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Title	Process-based modelling of phosphorus removal in a novel constructed wetland system using dewatered alum-sludge as substrate
Authors(s)	Kumar, J.L.G., Zhao, Y.Q., Babatunde, A.O.
Publication date	2011
Publication information	Kumar, J.L.G., Y.Q. Zhao, and A.O. Babatunde. "Process-Based Modelling of Phosphorus Removal in a Novel Constructed Wetland System Using Dewatered Alum-Sludge as Substrate" 64, no. 3 (2011).
Publisher	IWA Publishing
Item record/more information	http://hdl.handle.net/10197/4019
Publisher's statement	©IWA Publishing 2011. The definitive peer-reviewed and edited version of this article is published in Water Science & Technology Vol 64 No 3 pp 774–780 [DOI doi:10.2166/wst.2011.711] and is available at http://www.iwaponline.com/wst/06403/wst064030774.htm .
Publisher's version (DOI)	10.2166/wst.2011.711

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Process-based modelling of phosphorus removal in a novel constructed wetland system using dewatered alum-sludge as substrate

J.L.G. Kumar, Y.Q. Zhao* and A.O. Babatunde

*Centre for Water Resources Research, School of Architecture, Landscape and Civil Engineering,
University College Dublin, Newstead, Belfield, Dublin 4, Ireland*

**Corresponding author: Tel: +353 1 7163215; Fax: +353 1 7163297; e-mail: yaqian.zhao@ucd.ie*

ABSTRACT

A process-based model that can evaluate the transport and the fate of phosphorus (P) in agricultural wastewater was developed for a novel 4-stage dewatered alum sludge cakes (DASC) based constructed wetlands (CWs) system using STELLA software (version 9.1.4). The model considered adsorption, plant and microbial uptakes as the major forms of P involved in the transformation chains. The results were obtained by experimental procedure through laboratory measurement, from literature and/or calibration. The observed effluent P concentration in the CWs ranged from 3.62 to 8.50 mg/L (stage 1), 2.00 to 4.45 mg/L (stage 2), 1.39 to 3.76 mg/L (stage 3) and 0.52 to 2.36 mg/L (stage 4) whereas the simulated values ranged from 2.12 to 10.99 mg/L (stage 1), 1.32 to 5.65mg/L (stage 2), 0.84 to 3.64 mg/L (stage 3) and 0.53 to 2.25mg/L (stage 4), respectively. The simulated and observed values of P removal in CWs system were in good agreement. A mass balance analysis was performed for all the major processes which resulted in a major pathway of P removal through adsorption (64-75%, 58-66%, 57-63% and 49-58%) followed by plant uptake (7-11%, 8-14%, 14-17% and 9-19%) and microbial uptake (3-7%, 3-5%, 9-12% and 7-12%) for stage 1, stage 2, stage 3 and stage 4, respectively. Thus the mathematical model developed in this study could be used to explain the removal processes and simulate the fate of P in the DASC-based CWs system.

Key words: Alum sludge, phosphorus removal, constructed wetlands, STELLA, modelling

INTRODUCTION

Constructed wetlands (CWs) can be effectively used to treat a wide variety of wastewaters (Kadlec & Wallace 2009). However, removal efficiency of phosphorus (P) in many types of CWs is relatively low unless special substrates with high P-immobilization capacity are used

(Vymazal 2007). Accordingly, a CWs system employing dewatered alum sludge cakes (DASC) as main substrate to enhance P removal has been developed (Zhao *et al.* 2009; 2010). DASC is a by-product generated in drinking water treatment processes (using aluminium sulphate as a coagulant). It has been demonstrated that DASC can be used as a P adsorbent (due to the strong chemical affinity of Al and P) and a carrier for biofilm development in CWs (Babatunde *et al.* 2009). More significantly, the use of DASC in CWs will transform the DASC from a 'waste' into useful material.

