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NITROGEN DYNAMICS IN A MATURATION WASTE STABILIZATION POND SYSTEM RECEIVING INDUSTRIAL WASTEWATER IN MABIBO AREA DAR ES SALAAM, TANZANIA

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ABSTRACT: A mathematical model describing the dynamics of Nitrogen transformation and removal in a maturation Waste Stabilization Pond (MWSP) system receiving industrial wastewater was developed. Simulation of the processes was done using STELLA 8_1®, based on the principle of conservation of mass. Besides, measurement of different parameters input to the model was made. Model simulation and mass balance analysis results show that nitrification was responsible for the majority of nitrogen transformation at 36.9% (38.1 $mgl^{-1}d^{-1}$), followed by plant uptake at 31.6% (32.55 $mgl^{-1}d^{-1}$); mineralization at 21.05% (21.65 $mgl^{-1}d^{-1}$); sedimentation/accretion at 9.3% (9.1 $mgl^{-1}d^{-1}$) transformation. Regression analysis indicates a good agreement between simulation results and actual measurements with R^2 of 0.749 for NO_3-N, 0.709 for NH_3-N, 0.985 for Org-N, and 0.973 for Soil/Sediment-N. These results suggest that the developed model is capable of simulating the dynamics of nitrogen transformation and removal in a Maturation Waste Stabilization Pond system receiving industrial wastewater, and can be utilized as a tool in assessing nitrogen levels at various pollution scenarios to aid decision making as regard to protecting water bodies receiving effluent from these systems.

Keywords: Industrial Wastewater; Maturation Waste Stabilization Ponds, Modeling; Nitrogen transformation

INTRODUCTION

The most appropriate wastewater treatment is that which will produces an effluent meeting the recommended microbiological and chemical quality guidelines both at low cost and with minimal operational and maintenance requirements [1]. Waste Stabilization Ponds (WSPs) are still regarded as the method of first choice for the treatment of wastewater world-wide. While in Europe WSPs are mainly used for small rural communities, one third of all wastewater treatment plants in the USA are WSPs, usually serving populations up to 5000 [2]. However in warmer climates (the Middle East, Africa, Asia and Latin America) ponds are commonly used for large populations (up to around 1 million). Many countries in tropical climates use WSPs for wastewater treatment (e.g., Tanzania, Kenya, Malawi, Uganda, Zambia, Botswana, Zimbabwe). In these tropical and equatorial regions, sewage treatment by WSPs has been considered an ideal way of harnessing the capability of natural processes to meet the benefits of achieving improved sewage effluents to the environment.

In an attempt to understand nitrogen transformation mechanisms for various ecological systems, extensive research has been carried out worldwide and models developed for various scenarios, including activated sludge treatment plants [3], waste stabilization ponds receiving domestic waste water [4,5,6], attached growth systems [7,8], river deltas and estuarines [9] constructed wetlands [5,10], natural wetlands [11], duckweed systems [12], water hyacinths ponds [10,13] and high rate ponds [14]. Some research studies have established the performance of individual waste stabilization ponds [14,15], A much better approach to further understanding of fates of nitrogen compound in WSP was based on using model, which has been largely used to stimulate the behavior of nitrogen in aquatic ecosystems that are free from industrial pollution. This study therefore aims at using modeling approach to study the dynamics of nitrogen transformation and removal in a situation whereby the system is subjected to pollution from industrial wastewater.

