| **Title** | STELLA software as a tool for modelling phosphorus removal in a constructed wetland employing dewatered alum sludge as main substrate |
|-----------|---------------------------------------------------------------------------------------------------------------------------|
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| **Publication Date** | 2011-06 |
| **Publication information** | Journal of Environmental Science and Health, Part A, 46 (7): 751-757 |
| **Publisher** | Taylor & Francis |
| **Link to publisher's version** | http://dx.doi.org/10.1080/10934529.2011.571600 |
| **This item's record/more information** | http://hdl.handle.net/10197/3105 |
| **Rights** | This is an electronic version of an article published in Journal of Environmental Science and Health, Part A, 46 (7): 751-757, available online at: http://dx.doi.org/10.1080/10934529.2011.571600. |
| **DOI** | http://dx.doi.org/10.1080/10934529.2011.571600 |
STEHLA software as a tool for modelling phosphorus removal in a constructed wetland employing dewatered alum sludge as main substrate

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ABSTRACT

A dynamic simulation model was developed for the removal of soluble reactive phosphorus (SRP) from the vertical flow constructed wetlands (VFCW) using a dynamic software program called STEHLA (structural thinking, experiential learning laboratory with animation) 9.1.3 to aid in simulating the environmental nature and succession of relationship between interdependent components and processes in the VFCW system. In particular, the VFCW employed dewatered alum sludge as its main substrate to enhance phosphorus (P) immobilization. Although computer modelling of P in treatment

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wetland has been well studied especially in recent years, there is still a need to develop simple and realistic models that can be used for investigating the dynamics of SRP in VFCWs. The state variables included in the model are dissolved phosphorus (DISP), plant phosphorus (PLAP), detritus phosphorus (DETP), plant biomass (PLBI) and adsorbed phosphorus (ADSP). The major P transformation processes considered in this study were adsorption, plant and microbial uptake and decomposition. The forcing functions which were considered in the model are temperature, radiation, volume of wastewater, P concentration, contact time, flow rate and the adsorbent (i.e. alum sludge). The model results revealed that up to 72% of the SRP can be removed through adsorption process whereas the uptake by plants is about 20% and the remaining processes such as microbial P utilization and decomposition, accounted for 7% SRP removal based on the mass balance calculations. The results obtained indicate that the model can be used to simulate outflow SRP concentration, and it can also be used to estimate the amount of P removed by individual processes in the VFCW using alum-sludge as a substrate.

**Keywords:** Constructed wetland, phosphorus, alum sludge, tidal flow, STELLA.

**INTRODUCTION**

Treatment wetlands are engineered systems designed to remove pollutants from contaminated water. Understanding of the removal mechanisms has expanded concurrently with increased adoption and usage of treatment wetlands. Varieties of removal mechanisms including sedimentation, filtration, precipitation, volatilization, adsorption and plant uptake are well documented. The primary soluble reactive
phosphorus (SRP) removal mechanisms in vertical flow constructed wetlands (VFCW) systems are substrate adsorption, microbial anabolism and plant uptake. However, substrate SRP adsorption represents the main removal pathway.\cite{3} Therefore to ensure efficient SRP removal, it is important to use substrates with high SRP removal capacity and suitable physiochemical properties. A low-cost material that can enhance SRP removal is aluminium salt-coagulated water treatment sludge (or alum sludge, as it generally called in the water treatment industry). It is the most widely generated water treatment residual worldwide and is mostly landfilled at huge costs since it is regarded as a waste with little known reuse value. However, the chemical composition of alum sludge gives it a highly reactive surface and a strong affinity for P.\cite{4, 5} On the other hand, an innovative approach of “tidal flow” operation regime has demonstrated the improved ability of constructed wetland (CW) system to enhance oxygen transfer and consequently enhance the biological process for the removal of pollutants including SRP from wastewater.\cite{6, 7}