Although previous studies to improve P removal in the DASC-based CWs had been successful in authors' group, it is acknowledged that design of the system is challenging due to the complexity of the treatment processes involved. Kadlec & Knight (1996) introduced simple black-box type models for estimating treatment efficiencies of CWs without any consideration of the process involved. However, detailed understanding of CWs functioning is desirable because physical, chemical and biological processes occur in parallel and influence each other in CWs. In recent years, applications of dynamic compartmental models in CWs have shown promising results to help the understanding of the treatment processes (Brasil *et al.* 2007; Langergraber 2008; Pimpan & Jindal 2009; Giraldo *et al.* 2010). Among the dynamic compartmental models, STELLA (structural thinking experiential learning laboratory with animation) is becoming a popular tool in CWs since it allows for a process-based analysis to understand the treatment behaviour (Kumar & Zhao 2011).

In a previous study Kumar *et al.* (2011) developed a mathematical model using STELLA to simulate the P effluent concentration and the fate of P in a single-stage DASC-based CWs. In this study, a P simulation model for a 4-stage DASC-based laboratory scale CWs system treating high strength agricultural wastewater was established using STELLA. Furthermore, the fate of P was studied in each of the individual stages of the CWs system based on the simulation and the mass balance analysis using STELLA.

METHODOLOGY

Experimental study

The laboratory scale CWs consists of 4 interlinked stages (Figure 1) using Pyrex columns with an internal diameter of 95mm and a height of 900mm. DASC, collected freshly from a local water treatment plant, was air-dried and ground and sieved to have a d_{10} and d_{60} of 0.5 mm and 1.8 mm, respectively. The DASC was then filled into the CWs up to a depth of 500mm with a support base of 100mm-depth of gravel (with size of 6-10mm). The DASC contains Al (170 mg/g (dry mass)), TOC (173 mg-C/g) and minor Ca, Fe, Mg, Si and P etc. and its characteristics were examined in detail (Zhao and Yang; 2010). Young reeds *Phragmites australis* were planted on top of each stage. The CWs was operated using the tidal flow strategy which was carried out in cycles with a hydraulic loading rate (HLR) of $1.27\text{m}^3/\text{m}^2\cdot\text{d}$. More details about the experimental set-up and performance analysis have been described in Babatunde *et al.* (2010).

Figure 1 Schematic view of the laboratory scale 4-stage DASC-based CWs system

Description of the model

STELLA is a modelling tool for building a dynamic modelling system by creating a pictorial diagram of a system and then assigning the appropriate values and mathematical functions to the system (ISEE Systems 2006). The 4-stage CWs system for P removal was modelled using a series of differential equations. These equations were implemented and solved using the STELLA graphical systems modelling package. The essential features of the modelling system are defined in terms of stocks, flows, converters and connectors. As a graphical programming language, it allows a modeller using the program's special tools and functions to build dynamic models (Pimpan & Jindal 2009). 4th order Runge-Kutta method was chosen to create an estimate for the change in stock over the delta time (DT).

Model formulation

Figure 2 shows a conceptual model for the fate of P in the CWs system pertaining to this study. The major mechanisms for P dynamics in the CWs system studied are adsorption via wetland substrate (i.e. DASC), plant uptake and microbial uptake. The state variables include dissolved P (DISP), plant P (PLAP), detritus P (DETP), plant biomass (PLBI) and adsorbed P (ADSP). The processes (as shown in Figure 2) are: uptake of P by *Phragmites australis* (1); growth of *Phragmites australis* biomass (2); adsorption of P in DASC (3); microbial uptake/consumption (4); mineralization (5); inputs/outputs (6,7); solar radiation (8); mortalities (9,10) and settling of detritus (11). In addition, adsorbent (DASC), tidal flow, temperature, P concentration and radiation are considered as a forcing function in the model. The process-equations and their descriptions are shown in Table 1. The final values obtained by experimental procedure, laboratory measurement, literature and/or calibration are shown in Table 2.