MATERIALS AND METHODS
Description of the Study Area

The study of the research was conducted at Mabibo ponds located at Mabibo ward in Kinondoni district in Dar-es-salaam city at $6°48'$S and $39°13'$E (Figure 1). To the West the ponds are bordered by Ubungo Maziwa, Mburahati to the East, Mabibo External to the South and to the North the ponds are bordered by the Manzese area.
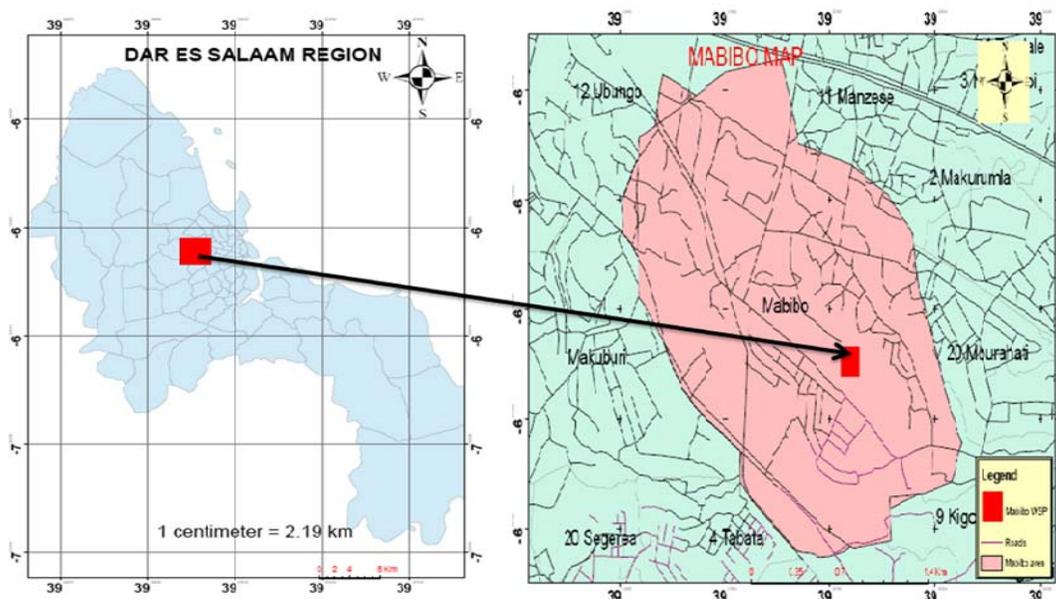
Figure 2: Location of Study Area in the Dar es Salaam Map

The Mabibo WSP system is comprised of six ponds which receive wastewater from the Ubungo industrial area, majority of which are from textile industries. Figure 2 shows the layout plan of the satudy area and water sampling points 1 and 2 (S_1 and S_2). Sampling point S_1 is located at the entrance of the maturation pond while S_2 is located at the pond outlet where the effluent is discharged to the receiving environment.
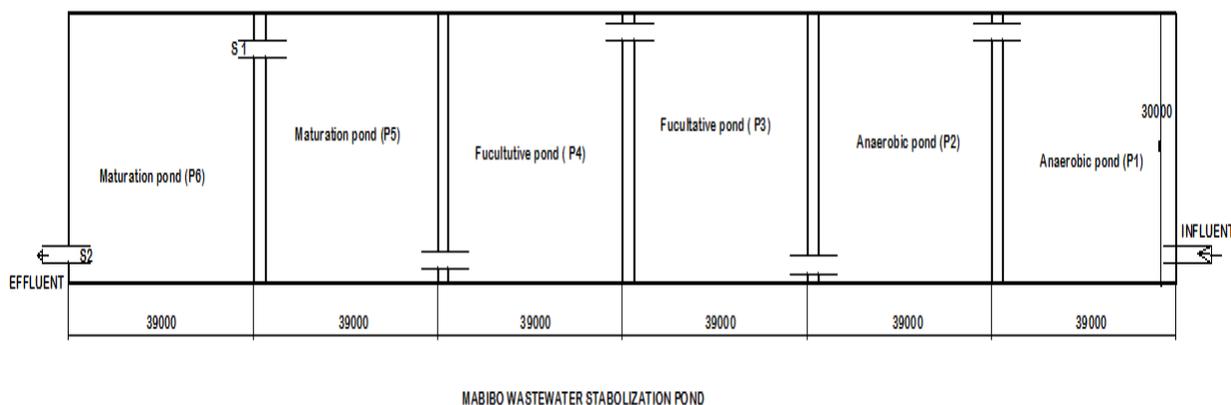
Figure 2: Location of Sampling Points along the Pond System

In situ measurements

Temperature, pH and Dissolved Oxygen (DO) concentration were all measured *in situ*. Temperature was measured using mercury-filled Celsius thermometer which had $0.1°$C scale etched on capillary glass, and the measurement was taken at about 30cm depth from water surface. pH was measured using HACH[®] 704 electrode pH meter. DO measurement was done using HACH[®] SENSION 156 electrode. Flow rate (Q) was measured using Float method, which determines surface velocity, Mean velocity was obtained using a correction factor. A suitable straight channel of 250 x 60 cm length to width was chosen to reach with minimum turbulence then the object was dropped from one point to the end point and the time was recorded for determination of flow. All measurements were done between 10.00 am and 12.00 noon on daily basis for 14 days.