P uptake by macrophytes in constructed wetland is usually highest during the beginning of growing season before maximum growth is attained.\cite{8, 9} An important response to season is the translocation of nutrients within the plant. Prior to autumn senescence, the majority of imported ions are translocated from shoot portions to the roots and rhizomes. These stored nutrients are used during early spring growth.\cite{10, 11} Microbiota uptake is very fast, but the magnitude (amount stored) is very low. The uptake by microbiota (bacteria, fungi, algae, microinvertebrates etc.) is rapid because these organisms grow and multiply at high rates.
Modelling P removal in CW is important with regards to understanding the P behaviour in the integrated treatment processes. In recent years, P removal has been described in detail in different ways in treatment system. Various approaches have been adopted, particularly on the potential use of wetlands for P removal from wastewater.\textsuperscript{[12]} An average phosphate removal of 26\% was reported for a hybrid constructed reed bed treatment system treating municipal wastewater and employing pea gravel as a media.\textsuperscript{[13]} A review of total P removal in various types of CWs was done by Vymazal.\textsuperscript{[14]} It is noted that the STELLA software has been widely used in biological, ecological and environmental sciences including its application in CW.\textsuperscript{[15-17]} As a so-called novel alum sludge-based constructed wetland system was developed in our research group,\textsuperscript{[18]} and understanding P removal in the system is desirable especially for modelling and prediction purposes. This forms the basis of the study.

The purpose of this study was to develop a model for the fate of P in a VFCW using the commercial available software package of STELLA. The key objectives were: (1) develop a dynamic model for predicting adsorption, plant and microbial uptake from the newly developed VFCW, which uses dewatered alum sludge as main substrate; (2) calibrate the model using the available experimental data; and (3) apply the model to predict the fate of P in the VFCW.

**MATERIALS AND METHODS**

*Set-up of alum sludge-based VFCW*

A laboratory scale novel VFCW system was set up and operated for a period of two years. The system used dewatered alum sludge cakes (DASC) as the main wetland medium. The DASC were collected from a local water treatment plant, which uses
aluminium sulphate as coagulant. Characteristics of the alum sludge and its suitability as a CW substrate has been well investigated from our previous study.\[^{19}\] *Phragmites australis* were planted at the top of DASC. Details of the VFCW system and its operation as well as the performance for two years have been well described in the previous publication.\[^{20}\]

**Description of the model**

The first step in the modelling processes was to develop a basic structure to capture the processes and procedures described using STELLA. After setting up the model in a flow diagram form, STELLA program converts the graphical representation to the basic equations.\[^{21,22}\] The developed model has five state variables as shown on the STELLA diagram (Fig. 1). These five state variables include dissolved phosphorus (DISP), plant phosphorus (PLAP), detritus phosphorus (DETP), plant biomass (PLBI) and adsorption (ADSP). The major P transformation processes considered in this study were adsorption, plant and microbial uptake. All are expressed in the unit of mg P/day in this study. Adsorbent (alum-sludge), contact time and tidal flow are the major forcing functions. Temperature, SRP concentration and radiation were also considered in the model. Detailed description of each mechanism responsible for removal and P dynamics are presented below. The state variables, processes, parameters and auxiliary variables used in the model are shown in Table 1. Readers could consult the STELLA users’ guide for details.\[^{23,24}\]

**Adsorption**
In water quality models, the selected time step is usually days or weeks.\textsuperscript{[25]} However, adsorption and ion exchange are fast processes, reaching equilibrium in minutes or hours. It has been observed from the current trial that the P adsorption in the alum sludge media is an extremely fast process and therefore the time step has been chosen at 0.02 Delta Time (DT). DT refers to the time interval between calculations in the STELLA software.

Adsorption process in the alum-sludge can be estimated using Equation 1.

\[
Ad = F_a (DISP - P_e \times V)
\]  

(1)

where, \(F_a\) is a factor, \(P_e\) is the equilibrium concentration (mg/L) while \(V\) is the volume of wastewater (L/day).

\(P_e\) can be calculated by using the followings:

\[
P_e = \left( \frac{ADSP}{T_A \times K_F} \right)^n
\]  

(2)

where, \(T_A\) is total amount of adsorbent (g), \(K_F\) is Freundlich constant (L/g), \(n\) is heterogeneity factor.

Freundlich adsorption model was used to describe the P adsorption behaviour. The \(K_F\) and \(n\), which is a measure of the deviation from linearity of the adsorption, were pre-determined by the batch tests. From the Freundlich adsorption isotherm experiment it has been found that the relationship between \(P_e\) and the mass of P adsorbed (alum-sludge) at equilibrium is strong \((R^2 = 0.93)\).\textsuperscript{[26]} The adsorption continues as long as the DISP is bigger than the \(P_e\). The driving force is DISP minus \(P_e\). Accordingly, the adsorption process was multiplied with a factor (in our alum-sludge based VFCWs the factor \((F_a)\) of 50 was used
based on experimental results) because the adsorption is fast and therefore the equilibrium is reached very quickly. It is expected that this factor will vary according to the type of substrates, pollutant concentrations, type of wetlands etc. Hence, careful attention should be given while selecting a factor for the adsorption process especially when calculating using STELLA software.