Figure 2 Conceptual model for the P removal in DASC-based CWs

Adsorption process was described by the equilibrium between P in water and P in adsorbent. P adsorbed-equilibrium has been previously studied and the expression is listed in Table 1. Plant growth (*Phragmites australis*) was described as a function of maximum growth rate at the optimum temperature and radiation. The plant growth is also dependent on the amount of P in the plant and therefore $(P_P - P_{min}) / (P_{max} - P_{min})$ is adopted (see Table 1). It can be seen from Table 1 that the plant growth is a first-order reaction of PLBI with a parameter (coefficient) G_m . Furthermore the growth is also expressed by Michaelis-Menton equation of radiation. Overall, the growth equation is taking into account the amount of plant PLBI, the radiation (Michaelis-Menton equation) and the P in plants. Plant uptake (*Phragmites australis*) is described as a function of maximum uptake rate at the optimum temperature. For plant uptake the need of P can be explained as proportional to $(P_{max} - P_p) / (P_{max} - P_{min})$. Again, the PLBI is expressed in first-order reaction and the uptake is described by Michaelis-Menton equation of dissolved P. Microbial uptake is considered as a temperature dependent by an Arrhenius function. Michaelis-Menton equation of dissolved P was used to describe the process of microbial activities. The mortality of plant mortality of biomass and the detritus are all expressed in first-order reaction with Arrhenius function of temperature.

Table 1 P-processes, mathematical equations and its descriptions for the novel 4-stage DASC-based CWs system

Processes	Equations	Description	References
Adsorption (Ad)	$Ad = F_a (DISP - P_e \times V); P_e = \left(\frac{ADSP}{T_A \times K_F} \right)^n$	F_a : Ad parameter; DISP: Dissolved P; P_e : P equilibrium concentration; V: volume of wastewater; ADSP: adsorbed P; T_A : total amount of adsorbent (g), K_F : Freundlich constant (L/g); n : heterogeneity factor.	Zhao <i>et al.</i> (2007)
Growth (Gr)	$Gr = \frac{G_m \times PLBI \times R_a \times (P_p - P_{min}) \times 1.05^{(T-20)}}{(R_a + K_r) \times (P_{max} - P_{min})}$	G_m : Maximum P growth rate of plants; PLBI: Plant biomass; R_a : Radiation/Light required for plant growth; P_p : P in plants; P_{min} : Minimum P in plants; T : temperature; K_r : Plant growth rate (Michaelis-Menton half saturation constant for growth); P_{max} : Maximum P in plants.	Kumar <i>et al.</i> (2011)
Uptake (Up)	$Up = \frac{U_{max} \times PLBI \times (P_{max} - P_p) \times DISP \times 1.05^{(T-20)}}{(DISP + K_u) \times (P_{max} - P_{min})}$	U_{max} : Maximum uptake rate of plants; K_u : Uptake rate of P (Michaelis-Menton half saturation constant for uptake)	Kumar <i>et al.</i> (2011)
Microbes (Mi)	$Mi = \frac{B_g \times DISP \times 1.05^{(T-20)}}{DISP + K_b}$	B_g : Bacterial growth; K_b : Bacterial growth rate (Michaelis-Menton half saturation constant for microbial growth)	Kumar <i>et al.</i> (2011)
Plant Mortality (Mp)	$Mp = PLAP \times M_r \times 1.07^{(T-20)}$	PLAP: Plant P; M_r : Mortality rate	Zhang <i>et al.</i> (2003)
Biomass Mortality (Mb)	$Mb = PLBI \times M_r \times 1.07^{(T-20)}$		Jørgensen (1998)
Detritus (De)	$De = DETP \times M_{max} \times 1.07^{(T-20)}$	DETP: Detritus P; M_{max} : Maximum P mineralization	Jørgensen <i>et al.</i> (1997)
Adsorption Efficiency (Ae)	$Ae = \left(\frac{Ad}{Ip} \right) \times 100$	Ip : total amount of P coming into the system	Calculation
Uptake Efficiency (Ue)	$Ue = \left(\frac{Up}{Ip} \right) \times 100$		Calculation
Microbial Efficiency (Me)	$Me = \left(\frac{Mi}{Ip} \right) \times 100$		Calculation

Table 2 State variables, forcing functions and parameters for the novel 4-stage DASC-based CWs system

