipitation is found to be 0.8 times the suspended phosphorus. By this equation the precipitation will be the same fraction of the suspended phosphorus, regardless of the inlet concentration and flow.

Uptake to plants – Based on Asaeda *et al.* (2002), the maximum specific growth rate of roots at 20° C is said to be  $7 \times 10^{-3}$  g/(g.day). By calibration, a value of  $7 \times 10^{-4}$  g/(g.day) is found to give a better output.

Based on the literature, the average quantity of phosphorus in plants is  $2.5 \times 10^{-3}$  g/g. An initial value of total phosphorus in plants of 2.06 kg is used. This is related to the content of  $2.5 \times 10^{-3}$  g/g, and that there are approximately 3000 plants in the wetland (Mbwette *et al.*, 2001). From our observation, it was found that the average dry weight of a plant is 275 g. Overall, therefore, this gives a value of 825 kg of biomass, which is equal to the 2.06 kg of total phosphorus in plants.

Loss of Biomass -- Asaeda *et al.* (2002) give a value for mortality of roots, leaves and stem for *Phragmites australis*, which are the species planted in the wetland. The phosphorus loss rate was  $2.84 \times 10^{-3}$  g P/(g P.day) (see Table 7).

Table 7. Calculation of Plant Phosphorus Loss Rate

	Loss rate (g/g.day)	Percentage of the plant	Weighted P loss rate (g P/g P.day)
Roots	0.00015	5.5	
Stem + leaves	0.003	94.5	
			$2.84E^{-03}$

Conversion of suspended phosphorus into reactive phosphorus -- Suspended phosphorus is transformed into reactive phosphorus by bacterial activity, among other processes. According to Jørgensen and Bendoricchio (2001), the conversion can be described as a 1<sup>st</sup>-order reaction. With respect to the temperature, the relevant equation is:

$$\text{Susp P to reactive P} = \text{Susp P} \times e^{(k \cdot t)}$$

$$\text{where } k = k_{20} * \_ (\text{temp}^\circ \text{C} - 20)$$

The terms  $k_{20}$  and  $\_$  are constants specific to the conditions. By calibration,  $k_{20}$  is determined to be 0.05 and  $\_$  to be 1.14. For further calibration, the equation is multiplied by 2.

Flow rate – The inlet flow rate was initially set to 2 m<sup>3</sup>/day. It was subsequently inserted as a set of data that matched the data inserted for the two species of phosphorus.

## Model Simulations

The results of the model simulations are presented below. In all graphs, the blue line (noted by the number 1) gives the predicted results obtained from the model, while the red line (noted by the number 2) illustrates the results from actual measurements made at the wetland. In regard to phosphorus uptake by plants and adsorption to gravel, only the values from the model are illustrated.

### *Suspended phosphorus*

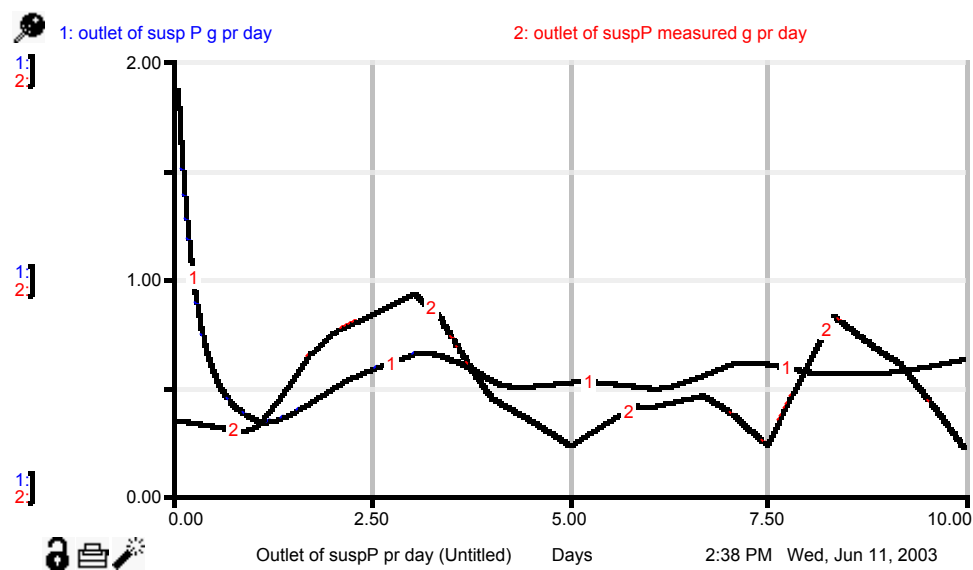


Fig. 2. Outlet of suspended phosphorus (g/day).

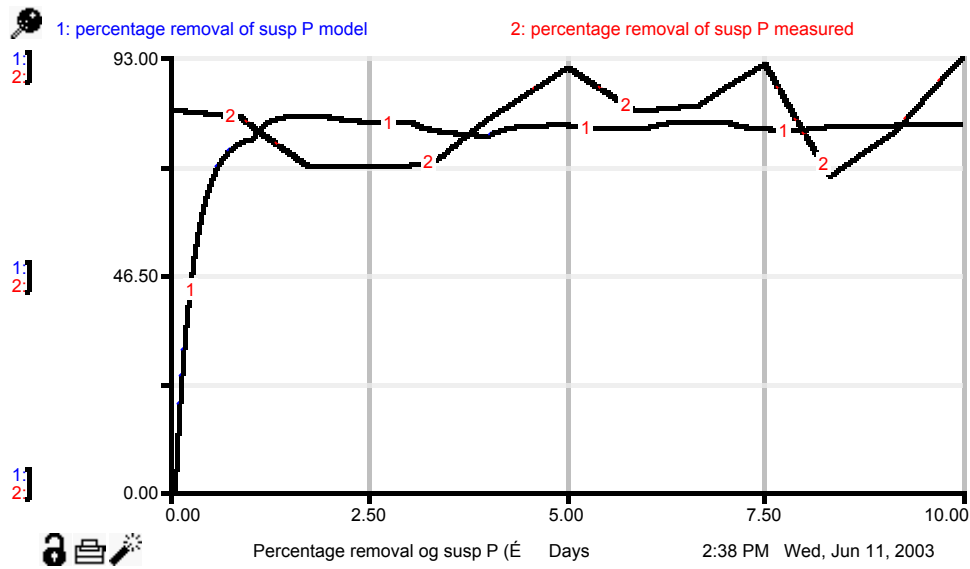


Fig. 3. Percentage removal of suspended phosphorus.

**Reactive phosphorus**

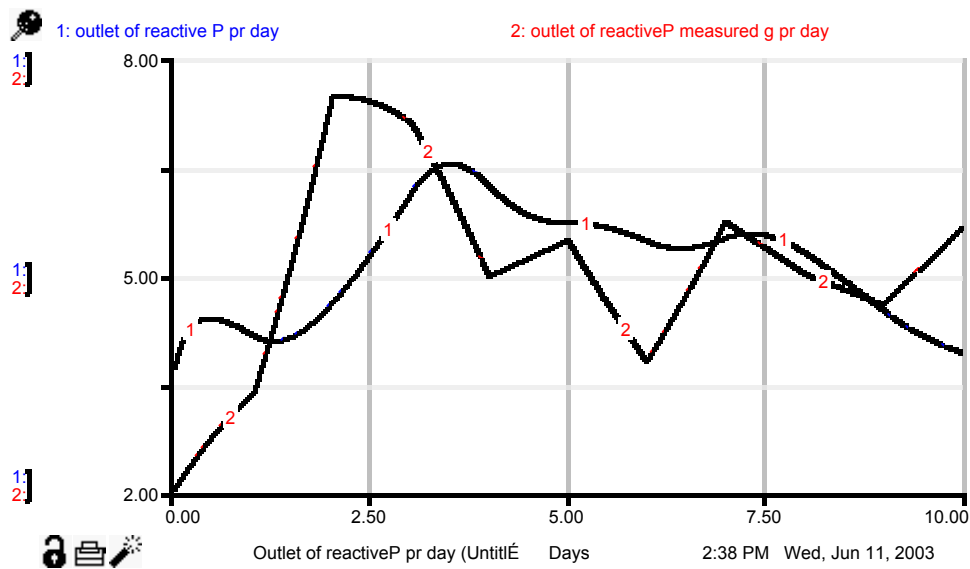


Fig. 4. Outlet of reactive phosphorus (g/day).