**Other process equations**

Most models in environmental sciences and ecology are ‘lumped models’ which imply that one parameter represents the average values of several species. As each species has its own characteristic parameter value, the variation in the species composition with time will inevitably give a corresponding variation in the average parameter used in the model.\(^{[24]}\) The following equations were used to describe the plant growth (Eq. 3), plant uptake (Eq. 4), microbial uptake (Eq. 5), mortality of plant (Eq. 6), mortality of biomass (Eq. 7) and decomposition (Eq. 8) for the alum sludge-based VFCWs. Process equations mainly were formulated using first-order and Michealis-Mentons expressions.\(^{[24]}\) Water temperature is one of the important cyclic stimuli, but inlet flow rates and concentrations and several features of the annual biogeochemical cycle also can contribute to the observed patterns of nutrients and pollutant removal. A simple Arrhenius expression (Eq. 9) was used to represent temperature influence in the model.\(^{[22]}\)

\[
Gr = \frac{G_m \times PLBI \times R \times (P_p - P_m)}{(R + K_r) \times (P_{mx} - P_m)} \times 1.05^{(T-20)}
\]

(3)

\[
Up = \frac{U_m \times PLBI \times (P_{mx} - P_p) \times DISP \times 1.05^{(T-20)}}{(DISP + K_u) \times (P_{mx} - P_m)}
\]

(4)
\[
Mi = \frac{Bg \times DISP \times 1.05^{(T-20)}}{DISP + K_b}
\]  
(5)

\[
Mp = PLAP \times M_r \times 1.07^{(T-20)}
\]  
(6)

\[
Mb = PLBI \times M_r \times 1.07^{(T-20)}
\]  
(7)

\[
De = DETP \times M_m \times 1.07^{(T-20)}
\]  
(8)

\[
K_T = K_{20} \theta^{(T-20)}
\]  
(9)

where, \(K_T\) is the removal rate constant at \(T\) °C, \(K_{20}\) is removal rate constant at 20 °C, \(\theta\) is dimensionless, \(T\) is water temperature (°C). The value of \(\theta\) is 1.05 for organic matter decomposition, plant growth, plant uptake and microbial uptake whereas mortality of plant, mortality of biomass and decomposition is more sensitive to temperature changes. Therefore, \(\theta\) value can be taken within the range of 1.07-1.08 \[^{24}\]

**Calibration and sensitivity analysis**

The calibration was carried out using a standard trial and error procedure. It is expected to yield a model that fits fairly well with observations. Calibration was done by adjusting the selected parameters in the model to obtain a best fit between POUT (simulated output) and POBS (experimental output). Sensitivity analysis was carried out to aid in the model calibration. This was done by examining the relative change in model output (\(X\)) divided by relative change in the value of the parameter tested (\(P_a\)) (Eq. 10).
\[ S_x = \frac{\partial X / X}{\partial P / P_u} \]  

(10)

The higher the value of \( S_x \), the more sensitive the model in the changes to the parameter is. \(^{[24]}\) The relative change in parameters is chosen on the basis of experimental knowledge as to the uncertainty of the parameters.

RESULTS

Simulation of SRP using STELLA software

Experiment was carried out for the period of two years. An attempt was made to calibrate the model using the first year (0 to 350 days) data and the remaining 350 days data were used for validation of the model. Input parameter values used in the model calibration were either obtained from experimental measurements, theoretical calculations, or published literature. The calibration was accomplished by adjusting the key parameters until the model predicted the SRP concentration in the outflow as compared with the outflow concentration reasonably. The measured (POBS) SRP concentration ranges from 0.3mg/L to 3.5mg/L whereas the simulated (POUT) ranges from 0.78mg/L to 2.67 mg/L. The maximum value simulated by the STELLA software is very close to the measured outflow SRP except for few data points. However, it has been found that the experimental data were slightly higher than the simulated values. It is also worth noting that the model did not simulate the very low values as well, but this variation is highly insignificant as compared with the measured and simulated data for the alum sludge-based VFCW. Figure 2 shows the entire trend of model calibration and validation. From days 240-260
the outflow concentration was significantly higher while comparing the normal set of data. It is thought-provoking to notice the validated data of the model which shows almost close simulations for the period of one year despite the fact that a reasonable variation occurred in the first few months (Fig. 2). Nevertheless, the variation observed is less than one mg/L and therefore it is acceptable. This reasonable fluctuation in the model simulation and the experimental results might be due to experimental error or accumulation of biomass within the VFCW and the plants are not harvested throughout the experimental period. Since this experiment has been conducted in a lab-scale environment, most of the forcing functions were assumed to be a constant and this may have also had an overall effect of the model simulations. The other possible reasons could be that apart from adsorption process, the other processes considered in the model are most likely temperature and light dependent.