Symbol	Values/Units	Literature range	Source
State Variables			
DISP	mg		
PLAP	mg		
DETP	mg		
ADSP	mg		
PLBI	mg		
Forcing functions			
Adsorbent (DASC)	mg/g P		
Flow (tidal-operation)	m ³ /d		
Solar radiation	Joules/m ² .d		
Temperature	°C		
Inflow P	mg/d		
Volume of wastewater	L/d		
Contact time of wastewater	h		
Resting time of the system	h		
Parameters and Coefficients			
P_{max}	0.08 g/100g		Estimated
P_{min}	0.008 g/100g		Estimated
U_{max}	0.08/d	0.003-0.01	Jørgensen (1998)
K_r	0.07 mg/L.d	0.001-0.005	Calibration
B_g	0.6 /d	-	Calibration
K_b	0.76 mg/L.d	-	Calibration
M_{max}	0.3/d		Jørgensen (1998)
M_r	0.003 mg P/d	-	Calibration
G_m	0.9 mg P/d	0.1-0.6	Calibration
K_u	0.009 mg/L.d	0.001-0.005	Calibration
F_a	85		Estimated
H_r	1.27m ³ /m ²		Experiment
V_w	6.9 L		Experiment
K_F	0.53 L/g		Experiment
n	1.24		Experiment
T_A	2600g		Experiment

RESULTS AND DISCUSSION

P simulation in CWs system

Prior to the P modelling in this 4-stage DASC-based CWs, it has been demonstrated that the DASC-based CWs is capable of enhanced P and organic matters removal, particularly from

medium and high strength wastewater. The results obtained in this 4-stage DSAC-based CWs system suggested that high removal efficiency for soluble reactive phosphorus of 89% can be achieved (Babatunde *et al.* 2010). Distinctively, the system showed a superior P removal performance due to the strong chemical affinity of Al and P when compared to other systems in literature. Sun *et al.* (1999) and Cerezo *et al.* (2001) reported respectively 55% and 60% P removal efficiency while using multi-stage gravel-based CWs system. Effort has been made in this study for the insight of pollutant dynamics to study the fate of P processes and the simulation of effluent P concentration. The model was run with STELLA 9.1.4 software using a time step of 0.02 hours for 3 months.

Since there is no notably parameter values available from the literature for the DASC-based CWs, authors calibrated the parameter values for growth, uptake, microbial, biomass and mortality equations from the similar studies of CWs. Calibration of dynamic model for the 4-stage CWs system has been carried out in a usual way of “trial and error” method, it means that the set of parameters which give the best fit between observed and simulated results. Calibration of the model was performed with the previous single-stage CWs data (Kumar *et al.* 2011). The observed effluent P concentration ranged from 3.62 to 8.50 mg/L, 2.0 to 4.45 mg/L, 1.39 to 3.76 mg/L and 0.52 to 2.36 mg/L for stage 1 to stage 4 of the CWs system, respectively, whereas the simulated values ranged from 2.12 to 10.99 mg/L, 1.32 to 5.65mg/L, 0.84 to 3.64 mg/L and 0.53 to 2.25 mg/L for stage1 to stage 4, respectively (Figure 3). It can be observed that there is a trivial deviation of simulation in all the stages of the CWs system. But on the other hand, the mean concentration values of P for observed and simulated were found very close and therefore the overall simulation is acceptable. It is worth noting that the deviation caused in the simulation probably over simplification of pant and microbial uptake processes in the model. It is interesting to note that the P removal was more or less constant in the system which leads to simulate the complex behaviour quite successfully. It is because of the fact that DASC-based CWs can significantly adsorb P from aqueous solution through complexation and ligand exchange mechanism (Babatunde *et al.* 2009).