Analytical Methods

Water samples were analyzed for NO_3-N, NH_3-N, Organic-N, Algal-N and Soil-N at the Ardhi University Environmental and Water Quality Laboratory using standard methods (AWWA, 1992). Both NO_3-N and NH_3-N were respectively analyzed using Spectrophotometer with Cadmium Reduction and Turbid metric methods. Nitra Ver 5 and Nessler reagents were used for NO_3-N and NH_3-N analysis respectively. Total Kjeldahl Nitrogen (TKN) was used for the determination of Organic Nitrogen. Algal nitrogen (Algal-N) and nitrogen in sediments (N Sediments) were determined by using Semi-micro-Kjeldahl method at the College of Engineering and Technology, University of Dar es Salaam in accordance with Standard Methods (AWWA, 1992).

MODEL DEVELOPMENT

The Conceptual model

The conceptual model for Nitrogen transformation and removal in a MWSP system has been formulated based on the principle of conservation of mass (Figure 3). State variables incorporated include Organic-N, NH_3-N NO_3-N, and N-Soil. The transformation processes included in the model include mineralization, nitrification, denitrification, sedimentation, uptake of inorganic nitrogen (ammonia and nitrates) by algae, and ammonia volatilization. Major assumption for the analysis of transformation processes was first order kinetics in a completely mixed flow system. STELLA® 8_1 programme was used to simulate the processes influencing the transformation and removal of nitrogen in the MWSP system.

Mathematical description of mass fluxes

The transient behaviors of mass fluxes that define nitrogen transformation and removal in a MWSP system are presented in equations 1 through 20. The model comprises of four state variables namely organic nitrogen (Org-N), Ammonia (NH_3-N), Nitrate (NO_3-N) and Nitrogen in soil(Soil-N) are shown based on the conceptual diagram (Figure 3) and the differential equations for each state variable as indicated in the nitrogen cycle in WSP system as described in equations 1 through 18.
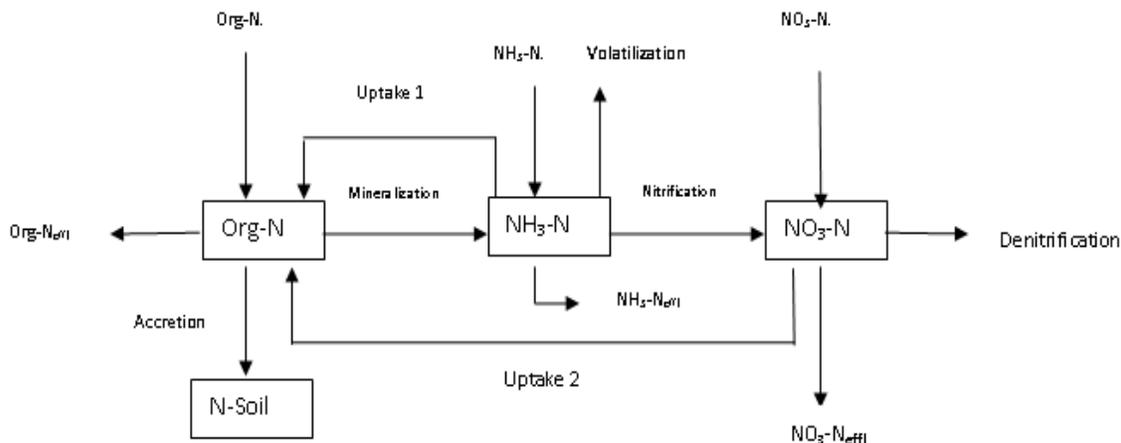
Figure 3: Nitrogen transformation processes in a MWSP

Organic nitrogen (Org-N)