**Sensitivity analysis**

A sensitivity analysis attempts to provide a measure of the sensitivity of parameters, forcing functions, initial values of the state variables of the sub models to the state variables of greatest interest in the model.[27] However, effort has been taken in this study to analyze the sensitivity for 9 parameters which is most likely to be important for the model simulation in the VFCW. These 9 parameters are \( G_m, M_m, U_m, K_h, K_r, K_m, P_{mx}, P_{mi} \) and \( M_t \) (see Table 1). The changes of the parameter values may be chosen proportionally to the value of the parameter and was also dependent on the possible range of the parameter. In this study, changes were made of ±20%. The details of the sensitivity analysis of the parameters are shown in Table 2. It has been observed that the increase and decrease of \( G_m \) made a significant change in the corresponding state variables of the model. Similarly the change in \( M_t \) also made a significant change in the model output and the corresponding state variable. The rigid structure and fixed set of parameters do not
reflect the real changes in the VFCW. However, \( G_m \) and \( M_r \) is sensitive for the SRP removal in a single VFCW. The lower and higher values of the model are almost identical in model simulation. However, the changes of parameter values \( G_m \) and \( M_r \) have shown difference in the entire model simulation. The other parameter doesn’t show much significant transformation because of the reason that the model considered only the constant ‘T’ for the entire run of simulation.

**Fate of P in VFCW**

The elimination pathways for P in CWs include precipitation, adsorption, plant/microbial uptake, fragmentation and leaching, mineralization and burial.\[^{14}\] The major P transformation processes considered in this study were adsorption, uptake by plants, microbial consumption/uptake and decomposition of detritus. As described earlier, this model consists of five state variables which are all expressed in the unit of mg/day. STELLA as the modelling environment uses a finite difference numerical scheme for computations. The aforementioned mathematical equations for mass balance of adsorption, uptake by plants, microbial consumption/uptake and decomposition of detritus along with forcing functions were entered in STELLA software. The input data of P were inserted into the STELLA software during model calibration and integrated by using second order Runge-Kutta method with a time step of 0.02 day. The best values of unknown coefficients were obtained through calibration. Once the model finishes its run (i.e., at the end of 350 day) the amount of P gets accumulated into the state variables and the processes of the model shows how much amount of P get removed by individual paths. After attaining this stage it is possible to calculate the efficiency of the individual processes such as \( Ad \) (Eq. 1), \( Up \) (Eq. 4) and \( Mi \) (Eq. 5) & \( De \) (Eq. 8). In STELLA software, a circle icon can be used for instance to calculate the efficiency by feeding the appropriate mathematical equations. The
model efficiency for \(Ad\), \(Up\) and \(Mi\) were calculated and the results indicates the percentage of the inflowing P which is adsorbed by the processes for each time step as a function of time. A mass balance estimation revealed that for the simulation conditions used in this study about 72% for \(Ad\), 20% for \(Up\) and 7% for \(Mi\) and \(De\) were, respectively, were obtained.