Fate of P

The major P processes and P removal in each stage of the system are shown in Table 3. The results were obtained by running the STELLA software to simulate the P transformation processes in accordance with mass balance basis. The key P removal mechanisms identified in descending order are adsorption, plant uptake and microbial uptake. In this study, approximately the maximum influent, 577 ± 78 mg P/d (mass), was pumped into the system (stage 1). It has been observed that the mass of P flowing through the system as influent was approximately 103 ± 27 mg P/d, 21 ± 12 mg P/d and 4.5 ± 2 mg P/d for stage 2, 3 and 4, respectively. Subsequently, the processes such as adsorption, plant uptake and microbial uptake efficiencies were calculated via mass balance for each individual stage (Table 1)

Figure 3 Comparison of observed (OBS) and simulated (SIM) P removal using DASC-based CWs: (a) stage 1, (b) stage 2, (c) stage 3 and (d) stage 4

Table 3 Mass balance analysis of P processes in all stages of DASC-CWs

CW Stages	P Adsorption (%)	Plant uptake (%)	Microbial uptake (%)
1	64-75	7-11	3-7
2	58-66	8-14	3-5
3	57-63	14-17	9-12
4	49-58	9-19	7-12

A comprehensive explanation of P adsorption is given in the single stage P model (Kumar *et al.* 2011). In all the 4-stage CWs system the P adsorption efficiency was quite dominant as compared to other processes because DASC has considerable P adsorption capacity (Zhao and Yang 2010). Through this study STELLA simulation provides a better understanding of P removal through adsorption in DASC-based CWs although other researchers, such as Ouyang *et al.* (2010) and Pimpan & Jindal (2009) used STELLA simulation for adsorption studies for atrazine and cadmium. Plant uptake efficiency (Table 3) shows that the first two stages have relatively similar removal efficiencies through plant whereas the last two stages were slightly higher based on the simulation. As compared to adsorption removal efficiency, the plant removal efficiency was significantly lesser amount. It may be due to the reason that P is probably limiting for the growth of plants.

In this model, growth of plant was explicated as a two-step process: First process is the uptake of nutrients by plant, this process is determined mainly by the intracellular concentration. Second process is the growth of plant, which is determined partially by the intracellular concentration. As far as the removal of P through plants is concerned it is crucial to describe the growth of the plants independently from P and in accordance to temperature and radiation. Therefore a growth equation was formed which is dependent on radiation and temperature. The growth of plant biomass was described by first-order reaction along with the influence of temperature with simple Arrhenius expression. The influence of light is explained by Michaelis Menton expression. While transferring biomass in STELLA program, it transfers the entire biomass, rather than P itself. Since STELLA is based on mass conservations it is necessary to say “book-Keeping” of P and biomass independently because the uptake parameter is taken from the growth rate, but the equation considers the maximum P, minimum P and P in water. Thus P in plant is the ratio of PLAP and PLBI. The detail explanation of growth and uptake equation is shown in Table 1.

Michaelis-Menton equation of dissolved P was used to describe the process of microbial activities. Detritus P has been explained as a first-order reaction along with the Arrhenius function. Simulation results in Table 3 show reasonable amount of P removal through microbes

in DASC-based CWs. The DASC thus acts as a carrier for biofilm development and also provides a surface for biofilm attachment which served to enhance microbial activity (Babatunde et al. 2009; Zhao *et al.* 2009). Only few studies have been undertaken on biological P removal using CWs system. It is recommended to have further research to study the dynamics of microbes especially in the DASC-based CWs.

CONCLUSIONS

The mathematical model (based on STELLA) proposed in this study is able to simulate P transformations in a 4-stage DASC-based CWs system with a reasonable accuracy. From the model outputs, the following conclusions can be made: (1) The simulated effluent P concentration in all the 4-stages had a considerably good agreement with the observed results; (2) The major P transformation pathways are adsorption, plant uptake and microbial uptake. (3) The fate of P in all the four stages clearly shows that adsorption played a pivotal role in each stage of the system due to the use of the alum-sludge as a substrate. P adsorption by wetland substrate/DASC represents 59-75% of total P reduction. Subsequently, plant uptake and microbial uptake have significantly less portions regarding P removal (as compared to adsorption). This 4-stage CWs system model can be accepted with the current calibration conditions. However further calibration will be incorporated when extensive data are collected via the operation of the DASC-based CWs system.

ACKNOWLEDGEMENT

Authors gratefully acknowledge financial support obtained from the Irish Department of Agriculture, Fisheries and Food under the Research Stimulus Fund Programme (grant no: RSF07-529).

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