The amount of organic nitrogen in the Maturation waste stabilization can be determined by mathematical differential equations as shown in equation 1:

$$\frac{d[Org-N]}{dt} = \frac{Q_i}{V}(Org-N) - \frac{Q_{out}}{V}(Org-N) + (gw_1 + gw_2) - r_m - r_a + r_{dc} \dots\dots\dots\dots\dots\dots(1)$$

Whereby: Q = Flow rate (m^3d^{-1}), V = Volume of the Pond (m^3), r_{dc} = Rate of decaying of organic matter ($mgl^{-1}d^{-1}$), r_a = Accretion rate of organic nitrogen in soil ($mgl^{-1}d^{-1}$), r_m = Mineralization rate ($mgl^{-1}d^{-1}$), rdc=rate of decay of organic matter ($mgl^{-1}d^{-1}$), gw_1 = Ammonia uptake by microorganism for growth ($mgl^{-1}d^{-1}$), gw_2 = Nitrate uptake by microorganism for growth ($mgl^{-1}d^{-1}$).

Decay rate
Decay process is assumed to obey first order kinetics as shown in equation 2:

$$r_{dc} = D_{rate} \ (N\text{-}Plant) \ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots..(2)$$

Whereby: D_{rate} =   Decay rate of organic nitrogen (d^{-1}).

Mineralization rate
Mineralization of organic nitrogen is the biological transformation of organically bound nitrogen to ammonia through degradation [16]. Mineralization process is also assumed to obey first order kinetics as indicated in equation 3.

$$r_m = A_m(Org - N)\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(3)$$

Whereby: A_m =   anaerobic mineralization rate per day (d^{-1})

Accretion rate
The accretion of organic nitrogen of the sediments depends on the concentration of organic nitrogen in accordance with equation 4.

$$r_a = AC_R(Org - N)\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(4)$$

Whereby: AC_R =Coefficient of accretion (d^{-1}).

Ammonia and Nitrate uptake rates are described in equations 5 and 6.

Ammonia uptake by microorganism for growth

$$gw_1 = \mu_{max(20)}\theta^{T-20}\left(\frac{NH_3 - N}{K_3 + NH_3 - N}\right)(Org - N).P_1\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(5)$$

Whereby: $\mu_{max(20)}$ = Maximum growth rate of bacteria at 20^oC, P_1=Ammonia uptake preference factor, K_3=Ammonia uptake half saturation constant mgl^{-1}, θ =Microorganism growth temperature coefficient [-].

Nitrate uptake by microorganism for growth

$$gw_2 = \mu_{max(20)}\theta^{T-20}\left(\frac{NO_3 - N}{K_4 + NO_3 - N}\right)(Org - N).P_2\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(6)$$

Whereby: P_2-Nitrate uptake preference factor, K_4-Nitrate uptake half saturation constant mgl^{-1}
Ammonia nitrogen (NH_3-N)
The amount of ammonia nitrogen in the Maturation waste stabilization pond was determined by mathematical differential equations as shown in equation 7:

$$\frac{d[NH_3 - N]}{dt} = \frac{Q_i}{V}(NH_3 - N) - \frac{Q_i}{V}(Org - N) + r_m + r - gw_1 - v - n - p_1\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(7)$$

Whereby: n= Nitrification rate of ammonia ($mgl^{-1}d^{-1}$), r= Regeneration rate of NH_3-N from soil ($mgl^{-1}d^{-1}$), v= Volatilization rate ($mgl^{-1}d^{-1}$), p= Plant uptake rate ($mgl^{-1}d^{-1}$).