**DISCUSSION**

*P adsorption in modelling*

Adsorption process in STELLA was described in such a way to calculate the \(P_e\) concentration using the Freundlich isotherm. The rate of exchange between \(P_e\) and \(T_A\) will be proportional to any difference from the above mentioned equilibrium. As stated before adsorption is a fast process; therefore DT has been choosen as 0.02 while running the model. It is worth noting that the model ran efficiently when the DT was set as 0.02. However, while increasing the DT especially for the adsorption process the model fails to run due to the reason that the amount of P adsorbed in the alum sludge is significant. From the model simulation, the maximum P adsorbed during the initial stage of the model run was about 62.3 mg and the corresponding inflow P amount was 86.4 mg. It has been observed that the overall simulation of \(Ad\) is reasonably good in STELLA especially for the adsorption process. It is worth noting that as per the lab experiment of batch isotherm test over 40% of P was removed within the first hour, irrespective of the initial P concentration or the adsorbent dosage.\(^{[28]}\) The initial rapid rate of adsorption however decrease with time, giving way to a very slow rate of approach to equilibrium, and equilibrium concentration are generally reached within 6 to 24 hours depending on the alum sludge dosage and the initial P concentration. Due to infancy stage of this model development there is no direct literature to compare the results especially for the use of
alum sludge in CW. However, several authors used STELLA program to describe the adsorption process in CWs, which use different kinds of media/substrate. The maximum cadmium removal simulated by the STELLA software occurred through the accumulation in the soil with mass fraction values of 33.6-56.3%. \(^{[22]}\) Furthermore it was reported that the maximum adsorption rate was about 8g/day and reached an equilibrium condition in about 100 days \(^{[21]}\) which is predicted by the STELLA software. Conversely it is worth emphasizing the use of the STELLA software for the alum sludge-based VFCW which can be able to simulate well as compared to the other methods. Moreover STELLA helps to understand the P behaviour inside the CW especially for adsorption and other relevant processes too.

**P uptake by plants**

Plant uptake \((U_p, \text{see Eq. 4})\) expresses first order equation for PLBI and the uptake by the need of P from water for its growth, i.e. \((P_{mx}-P_p)/(P_{mx}-P_{mi})\), which is described by Michaelis-Menton expression of the DISP. Therefore the \(P_p\) is the ratio of PLAP/PLBI. In general P in plant is high at mid summer but it is used to change in lower in late September and it also keeps low in the beginning of the new season. This variability in P is in accordance with the physiology of plants. However this P variability is not considered in the current study. DETP is also a state variable included in the model. The decomposition rate for detritus was found relatively low, indicating that the contribution from detritus decomposition is low. The results from the STELLA indicated that the mass of P by uptake varied from time to time during the simulation period. However maximum efficiency was found to be approximately 20%. It has been reported that the simulated mass fractions of cadmium accumulated in plants ranged between 21.8- 24.9% based on the simulation using STELLA software. Several authors \(^{[29,30]}\) studied the P uptake by plants and only few
literatures are available using STELLA software for the simulation of \( Up \). Unfortunately, no data from the use of alum sludge as substrate in CW were found in the literature.

\textit{P consumption/uptake by microbial activities}

The uptake of P by microbiota (bacteria, fungi, algae, microinvertebrates, etc.) is rather complicated as the bioorganisms grow and multiply through a very complicated process. The magnitude of P uptake, i.e. the amount stored in bioorganisms is very low and it may also depend on the trophic status of the wetland system. For instance, in less P enriched sites, the microbial uptake may be more significant than in more eutrophic sites.\[^{31}\]

Microbial uptake (Eq. 6) has been expressed using Michaelis-Menten equation in the modelling. The maximum efficiency was found approximately 7\% for \( De \) (see Eq. 8) and \( Mi \) (see Eq. 5) which is quite low. The biofilm contributes to P removal by incorporating P into biomass for cell synthesis, maintenance and energy transport.\[^{32}\] In the wetlands, the microbial uptake is the smallest process among the other removal processes. Thus the microbes have minimal effect on the removal of P in the wetlands.\[^{33}\]

**CONCLUSIONS**

A model for SRP fate in wastewater treatment using a novel alum sludge-based CW was developed using STELLA. The experience gained by this study demonstrates that it is indeed possible to construct a model for the SRP removal in VFCWs. The mechanisms used in this modeling included adsorption, uptake by plant and microbial processes. The model was calibrated in order to attain closer predictions as compared to the experimental data. A reasonable agreement was obtained between the measured and the predicted results. This study revealed that alum-sludge can be used as a wetland substrate for the removal of SRP concentration via VFCW for significant removal of P. A mass balance
showed that up to 72% of the removal of SRP is through adsorption which is highly significant whereas removal through plants is about 20% and the remaining processes such as microbial P utilization and decomposition accounted for 7% SRP removal in VFCW.