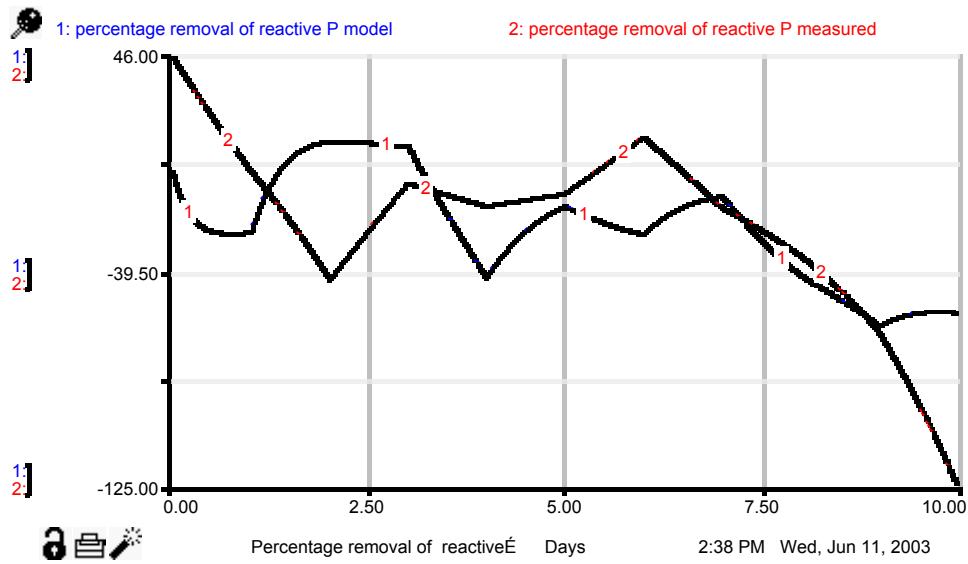


Fig. 5. Percentage removal of reactive phosphorus.

### Plant uptake

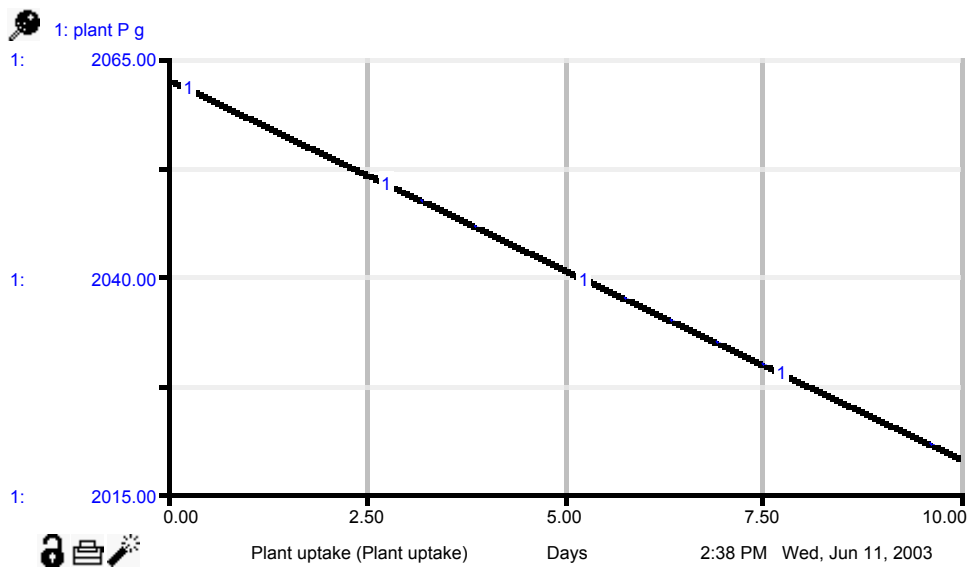


Fig. 6. Uptake of phosphorus to plants (actually a release).

## Adsorption to gravel

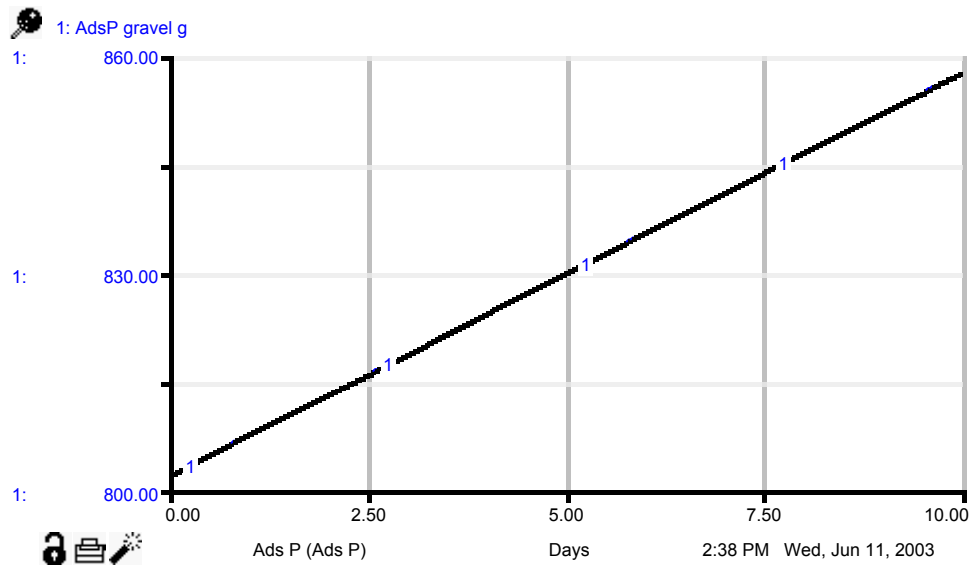


Fig. 7. Adsorption of phosphorus gravel (mg/day).

## Mass Balance

Figure 8 illustrates two phosphorus mass balances. The first (Fig. 8a) is obtained from the measured values (which is a picture of total phosphorus), while the second (Fig. 8b) is calculated from the model outputs. The two mass balances are consistent to a certain extent; approximately the same uptake to plants is obtained (i.e., measured value of 1.9 g P/day vs. model prediction of 1.4 g P/day). The gravel uptake by the model is only half the uptake calculated from the mass balance (0.5 g P/day and 0.9 g P/day, respectively). The difference could be attributed to high concentrations of condensed phosphates, which are difficult to determine, and were not included in the model.

The uptake of phosphorus to gravel is not correlated to the mass balance. The model indicates a total uptake of 5.7 g P/day, with 0.9 g/day being calculated from the mass balance. The reason for the difference between the two uptakes is that dead biomass adds to gravel, based on the model, while this factor is not included in the calculated mass balance. What is really happens at the wetland is that the dead plants fall to the top of gravel, where they are mineralised while going through the gravel.

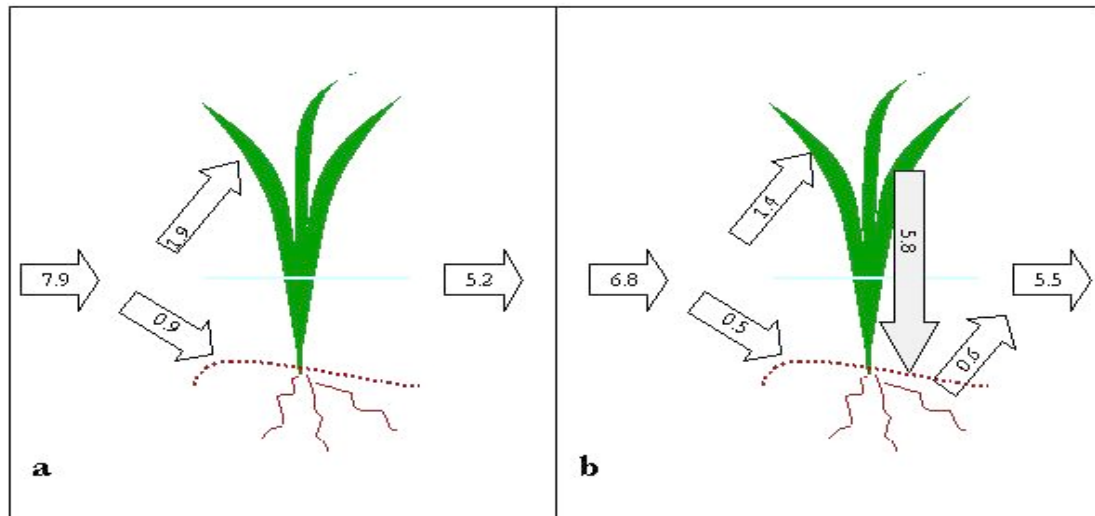


Fig. 8. Phosphorus mass balances (Fig. 8a = mass balance calculated from the measurements; Fig. 8b = mass balance obtained from the model; phosphorus leaking from plants is not included in the mass balance; units are g P/day).