Regeneration rate

The decomposition of N-soil which is the liberation of NH₃-N from organic nitrogen accumulated in the soil, was also modeled using first order kinetics with respect to N-Soil in accordance with equation 8:

$$r = regRate(N - Soil)\text{..(8)}$$

Volatilization rate

The rate of ammonia volatilization depends on the concentration of ammonia gas in the liquid, temperature and depth pH of the water, NH₃-N in water exists as dissolved ammonia gas or ammonium. The amount of volatilization may be described by equation 9:

$$v = \frac{0.0566}{d} e^{(0.13(T-20))} \left(\frac{NH_3 - N}{10^{(10.05 - 0.032T - pH)}} \right) \text{...(9)}$$

Nitrification rate

The rate of nitrification (n) which is governed by the growth of chemoautotrophic nitrifying bacteria, depends on the pH, Temperature and concentration of ammonia and dissolved oxygen as indicated in equation 10:

$$n = \frac{\mu_n}{Y_n} \left(\frac{NH_4 - N}{K_N + NH_4 - N} \right) \left(\frac{DO}{KDO + DO} \right) \times C_T \times C_{pH} \text{...(10)}$$

Whereby: C_{pH} = Nitrosomonas growth limiting factor for pH, K_N = Half rate saturation constant for Nitrosomonas (Nielsen et al., 1999) as shown in equation 11:

$$K_N = 10^{0.051(T-1.58)} \text{..(11)}$$

Y_n= Yield coefficient, of nitrosomonas, μ_N= Maximum Nitrosomonas growth rate, C_T=Temperature correction factor.

Downing (1966) reports that for pH ≥7.2, no significant inhibition, therefore C_{pH} = 1; when pH falls below 7.2, the existence of free ammonia inhibits growth of nitrifying bacteria. Accordingly, nitrification rate is corrected by introducing C_{pH} in accordance with equation 12.

$$C_{pH} = 1 - 0.833(7.2 - pH)\text{..(12)}$$

Nitrification rate is also temperature-dependent. An exponential function shown in equation 13 describes the temperature correction factor.

$$C_T = e^{\alpha(T-T_o)} \text{...(13)} \quad \text{Whereby:}$$

T_o = reference temperature and α is empirical constant

Nitrate nitrogen (NO₃-N)

The amount of Nitrate nitrogen in the maturation waste stabilization pond is modeled using a differential mass balance equation 14:

$$\frac{d[NO_3 - N]}{dt} = \frac{Q_i}{A}(NO_3 - N)_i - \frac{Q_i}{A}(NO_3 - N)_e + f + n - gw_2 - P_2 - dn\text{..........................(14)}$$

Whereby: dn = Denitrification rate (mgl⁻¹d⁻¹), n= Nitrification rate (mgl⁻¹d⁻¹), f = Fixation rate (mgl⁻¹d⁻¹), p₂ = Plant uptake rate from nitrate (mgl⁻¹d⁻¹), gw₂=Nitrate uptake by microorganism for growth (mgl⁻¹d⁻¹).

Denitrification rate

Denitrification has been modeled using first order Arrhenius kinetic in accordance with equation 15:

$$d_n = DC_{20}\theta^{(T-20)}NO_3 - N\text{..(15)}$$

The Arrhenius temperature coefficient θ varies from 1.02 to 1.09
DC_{20} = Denitrification constant at $20°C$

Nitrate uptake by plant (p₂)

NO_3-N is converted to biomass (Vegetative uptake) in accordance to the following relationship equation 16:

$$p_2 = N_{demand}\left(\frac{NO_3 - N}{Kh + NO_3 - N}\right)\left(\frac{NO_3 - N}{NH_3 - N + NO_3 - N}\right) \dots\dots(16)$$

Ammonia uptake by plant (p₁)
NH_3-N is converted to biomass (Vegetative uptake) in accordance to the following relationship equation 17:

$$p_1 = N_{demand}\left(\frac{NH_3 - N}{Kh + NH_3 - N}\right)\left(\frac{NH_3 - N}{NH_3 - N + NO_3 - N}\right) \dots\dots(17)$$

Nitrogen in soil (Soil-N)
The amount of change of Nitrate in plant in the MWSP can be determined by differential equation 18:

$$\frac{d[N - soil]}{dt} = a - r \dots\dots(18)$$ Whereby:

a=Accretion rate of organic nitrogen in soil ($mgl^{-1}d^{-1}$), r= Regeneration rate of NH_3-N from soil ($mgl^{-1}d^{-1}$).