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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FIGURE CAPTIONS

Figure 1. A STELLA diagram of the P model

Figure 2. Comparison of measured (POBS) and simulated (POUT) for SRP removal in a VFCW
Fig. 1
Fig. 2
Table 1. Summary of the state variables, processes, parameters and their associated units in the model development

| Symbol  | Description                                                                 | Value | Unit         | Source       | Literature range |
|---------|----------------------------------------------------------------------------|-------|--------------|--------------|------------------|
| **State variables**                                                                                     |       |              |              |                  |
| ADSP    | Amount of P adsorbed in alum sludge                                             | -     | mg P/day     | calculated   | -                |
| DISP    | Dissolved amount of P in alum sludge                                             | -     | mg P/day     | observed data | -                |
| PLAP    | Amount of P found in plants                                                     | -     | mg P/day     | estimated    | -                |
| PLBI    | Amount of P found in plant biomass                                              | -     | mg P/day     | estimated    | -                |
| DETP    | Amount of P found in detritus and used by bacteria                              | -     | mg P/day     | estimated    | -                |
| **Processes**                                                                                           |       |              |              |                  |
| Gr      | P requirement for growth                                                       | Eq. (4) | mg P/day | -           | -                |
| Up      | P removed through plants                                                        | Eq. (5) | mg P/day | -           | -                |
| Mb      | Mortality of biomass                                                           | Eq. (8) | mg P/day | -           | -                |
| Mp      | Mortality of plant                                                             | Eq. (7) | mg P/day | -           | -                |
| De      | Decomposition of detritus                                                       | Eq. (9) | mg P/day | -           | -                |
| Mi      | Microbial uptake                                                               | Eq. (6) | mg P/day | -           | -                |
| Ad      | P adsorption                                                                  | Eq. (1) | mg P/day | observed data | -                |
| **Parameters**                                                                                           |       |              |              |                  |
| P_{mx}  | Maximum P in plants                                                            | 0.06  | g/100g       | estimate     | -                |
| P_{mi}  | Minimum P in plants                                                            | 0.008 | g/100g       | estimate     | -                |
| U_{m}   | Maximum uptake of P from plants                                                | 0.07  | Per day      | [24]         | 0.003-0.01      |
| K_r     | Michaelis menton plant growth rate                                             | 0.05  | mg P/L day   | calibration  | 0.001-0.005     |
| B_{g}   | Bacterial growth                                                              | 0.8   | Per day      |              |                  |
| K_b     | Michaelis menton bacterial growth rate                                         | 0.5   | Per day      | calibration  |                  |
| M_m     | Maximum mineralization                                                         | 0.2   | Per day      | [24]         | 0.2-0.8         |
| P_e     | P equilibrium concentration                                                    | -     | mg P/L day   | calculated   | -                |
| P_p     | P in plant                                                                    | -     | mg/mg        | calculated   | -                |
| M_r     | Mortality rate                                                                | 0.001 | mg P/L day   | calibrated   |                  |
| G_m     | Maximum growth of plants                                                       | 0.07  | mg P/L day   | [24]         | 0.1-0.6         |
| K_u     | Michaelis Menton for uptake                                                    | 0.2   | mg P/L day   | calibration  | 0.001-0.005     |
| **Others**                                                                                  |       |              |              |                  |
| I_p     | Inflow of P                                                                    | TF*   | mg P/day     | observed data | -                |
| P_c     | P concentration of inflow                                                      | TF*   | mg P/L       | observed data | -                |
| R       | Light required for plant growth                                                | TF*   | µE/m²·sec     | met          | -                |
| T       | Temperature requirement of plant growth & microbial activities                  | TF*   | °C            | met          | -                |
Volume of wastewater 2.3 L/day experiment -
Wastewater contact with alum sludge in tidal flow regime 3 hours experiment -
Flow rate of wastewater into the CW 8 L/day experiment -
Amount of adsorbent in alum-sludge 2,500 mg/g P calculated -

*Note: TF is a Table Function which is incorporated into the model

| Changes of | Parameter values | POUT (+20%) (Model calibration) | POUT (-20%) (Model calibration) |
|------------|------------------|---------------------------------|---------------------------------|
| G_m        | 0.07             | 0.76-2.71                       | 0.73-2.66                       |
| M_m        | 0.2              | 0.78-2.49                       | 0.74-2.67                       |
| U_m        | 0.06             | 0.77-2.49                       | 0.73-2.67                       |
| K_p        | 0.5              | 0.74-2.67                       | 0.77-2.67                       |
| K_r        | 0.05             | 0.79-2.67                       | 0.74-2.67                       |
| K_u        | 0.2              | 0.74-2.67                       | 0.74-2.67                       |
| P_mx       | 0.06             | 0.76-2.67                       | 0.73-2.66                       |
| P_mi       | 0.008            | 0.74-2.67                       | 0.74-2.67                       |
| M_r        | 0.001            | 0.78-2.71                       | 0.73-2.61                       |