Based on the model, the plants have a negative growth; the overall phosphorus uptake is -4.4 g P/day. The uptake to plants is 1.4 g P/day, while the release is 5.8 g P/day. The calculated phosphorus mass balance gives an uptake of 1.9 g P/day, but does not provide any information about the phosphorus release from the biomass because it is not measured, even though the model is able to account for this process. The fact that the biomass is withering rather than increasing might be in relation to the real wetland, since it was not harvested for several years, and more old plants are seen than new shoots.

Based on simulations (Table 2), the model predicts the removal of suspended phosphorus and reactive phosphorus at different concentrations and flows. As expected, the removal rate of suspended phosphorus is 78% for all flows and concentrations. According to the model, the removal of suspended phosphorus is due mostly to precipitation, which is set to remove a certain part of the suspended phosphorus without taking the flow or concentration into account. This is done because the gravel possesses a filtrating effect, regardless of the flow, as long the flow is not too high. The reactive phosphorus is, as expected, affected both by the flow and concentration.

**Table 2. Results of model simulations**

Flow (m <sup>3</sup> /day)	Inlet (g/m <sup>3</sup> )		Outlet (g/m <sup>3</sup> )		Removal efficiency (%)		
	Conc. reactive P	Conc. susp. P	Conc. reactive P	Conc. susp. P	Reactive P	Susp. P	Total
1	1.0	0.5	0.58	0.11	42	78	54
1	2.0	1.0	1.86	0.22	7	78	31
1	4.0	2.0	4.48	0.44	-12	78	18
2	1.0	0.5	0.94	0.11	6	78	30
2	2.0	1.0	2.24	0.22	-12	78	18
2	4.0	2.0	4.85	0.44	-21	78	12
4	1.0	0.5	1.12	0.11	-12	78	18
4	2.0	1.0	2.42	0.22	-21	78	12
4	4.0	2.0	5.04	0.44	-26	78	9

Because of the plant uptake per time unit, the phosphorus removal increases when the flow decreases. The plants are exposed to the phosphorus for a longer period, thereby taking up more phosphorus. Similar, when the phosphorus concentration increases, the phosphorus removal decreases: The plants do not take up more than they need, with the percentage of the plant uptake getting smaller with a higher phosphorus inlet concentration. However, as the reactive phosphorus concentration gets higher, the suspended phosphorus concentration also gets higher, with more being converted into reactive phosphorus.

### Validation

Unfortunately, it has not been possible to validate the phosphorus model because of the small quantity of relevant data. However, a set of data from the rainy season would be perfect for model validation.

### Model Limitations

The model is described for a wetland that has not been harvested for a long time. The plants are withering, rather than growing. Water evaporation inside the wetland is not considered in the model, because this is not a problem, and the correct flow rates and concentrations of the two species might differ in relation to the actual situation.



## **Conclusions**

Except for the lack of model validation, the model has provided satisfactory results. By inserting measured values, and values from the literature, the model provides outputs that correlate with the wetland being analyzed.



## Nitrogen removal

The N-model was developed using collected data and the modelling program STELLA. The model is a deterministic causal model, which in contradiction to a ‘black box’-model also is internally descriptive. This means, that instead of just modelling the in- and outlet data (like a black-box model), it also models the transformations *within* the wetland. This approach gives the modelling engineer possibility to examine the internal processes, thereby giving a better understanding of possible limitations of different operating conditions. It also gives a possibility of predicting the effect on the nitrogen concentrations of up- or down sizing of the wetland.

### Model Framework

The state variables modelled are: Organic-N, Ammonium-N and Nitrate-N and the processes influencing these state variables are listed in table 1 below. The main nitrogen transformations included in the model are ammonification, nitrification and denitrification.

Organic-N (mg N)	$\frac{dN_{organic}}{dt} = inflow - amm. rate - outflow$
Ammonium-N (mg N)	$\frac{dN_{ammonium}}{dt} = inflow + amm. rate - nitr. rate - outflow$
Nitrate-N (mg N)	$\frac{dN_{nitrate}}{dt} = inflow + nitr. rate - denitr. rate - outflow$

Table 1. Differential equations for the state variables in the model. (Amm. = ammonification; nitr. = nitrification; denitr = denitrification).

The conceptual diagram next page (fig.1).gives an overview and basic understanding of the model framework presented in the following sections and shows the main flow paths of nitrogen in the wetland. In both the conceptual diagram and the model, boxes are state variables and ‘arrows’ are nitrogen flows.

There are five repetitive columns in the model (fig.1). Each column represents a subsystem and consists of three boxes representing the three different nitrogen species modelled. The subsystems are modelling the nitrogen transformations within a specific compartment situated between two sample stations in the CW as seen in figure 22. In the conceptual diagram horizontal arrows represent nitrogen transport with the water flow, and vertical arrows represent nitrogen transformations (process-equations). The flows out of each box are assigned different priorities in

the model, telling the program which flow to calculate first. Vertical flows (process equations) are given first priority and horizontal flows (water flows) are given second priority. This ensures that all chemical/physical process-equations built into each subsystem are calculated before the water continues to next compartment subsystem.

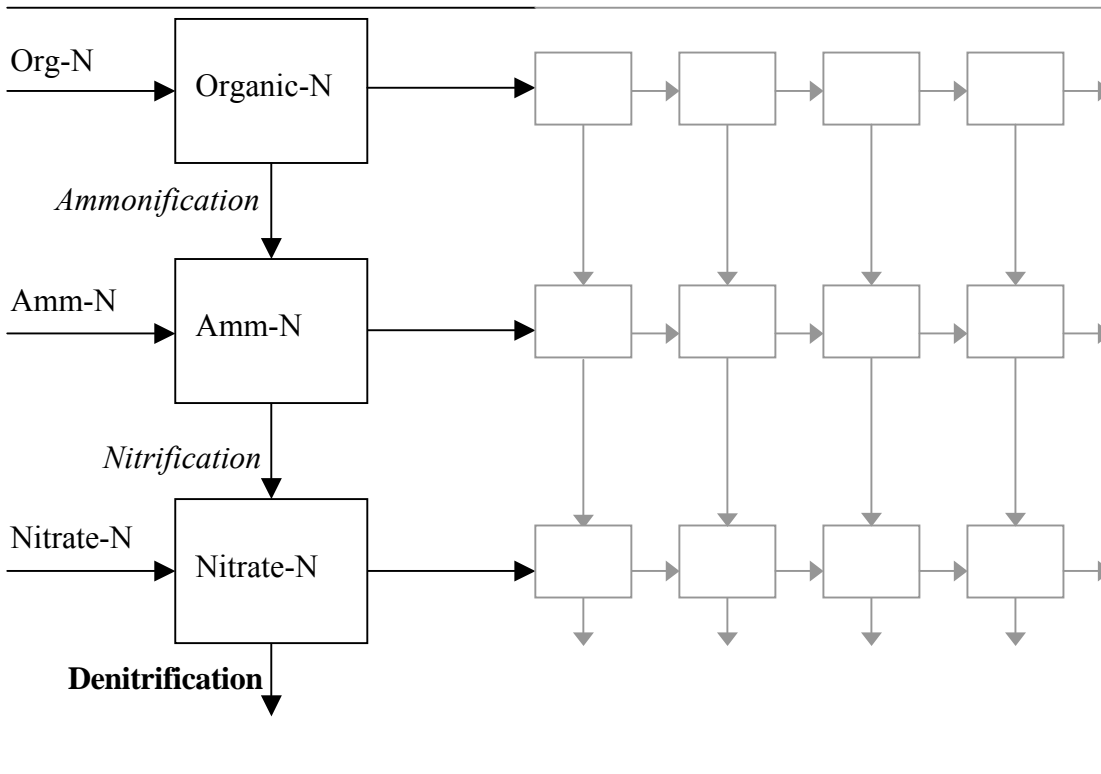
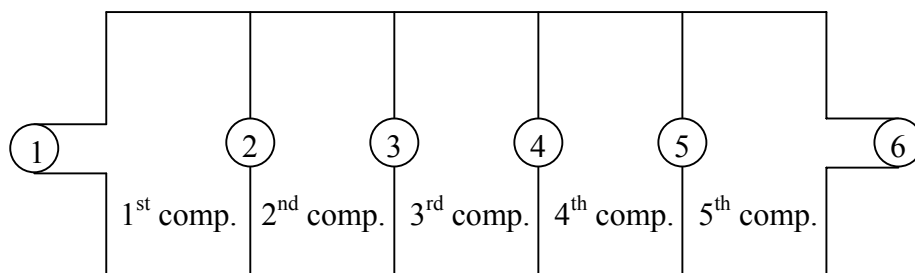