RESULTS AND DISCUSSION
Flow rate measurements
Flow rate measurements for wastewater through the MWSP system were recorded for 14 days. Results are shown in Figure 4. It can be seen that the flow rate has been fluctuating but within (836.67±9.94) m^3/d. As expected, the fluctuations are based on variations of water use in the industrial processes upstream.
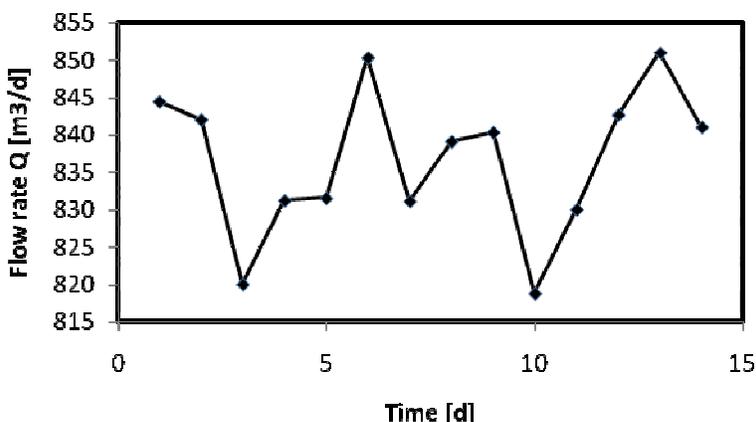
Figure 4: Water Flow trend in a MWSP system

Temperature, Dissolved Oxygen and pH
Average values for temperature, Dissolved Oxygen and pH are summarized in Table 1. For all parameters, average values between influent and effluent are nearly the same, which indicate very minor changes within the system which is assumed to be completely mixed. In general, pH was found to be in a slightly alkaline range, largely due to minimum decomposition processes in the pond system, as reported by Singo, supported by the low levels of DO, which indicate absence of photosynthesis processes in the MSWP system.

High pH also indicates the presence of nitrification process as reported by Painter [17] as the system is generally devoid of DO. Under this pH range, ammonia volatilization can also be active as reported by Reddy and Patrick [18]. Senzia [19] reports that increase of pH is also associated with depletion of CO_2 due to light intensity changes which in turn affect photosynthetic activities in the pond.

Table 1: Average values of temperature, DO and pH at Influent and Effluent of MWSP

Parameter	Sampling Points	
	Influent (S_1)	Effluent (S_2)
Temperature (°C)	30.05±0.52	30.28±0.44
Dissolved Oxygen	0.70±0.24	0.78±0.22
pH	8.71±0.69	8.56±0.46

n=10

Nitrogen Compounds

Table 2 shows average levels of nitrogen compounds in the MWSP system, at the two sampling points. There is a decrease in ammonia concentration between influent and effluent associated with slight increase of nitrate levels. Analysis of Organic Nitrogen in the MWSP system reveals remarkable consistent transient decrease from day 1 to day 10. Mineralization could explain the reason for this continual decrease.

Table 2: Average values of Nitrogen Compounds at Influent and Effluent of MWSP

Parameter	Sampling Points	
	Influent (S_1)	Effluent (S_2)
NH_3-N [mg/l]	27.76±6.10	10.40±3.37
NO_3-N[mg/l]	8.97±1.57	10.27±1.41
N-Algae[mg/l]	ND	193.07±107.25
N-Soil[mg/l]	ND	5.36±1.36

Model Simulation Results

The model simulation showed a decrease of NH_3-N concentration with time at the effluent end of the MWSP as shown in Figure 5. Conversely, as explained earlier, these results are in agreement with the observed results in the sense that nitrification is active in the system. There is also a general increase of NO_3-N in the system, which also in agreement the measured results (Figure 6).