Fig.1. Conceptual diagram showing the most important processes (in italic) build into the model. The entire framework of the model is shown as black and grey boxes together. The model is composed of 5 repetitive subsystems (the columns), each modelling the transformations of the particular compartment - compartment numbers are shown at the top. The first column is printed in black to illustrate the extent of one subsystem. The horizontal arrows represent water flow and the vertical arrows represent process-equations.

Each state variable (= each box) in the subsystems act as a completely mixed reactor, because no differentiation is made from beginning to the end of the compartments. This means, that the outflow of a compartment contains nitrogen equal to the (mean) concentration in that compartment. As the sample stations are situated at the boundaries between compartments the outflow concentration of preceding compartment is equal to the concentration at the following sample station. The unit of the state variables and the flows is  $mg\ N$ , but it can be converted to concentration, because the water volume is known.



*Fig.2. Illustration of the CW from above, showing the five compartments and the sample stations situated in between. The concentration in the sample stations equals the former compartments concentration (except inlet). Each compartment is in the N-model represented by a sub-model.*

## Hydrological Model

The hydrological model is the ‘backbone’ of the nitrogen-model and if not modelled properly it will distort the rest of the model thus giving less accurate outputs. This is because the flow of water and the detention time determine the period of time the wastewater is in contact with medium and hence the degree of treatment.

The theoretically ideal water flow in a wetland is a plug flow, where water flows through the CW in the exact same order as it enters. If a plot of plug flow is made, it looks like a rectangle or square with vertical sides and a flat top. In reality there are several factors like dispersion and canals with slower or faster flow (short-circuiting), which alters this ideal flow regime. This is also supported by our detention time study, showing increasing dispersion along the length of the CW (longer tails on the tracer curves).

In the N-model the hydraulics is modelled by a Tanks-In-Series model (Kadlec and Knight 1996). A delay is incorporated in the horizontal flow-arrows between the compartments, to ensure that water entering inlet (st.1) is seen in outlet one detention time later. With a detention time on 5.5 days the delay between the five compartments is  $5.5/5 = 1.1$  day. If another detention time is used the model automatically adjust the delays.

In the model the fraction ‘inflow/CWV’ (CWV = compartment water volume) determine the volume of water and thereby fraction of N-stock, which is transferred from one compartment to another. This ensures that inflow directly controls the outflow at the different stations.

## The Process Equations

The process equations constitute the relationships between the state variables, modelling the different nitrogen forms, and incorporating the effects of forcing functions. They are written after the hydrological model has been established. Data from campaign 1 and 2 are used for developing the N-model, whereas campaign 3 is used for validation.

The following process equations are basically first order reactions, but made dependant on temperature (Arrhenius expressions) and for nitrification and denitrification also on substrate availability (Michealis-Menten expressions). Temperature is often important as it is generally stated that a 10 degrees increase gives a doubling of the rate of bacterial growth when temperatures are below the optimum value (Madigan *et al* 2000). However in *this* particular study it is not that important as the temperature is rather stable around 26-28 degrees Celsius (see app. C, E, G and I), and the dependence of the process equation on temperature does thus not alter the basic first order expression. In for example temperate climates though, the temperature play a much more important role because of the seasonal fluctuations. All units used in flow arrows and state variables in the model are *mg N*.

**The ammonification** rate in the five compartments is defined as depending on the amount of organic nitrogen present and temperature. The first order equation ('ammrate' in model) determining the flow from box 'Org-N' to 'Amm-N' is as follows:

$$\text{Ammonification rate} = C_0 \cdot k \quad (1)$$

Units of the *Ammonification rate* is mg N/d.  $C_0$  is the amount of organic-N (mg N) present in the specific compartment at  $t = 0$ ,  $t$  is time. The parameter  $k$  is the temperature dependence defined by a modified Arrhenius expression:

$$k = k_{20_{AMM}} \cdot \theta^{(T-20)} \quad (2)$$

Where  $k_{20_{AMM}}$  ( $d^{-1}$ ) is the reaction coefficient for ammonification at 20°C, *theta* ( $\theta$ ) is the ammonification temperature coefficient, and  $T$  is the temperature in Celsius (Kadlec and Knight 1996). Because the temperature as mentioned above is almost constant in the CW the ammonification equation acts essentially as a plain first order equation.

**The nitrification** process has for simplification been modelled as a one-step process instead of a two-step process. The nitrification rate depends on the amount of ammonium present, the oxygen concentration and the temperature. Temperature is modelled in the same way as the ammonification and denitrification, while the ammonium and oxygen concentration is added in the equation by Michaelis-Menten expressions. The process equation ('nitrrate' in model) is as follows:

$$\text{Nitrification rate} = k_{20NIT} \cdot \theta^{(T-20)} \cdot C_0 \cdot \frac{[NH_4N]}{[NH_4N] + K_{NH_4^+}} \cdot \frac{[O_2]}{[O_2] + K_{O_2}} \quad (3)$$

Where the *Nitrification rate* is in mg N/d and  $C_0$  is the amount of ammonium-N (mg N) present in the specific compartment at  $t = 0$ .  $K_{NH_4}$  and  $K_{O_2}$  (mg N/L) are half saturation constants for ammonium and oxygen respectively. A modified Arrhenius relationship ( $d^{-1}$ ) describes the effect of temperature on nitrification.

The Michealis-Menten expressions in the equation are almost constants, due to the relative stable oxygen concentration and the very small  $K_{NH_4}$  compared to the ammonium concentrations in the wetland. The equation is therefore essentially a first order expression. However to broaden the models applicability to CWs with low ammonium concentration and other oxygen concentrations, the Michaelis-Menten expression has been added anyway.

**The denitrification** rate is described as depending on the amount of nitrate present and temperature. The process equation ('denitrate' in model) determining the flow from box 'AmmN' and out of the system is as follows:

$$\text{Denitrification rate} = k_{20DENIT} \cdot \theta^{(T-20)} \cdot C_0 \cdot \frac{[NO_3N]}{[NO_3N] + K_{NO_3^-}} \quad (4)$$

Where the *Denitrification rate* is in mg N/d and  $C_0$  is the amount of nitrate-N (mg N) present in the specific compartment at  $t = 0$ . A modified Arrhenius relationship ( $d^{-1}$ ) describes the effect of temperature on denitrification.  $K_{NO_3}$  (mg N/L) is the half saturation constant for nitrate. .

**The process-equations for plant-uptake** of ammonium and nitrate have *not* been incorporated into the model, because the study-site CW was not harvested and because the plants were assumed to have reached an almost steady state between N-uptake and N-release through decomposition. The

flow arrows in the model ('plantammrate' and 'plantnitrate') for plant uptake are therefore set to a zero-flow. This assumption is justified by many studies (Vymazal 1998, Brix 1997, Kadlec and Knight 1996). However, if the model is applied to data from CWs with regular harvesting, the model is still functional if the modelling engineer writes the equation for plant-uptake into the flow arrows. The logistic process equations can be written as follows (Jørgensen and Bendoricchio 2001):

$$Plant\text{-}uptake = r_{\max} \cdot C_0 \cdot \frac{K - C}{K} \quad (5)$$

Where the *plant-uptake* rates of ammonium (or nitrate) are in mg N pr day pr. compartment and  $C_0$  is the total N-content (mg N) in the plants present in the specific compartment at  $t = 0$ .  $K$  is the carrying capacity (total N-content at maximum biomass) for the plants in the system. The temperature dependence could be modelled by a modified Arrhenius expression ( $d^{-1}$ ). If the total concentration of amm-N and nitrate-N becomes too low in the CW, the plant-uptake will become limited, which should be applied to the plant-uptake equation by setting a minimum concentration for uptake. It should be mentioned that ammonium is preferred over nitrate in the uptake of plants and this should be considered in the modelling process.

**Retention of the particulate organic nitrogen** is caused by physical processes retaining particulate organic nitrogen in the first part of wetlands. This is modelled by multiplying the organic-N flow arrows between compartment 1 - 2 and 2 - 3, with constants that reduce the transport of nitrogen between these compartments. In the model these parameters are named PON C1 and PON C2 (Particulate Organic Nitrogen).

From the chlorophyll *a* measurements through the CW it can be seen that the filtration and sedimentation of algae happens in the first two compartments. The PON-parameters are only built into these compartments, as it is assumed that the removal of algae is a relative good indication of the overall filtration of particulate material. The larger amount of organic-N removed in these compartments compared to the rest of the CW, also supports this point of view.

**Processes not included in the model** are adsorption, volatilisation and other. Adsorption of ammonium to the bed matrix is assumed to be in a steady state, and thus not contributing to the net removal of nitrogen. Ammonia volatilisation is also considered negligible as the pH of the study-site wetland (and in most constructed wetlands) is below critical values for volatilisation.



Parameter	Final Calibrated value used	Literature value used	Other literature values	Unit
$\theta$ amm		1.04 <sup>b</sup>	1.02-1.08 <sup>a</sup> ;	-
$\theta$ nit		1.047 <sup>a</sup>	1.033 <sup>b</sup> ; 1.035 <sup>b</sup> ;	-
$\theta$ denit		1.09 <sup>b</sup>	1.08-1.10 <sup>b</sup> ; 1.045 <sup>a</sup>	-
$k_{20}$ amm	0.5		0.40 <sup>b</sup>	d <sup>-1</sup>
$k_{20}$ nit	0.8		0.39 <sup>b</sup>	d <sup>-1</sup>
$k_{20}$ denit	2.2		0.57 <sup>b</sup>	d <sup>-1</sup>
$K_{NH4}$		1 <sup>b</sup>		mg N/L
$K_{NO3}$		0.1 <sup>b</sup>	0.1-0.2 <sup>b</sup>	mg N/L
$K_{O2}$		1.3 <sup>b</sup>	0.15-2.0 <sup>b</sup>	mg N/L
PON C1	0.15			-
PON C2	0.15			-

Table 2. Literature and calibrated values of parameters used in the model - PON,  $K_m$ ,  $K_{20}$  and theta ( $\theta$ ). The first estimates calculated from data are also listed. a) Jørgensen and Bendoricchio 2001; b) Kadlec and Knight 1996

None of the modelled processes are described as depending on pH. This is not because pH has no influence on the biochemical processes involved, but because the pH experienced in the study-site wetland and in subsurface CWs in general, almost always is within a narrow range, where small changes do not affect the processes significantly (Kadlec and Knight 1996). Besides bacteria present in the CW are *adapted* to the range of pH values present.

### Literature Values and Estimation of Rate Constants ( $K_{20}$ )

A first estimate of the process rate constants from data is convenient to make, as it often makes calibration less time consuming compared to a calibration starting with literature values. Because of the relatively simple system (compared to for instance the N-cycle in a lake) and because extensive data from within the CW were available, it was possible to get good first estimates of the modelled process-rates as individual processes could be separated and estimated. Data from campaign 2 were used in these calculations. Literature and calibrated values used for the parameters  $K_{20}$ , PON,  $K_m$  and theta ( $\theta$ ) values are listed in table 2 above.

**Estimation of the ammonification rate** was straight forward as it easily could be derived from the organic-N removal through the wetland. A first estimate of the rate was obtained by calculating the relative decrease of organic-N based on campaign 2 data. This rate constant was then by simple

calculation built into the respective Arrhenius expression as a  $k_{20}$  value (in equation 1 and 4). This first estimate of the rate constant is then used in the calibration-process.

**Estimation of the nitrification rate** is possible in the wetland by looking at the total nitrogen removal and the changes in nitrate concentration. In this estimation it is assumed that denitrification is the only quantitatively important process that removes total nitrogen (TN) from a wetland without plant harvesting. This assumption is justified by several studies (Reddy *et al* 1989; Devol 2003; Kadlec and Knight 1996; Cronk 1996). The TN removal thus equals the denitrification rate, and nitrification provides the additional nitrate necessary for this calculated denitrification. The nitrification can be calculated as follows:

$$\text{Nitrification rate} = \text{TN removal} + \Delta \text{Nitrate} \quad (6)$$

Where '*TN removal*' is mg TN removed in a given compartment and '*Δ Nitrate*' is the change in mg nitrate-N of the compartment. From the nitrification rate (mg N/d) obtained from the above-mentioned equation (6) a first estimation of  $k_{20}$  can be calculated from equation (3) by knowing the ammonium concentration ( $C_0$ ) and provided that the Michaelis-Menten expressions are set to 1 and a literature value is used for theta ( $\theta$ ).

**Estimation of the denitrification rate** could be calculated from the TN removal in a given compartment. By knowing the nitrate concentration ( $C_0$ ) in the same compartment, an estimate of the rate constant could be obtained by equation (4) and this rate was then by simple calculation built into the respective Arrhenius expression as a  $k_{20}$  value (in equation 1 and 4). Like in the estimation of the nitrification rate the Michaelis-Menten expression in the denitrification is set to 1.

## Verification of the Model

To verify the model a couple of tests were performed. The intuitive assumption that an nitrogen-increase in inlet values should result in an increase of outlet values, was tested by increasing the concentrations of the different nitrogen species after turn and checking the outlet response for the given nitrogen specie. Another criterion was that no negative values were allowed to occur. This was assured by checking the function 'non-negative' values in the state variables telling the model not to allow any negative values. The last test was a check of the stability of the model.

In conclusion all verification tests were passed: no negative concentrations were observed, increase of inflowing nitrogen gave increases in the outflow and the model was stable in the range relevant to this study. In addition a sensitivity analyses were performed on all parameters, which among other things revealed that the process-rates were most sensitive to the Arrhenius expression.

## **Calibration of the N-model**

The calibration of the nitrogen model is based on trial and error changes in selected parameters. A sensitivity analysis made on all parameters identified  $k_{20}$  in the Arrhenius expression as the most important parameter to calibrate. The variation in oxygen and temperature was insufficient for a real calibration of parameters (like  $\theta$  and  $K_{O_2}$ ) that depend on these two variables. Instead literature values were used for these parameters. Values of  $k_{20}$  in the ammonification, nitrification and denitrification rates were calibrated starting with a first estimate calculated as explained in 'Estimation of Parameters'. A calibration sequence was selected starting with calibration of the ammonification rate, then the nitrification rate and lastly the denitrification rate. This specific order was chosen to follow the flow of nitrogen in the model, thus avoiding having to recalibrate a parameter because the process equation above was changed.