The model simulation indicates a general increase of N-Soil with time, suggesting that the accretion process is the transporting organic nitrogen to the soil/sediment (Figure 7). Figure 8 shows that N-Algae kept decreasing with time, supposedly due to mineralization and accretion to the soil/sediment matrix. Algae growth contributed to the pool of organic nitrogen in the system.
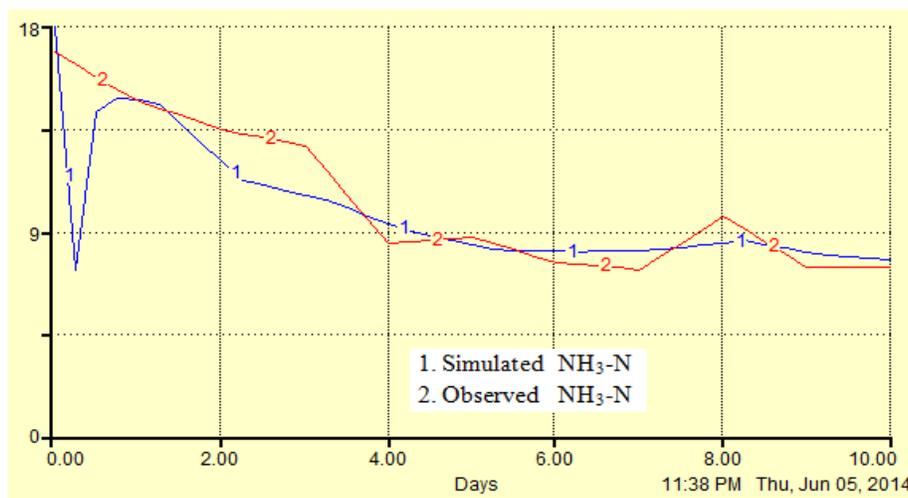
Figure 5: Ammonia Nitrogen in a MWSP system
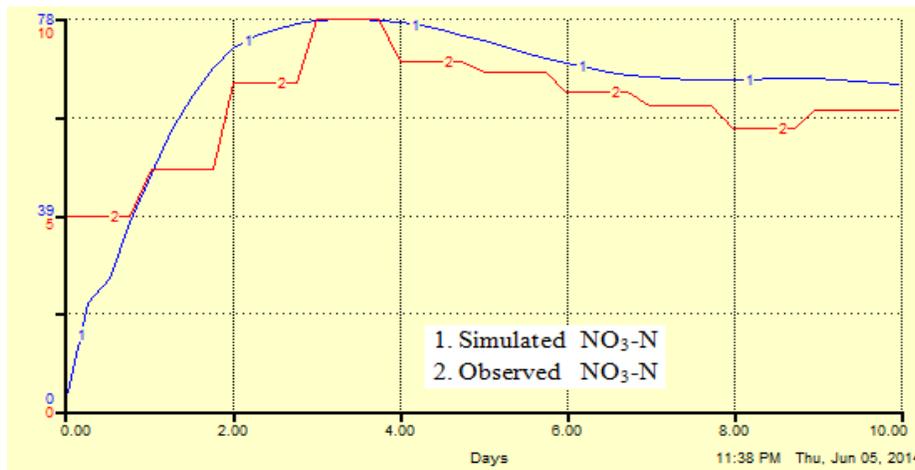
Figure 6: Nitrate Nitrogen in a MWSP System
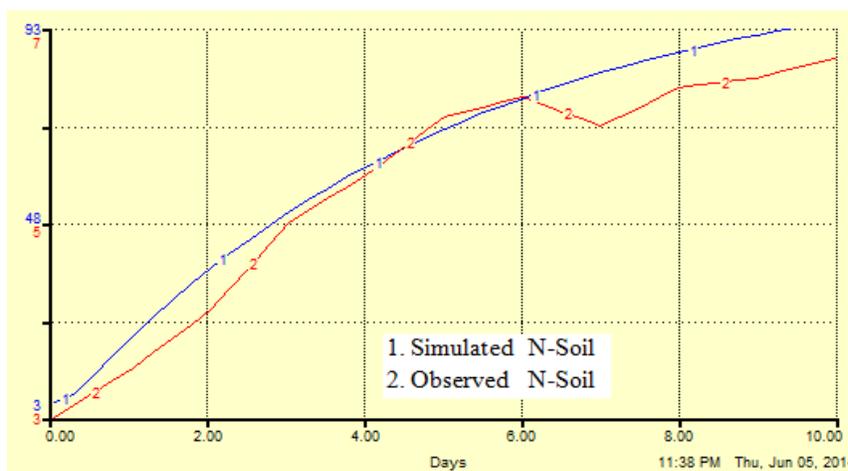
Figure 7: Soil nitrogen in soil
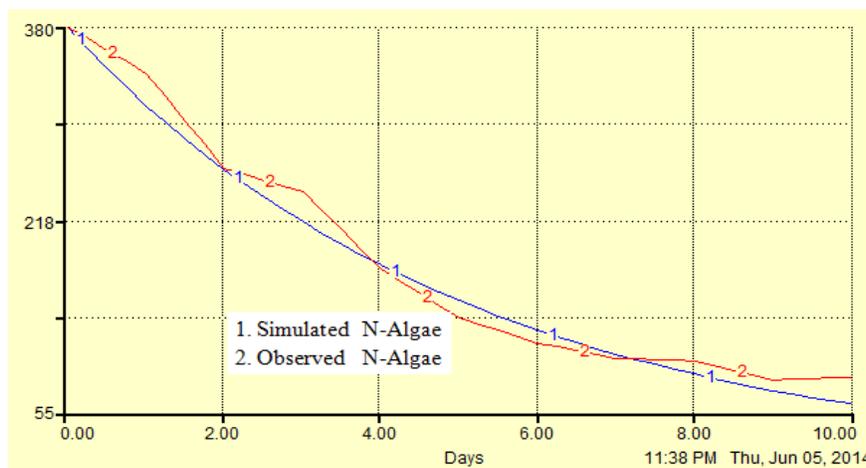
Figure 8: Organic nitrogen in plant biomass