It was possible to get almost exact results when calibrating on data from only *one* campaign. But to broaden this model's performance when applied to a wider spectrum of CW-data it was calibrated on *two* campaigns - campaign 1 and 2. In figure 3 model outputs after the final calibration are compared with observed average data (bars) from campaign 1 and 2. In the calibration the three process rates were adjusted in small steps each until the best possible model-fit to data in *both* campaign 1 and 2 was achieved. This was done by examining outputs of all possible combinations when changing the ammonification and nitrification rate -5%, 0% and +5%. The best combination was then fine-tuned further and the resulting percentage each rate should be adjusted with was build into the  $k_{20}$  value.

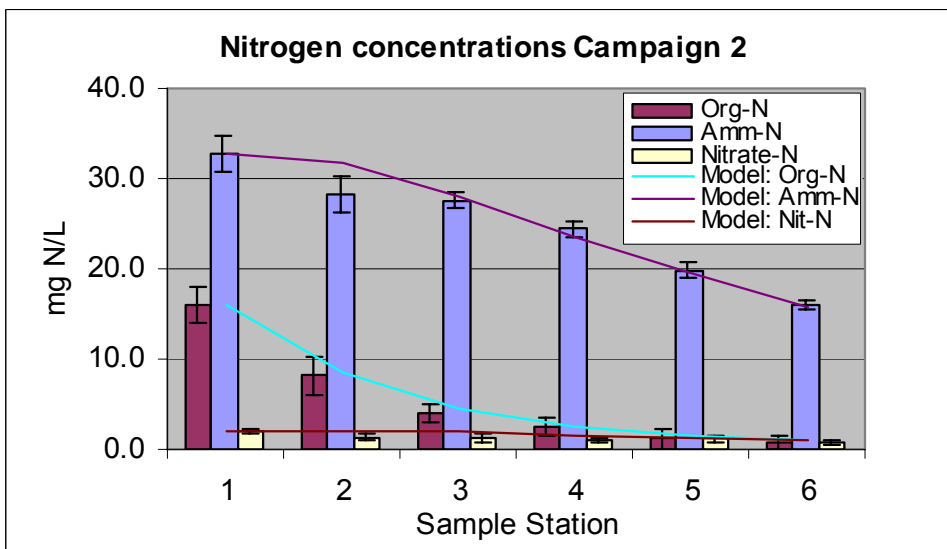
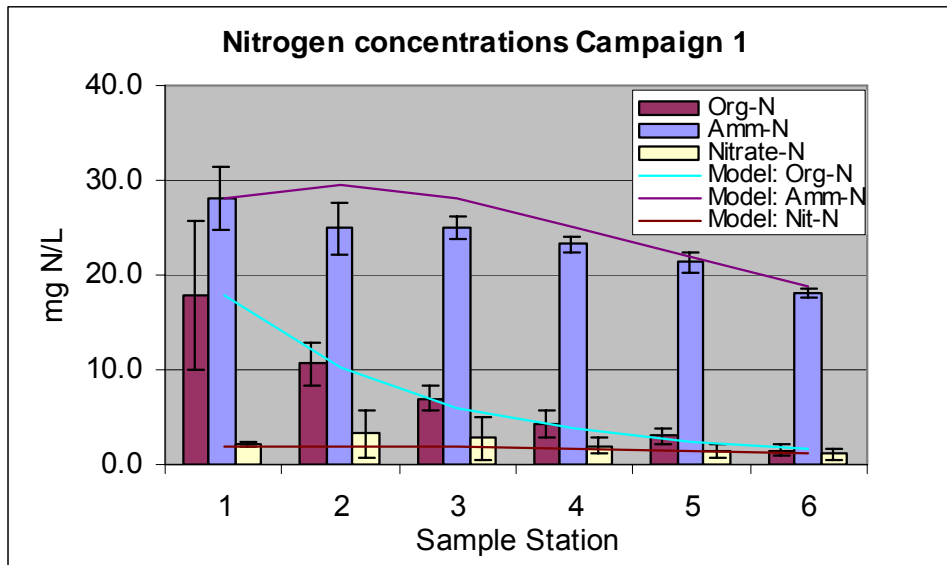


Fig.3. Calibration of the model. Model outputs (curves) compared with average sample station data (bars) from campaign 1 and 2 when conditions prevailing under these campaigns were applied to the model. Confidence intervals on 95% level are shown on observed data. Except for amm-N at station 2 the model-curve is fitting the observed data well with respect to all three nitrogen-species.

Table 3 lists quantitative measures of the goodness of fit between modelled and observed values. The slope ( $\alpha$ ) of the regression analyses and the correlation ( $R^2$ ) are both close to 1, which supports the good result of the model calibration seen in figure 22. In campaign 2 relative high deviations are seen in model outputs of org-N (26%) and nitrate (38%). This does not imply a bad fit of the model, but rather that the effluent concentrations of these N-species are very low (0.7 and 0.8 mg/L) magnifying percentage differences. What is important is, that the model is capable of reducing the concentrations to the low level observed.

Modelled versus observed outlet data Campaign 1 and 2	Average deviation (%) (mod. outputs vs. average obs.)		Modelled removal % (inlet to outlet)		Correlation (all obs. vs. mod. outputs)	
	C1	C2	C1	C2	C1	C2
TN	5%	2%	55% (57)	65% (61)	R <sup>2</sup> = 0.99 α = 1.096	R <sup>2</sup> = 0.99 α = 1.007
Organic-N	4%	26%	91% (91)	94% (95)		
Ammonium-N	4%	2%	36% (33)	52% (51)		
Nitrate-N	11%	38%	41% (35)	45% (60)		

Table 3. Modelled vs. observed outlet data in calibration of campaign 1 (C1) and 2 (C2). Numbers in brackets in the column 'Removal %' denotes the measured removals. The average deviation is calculated by following equation:  $(X_c - X_{ma})/X_{ma} * 100\%$ , where  $X_c$  are the computed value and  $X_{ma}$  are the average of the measured values.

When running the model with constant inlet concentrations, the concentration at the outlet does not stabilize entirely before 150-200 days has past. This is due to the internal mixing effect caused by the tanks-in-series model, which causes a pulse in the inlet to be blurred by being dissolved in the water already present in the wetland compartments. Also the initial values of nitrogen in the state variables have a significant effect on the time it takes to get a stable model output. In reality this effect is also expected to exist, as the internal mixing would create an adjustment phase if the nitrogen loading were changed. The concentration after 150 days was the one used when calibrating the model. However, in spite of this long-stabilization period the predicted concentrations after a model run on just 5-6 days are still quite close to the final stabilized outputs.

## Validation of the N-model

How precise does the model predict the values of a different, independent dataset? An answer to this question was given by validating on data from campaign 3. This campaign's elevated nitrate concentration in the inlet water is an advantage for the validation process, as it puts the model to a true test of its applicability outside the range of nitrate concentrations for which it was calibrated. The influent concentration of ammonium was also different in campaign 3, approximately two-thirds of the concentrations in campaign 1 and 2.

Model outputs are compared with data from campaign 3 (6 days average) in figure 3. As can be seen the model is capable of reducing the elevated nitrate level to the values observed within the wetland and outlet well. The internal decrease modelled from station 1 to 3 is however not as steep as the measured (modelled: 13.3→3.6→1.7; observed: 13.3→2.0→1.8). Like in the calibration of

campaign 1 and 2 the modelled organic-N transformations fits very nicely the corresponding measured average values in campaign 3. For ammonium the modelled concentrations are not as precise as in the calibration, but the model predicts a small local maximum of the ammonium concentration at station 2 even though it is not at station 3 as observed and not as distinct either (modelled: 20.8; observed 23.7).

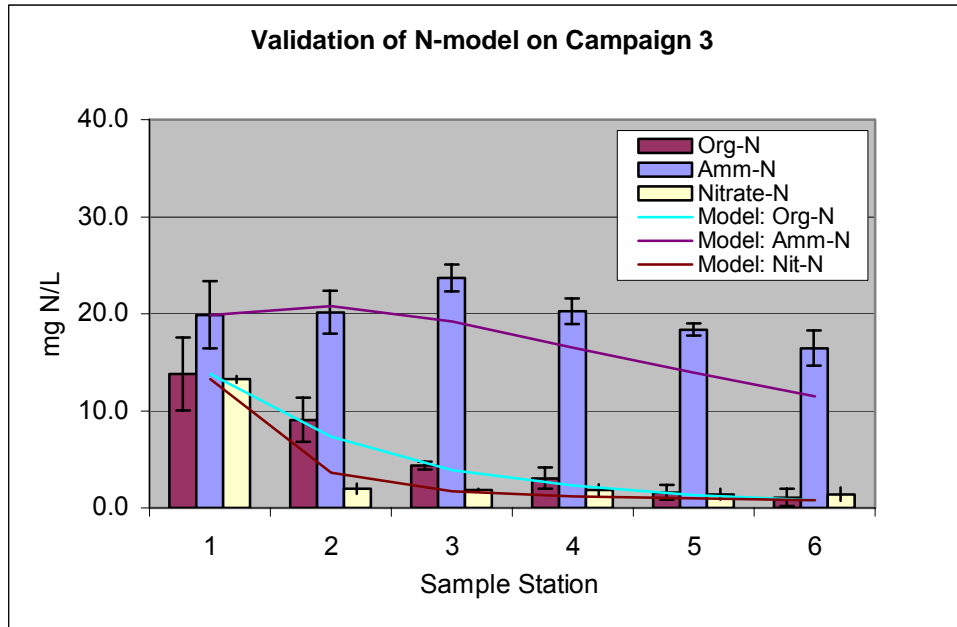


Fig.3. Validation of the N-model. The N-model performance when applied to a new dataset. Campaign 3 differ from the two other campaigns primarily because of elevated nitrate and lower ammonium levels in the inlet (and climate).

In table 4 model results are compared with modelled values. The slope ( $\alpha$ ) of the regression analyses and correlation ( $R^2$ ) are both relative close to 1, which supports the relatively good predictive capabilities of the model, found in the validation. In figure 24 the correlation between observed vs. modelled values of the campaigns are shown.

Modelled values versus observed outlet data - campaign 3	Average deviation % (mod. outputs vs. average obs.)	Modelled removal % (inlet to outlet)	Correlation (all obs. vs. mod. outputs)
TN	29%	72% (61)	$R^2 = 0.95$ $\alpha = 0.872$
Organic-N	26%	94% (92)	
Ammonium-N	30%	42% (17)	
Nitrate-N	44%	94% (89)	

Table 4. Validation of modelled vs. observed outlet data in campaign 3. Numbers in brackets in the column 'Removal %' denotes measured removals. The average deviation is calculated by equation:  $(X_c - X_{ma})/X_{ma} * 100\%$ , where  $X_c$  are the computed value and  $X_{ma}$  are the average of the measured values.

The high percent deviation of org-N and nitrate-N from the modelled values (table above) is somehow in contradiction to the intuitive impression from figure 3, where the modelled values seem to fit very well. However, like in campaign 2, the effluent concentrations are very low (1.1 and 1.4 mg/L), so small differences makes up a large percentage. For ammonium though the percent deviation tells more about the fit of the model. The difference here is quantitative significant. Below the regression analyses illustrates the good over-all correlations of modelled vs. observed data in the campaigns.

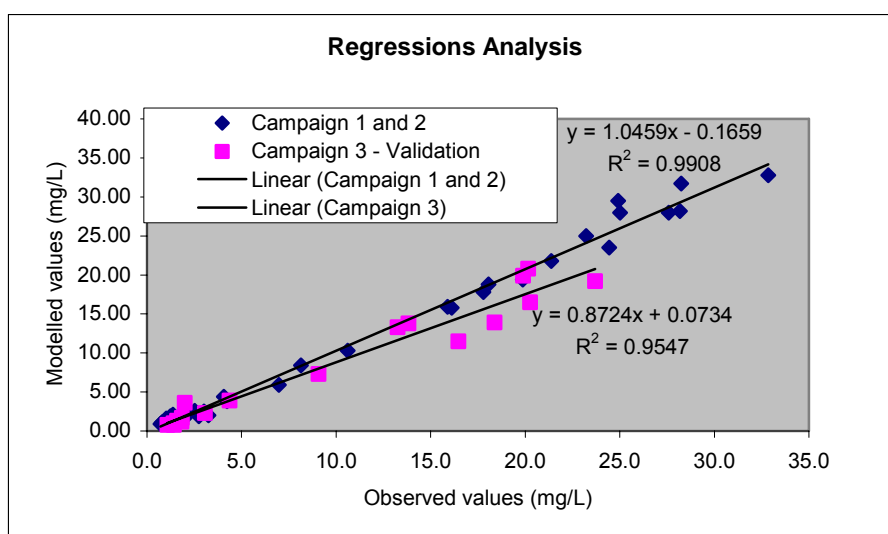


Fig.4. Regression analyses of campaign 1 and 2, and of campaign 3.

All in all the validation of the model on data from campaign 3 elucidate the high prediction capability of organic-N and nitrate-N in tropical subsurface wetlands, while the ammonium concentrations are somewhat too low. In this relative simple type of model where only three rates can be adjusted it is difficult to fit model outputs of ammonium better if a calibration of campaign 3 data was applied, as an increase of the ammonification and lowering of the nitrification rate here would imply a deviation from campaign 1 and 2 model results (fig.2). For a further validation data from other CWs with different temperature and oxygen regimes are needed, but this lies beyond the scope of this thesis.

## **How to use the model**

In the next two pages a figure of the model as it looks in STELLA and an explanation to the components involved are presented (see table 5 next page). In app. Q compartment 1's process equations as they look in STELLA are presented.

To run the model in STELLA values have to be filled into the nine converters (round circles) placed at the top. These inputs are then automatically transferred to the rest of the model and the model is now ready to be used.

The converters are: Inlet concentrations (mg/L) of organic-N, ammonium-N and nitrate-N, the average oxygen concentration in the bed (mg/L), bed volume of the CW (L), inflow and outflow rate of water (L/d), water temperature (°C) and porosity.