Mass Balance Analysis

The mass balance of the model shows, nitrification contribute 36.9% of nitrogen transformation in Maturation Waste stabilization pond, followed by plant uptake about 31.6%, mineralization which contribute about 21.05%, accretion with 9.3% transformation. The largest pool of nitrogen is stored in the form of Organic Nitrogen in the water phase of the pond, followed by loss to the soil/sediment.

The model simulation results indicate a good agreement between observed and simulated nitrogen species in the maturation ponds. Model verification showed the model behaves as expected with good linear regression coefficient (R^2) is 0.749 for nitrate, 0.709 for Ammonia, 0.985 for nitrogen in algae, 0.973 for nitrogen in soil or sediment. Despite the fact that this study used data collected under field conditions where various factors are difficult to control, the model was able to simulate the dynamics of nitrogen transformation in a MWSP system. This is a clear indication that the various process and formulation developed in model were valid to be applied in similar systems.

Model parameters Input to the Model

The data presented in Table 3 Shows different parameters used in model calibration

Table 3: Model Parameters

Parameters	Description	Range	Value	Source
Ar	Accretion coefficient	0.93-2.93	0.93	This study
Max growth20	Maximum growth rate of algae and bacteria at 20°C	0.62-2.62	2.62	This study
DC_{20}	Denitrification constant at 20°C (d^{-1})	0-2.1	0.1	Bacca and Arnett,1976
D_{rate}	Decaying constant (d^{-1})	0.189-2.189	0.189	This study
Mr	Mineralization rate constant of organic (d^{-1})	0.095-2.095	2.095	This study
Un	Maximum nitrosomonas growth rate (d^{-1})	0.130-2.13	1.3	Charley et al.,(1980)
Yn	Nitrosomonas yield coefficient	0.03-1.3	0.13	Charley et al.,(1980)
Kh	Nitrogen half saturation constant (mg/l)	0.1	0.1	Senzia,(2003)
KNO_2	The oxygen nitrosomonas half saturation (mg/l)	1.3	1.3	Dodwning,(1966)
θ	Sita	1.02-1.09	1.02	Bacca and Arnett,1976
Rer	Regeneration rate (d^{-1})	0.0150-20.15	0.015	This study
alfa	Alfa	0.098-2.098	1.058	This study
Ndemand		0.015-2.015	0.015	This study

CONCLUSIONS

Based on model simulation and mass balance analysis, it can be concluded that nitrification contribute 36.9% (38 mg/l.d) of nitrogen transformation, followed by uptake by algae at about 31.6% (32.55 mg/l.d). The results also showed that storage of organic nitrogen in the system water phase is 13.98 mg/d and deposition in the soil is 8.69 mg/d. Plant uptake by algae was low, probably caused by inhibition of photosynthetic activities in the system.

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