<b>STATE VARIABLES IN SUB-MODEL (STOCKS)</b>		
<i>Name in (sub) model</i>	<i>Unit</i>	<i>Explanation</i>
OrgN C1	mg org-N	Amount of organic-N in compartment 1
AmmN C1	mg NH <sub>4</sub> <sup>+</sup> -N	Amount of NH <sub>4</sub> <sup>+</sup> -N in compartment 1
NitN C1	mg NO <sub>3</sub> <sup>-</sup> -N	Amount of NO <sub>3</sub> <sup>-</sup> -N in compartment 1
<b>FLOW ARROWS IN SUB-MODEL (PROCESS EQUATIONS)</b>		
<i>Name in (sub) model</i>	<i>Unit</i>	<i>Explanation</i>
ammN st2	mg NH <sub>4</sub> <sup>+</sup> -N/dt	Amount of NH <sub>4</sub> <sup>+</sup> -N in outflow from compartment (= st.2)
ammN st1	mg NH <sub>4</sub> <sup>+</sup> -N/dt	Amount of NH <sub>4</sub> <sup>+</sup> -N in inflow
ammrate C1	mg org-N/dt	Amount of organic-N mineralised in compartment 1
denirate C1	mg NO <sub>3</sub> <sup>-</sup> -N/dt	Amount of NO <sub>3</sub> <sup>-</sup> -N denitrified in compartment 1
nitN st2	mg NO <sub>3</sub> <sup>-</sup> -N/dt	Amount of NO <sub>3</sub> <sup>-</sup> -N in outflow from compartment 1 (= st.2)
nitN st1	mg NO <sub>3</sub> <sup>-</sup> -N/dt	Amount of NO <sub>3</sub> <sup>-</sup> -N in inflow
nitrate C1	mg NH <sub>4</sub> <sup>+</sup> -N/dt	Amount of NH <sub>4</sub> <sup>+</sup> -N nitrified in compartment 1
orgN st1	mg org-N/dt	Amount of organic-N in inflow
orgN st2	mg org-N/dt	Amount of organic-N in outflow from compartment 1 (= st.2)
plantammrateC1	mg NH <sub>4</sub> <sup>+</sup> -N/dt	Amount of NH <sub>4</sub> <sup>+</sup> -N plant-uptake in compartment 1
plantnitrateC1	mg org-N/dt	Amount of organic-N plant-uptake in compartment 1
<b>FORCING FUNCTIONS (INFLOWS, CONSTANTS, CONCENTRATIONS)</b>		
<i>Name in (sub) model</i>	<i>Unit</i>	<i>Explanation</i>
ammconcC1	mg NH <sub>4</sub> <sup>+</sup> -N/L	[NH <sub>4</sub> <sup>+</sup> -N] in compartment 1
ammN conc st1	mg NH <sub>4</sub> <sup>+</sup> -N/L	[NH <sub>4</sub> <sup>+</sup> -N] in inlet
bed volume	L	Volume of CW (incl. gravels)
CDT	days	Compartment detention time
CWV	L	Compartment Water Volume
Detention time	days	Detention time in CW
inflow	L/dt	Inlet's inflow rate
inflow/CWV	-	Inflow rate in proportion to compartment water volume
nitconcC1	mg NO <sub>3</sub> <sup>-</sup> -N/L	[NO <sub>3</sub> <sup>-</sup> -N] in compartment 1
nitN conc st1	mg NO <sub>3</sub> <sup>-</sup> -N/L	[NO <sub>3</sub> <sup>-</sup> -N] in inlet
O <sub>2</sub> conc.	mg O <sub>2</sub> /L	[O <sub>2</sub> ] in CW (average)
orgN conc st1	mg org-N/L	[Organic-N] in inlet
outflow	L/dt	Outflow of the CW
Porosity	-	Porosity of the gravel bed
water temp	Celsius	Water temperature
<b>PARAMETERS IN SUB-MODEL</b>		
<i>Name in (sub) model</i>	<i>Unit</i>	<i>Explanation</i>
Arrh Amm	d <sup>-1</sup>	Arrhenius value for ammonification
Arrh Denit	d <sup>-1</sup>	Arrhenius value for denitrification
Arrh Nit	d <sup>-1</sup>	Arrhenius value for nitrification
K20amm	d <sup>-1</sup>	K <sub>20</sub> value for ammonification
K20denit	d <sup>-1</sup>	K <sub>20</sub> value for nitrification
K20nit	d <sup>-1</sup>	K <sub>20</sub> value for denitrification
Km amm	mg NH <sub>4</sub> <sup>+</sup> -N/L	K <sub>m</sub> value for [NH <sub>4</sub> <sup>+</sup> -N] in nitrification
Km nit	mg NO <sub>3</sub> <sup>-</sup> -N/L	K <sub>m</sub> value for [NO <sub>3</sub> <sup>-</sup> -N] in denitrification
Km O2	mg O <sub>2</sub> /L	K <sub>m</sub> value for [O <sub>2</sub> ] in nitrification process
PON C1	-	PON fraction retained by filtration in comp. 1
Theta amm	-	Theta value for ammonification
Theta denit	-	Theta value for denitrification
Theta nitrification	-	Theta value for nitrification

Table 5. Left: N-model in Stella. Above: Explanation to names used in one sub-model of the N-model. Only names from this sub-model (compartment 1) are explained as the rest of the model-names are similar, but with different compartment numbers. The parameter-values used are the

## Use of the N<sub>2</sub>- model for Constructed Wetlands design

The model is well calibrated and validated by a data set based on observations at the pilot plant at Dar es Salaam University. Therefore, it is possible to conclude that the model can be applied for wetland design. It is recommended to apply the following method:

1. Run the model with the known inflow concentrations of nitrate, ammonium and organic nitrogen.
2. Vary the inflow rate until the desired removal efficiency is obtained (the right outflow concentrations calculated on basis of the desired removal efficiency). The found inflow rate that yields the required outflow concentration is denoted IE.
3. The BOD removal is found in the following way considering that the organic matter contains 5-8% nitrogen in average 6.5% N. Multiply therefore the BOD<sub>5</sub>-in by  $(0.065/1.4) \approx 0.0464$  corresponding to the stoichiometric use of oxygen, 1.4 mg of oxygen per mg of organic matter, and run the model with this inflow concentration of organic nitrogen. If the removal of organic nitrogen is RON mg/l, **the BOD<sub>5</sub> removal is RON / 0.0464.**
4. The pilot plant wetland has an area of 35 m<sup>2</sup> but due to the low flow rate through the wetland, the water will easily form channels. The volume of the pilot plant wetland is  $35 \times 0.7 \text{ m}^3 = 24.5 \text{ m}^3$ . The porosity is 0.65 that implies that the void volume is about 16 m<sup>3</sup>. With a flow rate of 2 m<sup>3</sup> /24h a retention time of 8 days should be expected, but the retention time was determined to about 5 days. The effective area is therefore  $35 \times 5 / 8 \approx 22 \text{ m}^2$ . If the required flow rate for the CW under design is RI, the required wetland area to obtain the needed removal efficiency is therefore **RIx22 / IE**
5. To obtain a better utilization of the constructed wetland a flow rate of 10 – 25 m /24h is recommended, the highest flow rate and the highest concentration of suspended matter. If a depth of 0.7 m is foreseen the entrance width, W, for the entrance cross sectional,  $W \times 0.7 = \text{CSA}$ , should therefore be **W = RI/ (7- 17.5) with / for clear water and 17.5 for water with a high concentration of suspended solid.**
6. It is beneficial to use a length of 3 W. The right volume or area of the constructed wetland is found by the use of the flow pattern shown in Figure A.
7. Notice that the ammonium removal in a subsurface constructed wetland is low. If a high nitrogen removal is required it is therefore necessary before the constructed wetland to have a pre-treatment that nitrifies the ammonium, for instance maturation, a facultative or an aerated pond.

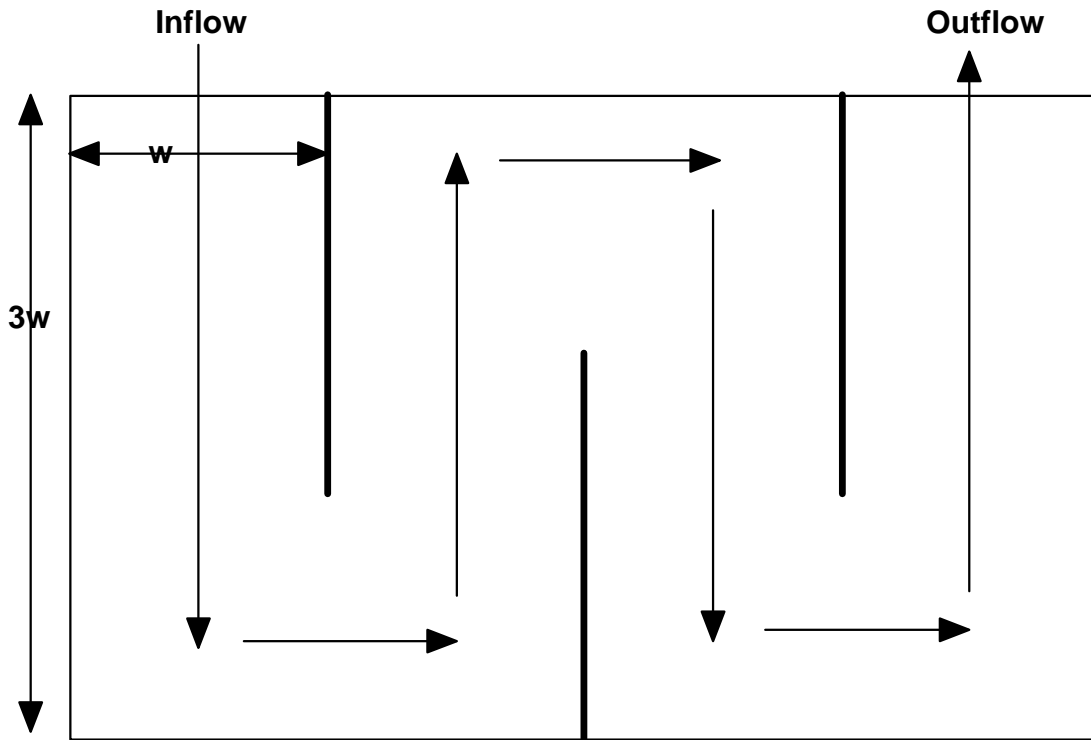


Figure A. Recommended flow pattern for CW.



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