Modelling heavy metals transformation in vertical flow constructed wetlands

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Abstract

Constructed wetlands are dynamic ecosystems for which we generally have poor predictive capabilities of the succession relationships between the interdependent components and the processes. In this study a dynamic simulation model that can evaluate the transport and fate of heavy metals in vertical flow constructed wetland systems was developed using a dynamic software program: Structural Thinking Experiential Learning Laboratory with Animation (STELLA) v9.0.2. The key heavy metals transformation processes considered in the study were adsorption and plant uptake; whilst the forcing functions considered were wastewater volume, temperature, heavy metals concentration, contact time, flow rate and adsorbent media. The model results indicate that up to 89%, 91% and 91% of Pb, Cr and Cd respectively, can be removed through adsorption process; whereas uptake by plants was 6%, 5.1% and 5.2% based on mass balance calculations. Sensitivity analysis also showed that the most sensitive areas in the model coincide with the adsorption parameter (the heterogeneity factor (n) and the Freundlich constant (Kf)). The results obtained indicates that the model can be used to simulate outflow heavy metal concentrations, and it can also be used to estimate the amount of heavy metal removed by individual processes in the system.

Keywords: Constructed wetland, ferric sludge, heavy metals, STELLA.

1. Introduction

Constructed wetland systems (CWs) have become a popular technical alternative worldwide for the treatment of various wastewaters. (Kadlec and Wallace, 2008). They are used not only to degrade organic substances and nutrients from wastewaters (Sun and Austin, 2007; Sun et al., 2005), but also to remove metals from several industrial wastewaters (Cheng et al., 2002; Zhao et al., 2009).

Unlike organic pollutants, heavy metals (HM) cannot be degraded through biological processes. Understanding the mechanism of HM removal has expanded concurrently with increased adoption and usage of treatment wetlands (Kosolapov et al., 2004). Marchand et al. (2010) indicated that there are four main processes of metals removal in CWs. These include adsorption to fine textured sediments and organic matter; precipitation as insoluble salts (mainly sulphides and oxyhydroxides); absorption and induced changes in biogeochemical cycles by plants and bacteria; and deposition of suspended solids due to low flow rates.

However, adsorption represents an important mechanism for removal of metals in CWs. Therefore, to ensure efficient HM removal, it is important to use substrates with high HM removal capacity and suitable physiochemical properties. A low-cost material that can enhance HM removal is ferric dewatered sludge (Mohammed et al., 2016). It is available worldwide and is mostly landfilled at huge costs since it is regarded as a waste with little known reuse value. However, the physicochemical properties of ferric dewatered sludge give it a highly reactive surface and a strong affinity for phosphorous and HM (Al-Tahmazi and Babatunde, 2016; Mohammed et al., 2016).

Plants also play an important role in CWs for the removal of pollutants. They take up nutrients and they are also able to adsorb and accumulate metals (Cheng et al., 2002). Moreover, *Phragmites australis*, known as common reed, is widely used in CWs for treatment of urban and industrial wastewaters containing metals (Bonanno and Lo Giudice, 2010).

The efficiency of CWs for wastewater treatment is often evaluated by a comparison between influent and effluent. However, this is a figurative black- box approach since there is no information on the biological and physicochemical processes occurring in the CWs Modelling of HM removal in CWSs is important with regards to understanding the HM behaviour in the integrated treatment processes. Various modelling tools including FITOVERT, CW2D, PHWAT and CWM1 have been used to understand the processes in CWSs (Kumar and Zhao, 2011). However, all these models have been used to simulate the hydraulic properties or degradation of pollutant. In this study the fate of Pb, Cr and Cd in a vertical flow constructed wetland (VFCW) was investigated through the development of a mathematical model using the Structural Thinking Experiential Learning Laboratory with Animation (STELLA) v9.0.2 software. The key objectives were: (1) to develop a dynamic model for simulating adsorption, plant uptake and plant growth from the VFCW which uses ferric dewatered sludge as main substrate; (2) to calibrate the model using the available experimental data; and (3) to apply the model to simulate the fate of HM in the VFCW.

2. Materials and methods

2.1. Set-up of vertical flow constructed wetland system

A laboratory scale VFCW system was set up outdoor using perspex columns that were 100 mm in diameter and 1000 mm in height. Each column was filled with 22±3 mm of round gravel to a depth of 150 mm from the bottom, which served as a drainage layer (see Figure 1). Air-dried ferric dewatered sludge with a particle size of 1-3 mm was used as the primary media layer (350 mm), followed by 7±2 mm washed gravel for a depth of 150 mm, giving an average porosity of 0.43. The ferric dewatered sludge consisted of Fe (193.85 mg g^{-1}); its detailed physicochemical properties have been published elsewhere (Mohammed et al., 2016). In brief, the specific surface area was 132 m^2 g^{-1} and the iron oxalate content was 162 mg g^{-1} which confirmed the amorphous nature of the ferric dewatered sludge. Each column experienced cyclic wet and dry period with the artificial landfill leachate. These periods were generated by peristaltic pumps. Each wet cycle was completed in three hours and fifty

minutes, giving each column 3:50 h of wastewater-media contact per cycle. Common reed, *Phragmites australis*, was planted on the top layer of the stage.

Experiments were carried out in two periods, namely Period 1 and 2. The initial purpose of the experiments was to investigate the removal rate of HM from landfill leachate. However, significant removal was not found in the performances of individual CW stages during Period 1. Accordingly, alterations to the experiment were made in Period 2. Only one CW stage (referred to as 'A' in Figure 1) was used in Period 1, whereas in Period 2 two CW stages (A + B), which were arranged in parallel, were used.

To simulate young landfill leachate, $CdSO_4.H_2O$ salt, $Cr(SO_4)_2.12H_2O$ salt and $PbCl_2$ salt, respectively for cadmium (Cd), chromium (Cr) and lead (Pb) were used to synthesise artificial landfill leachate in the laboratory. The initial concentrations of HM were (230 µg L^{-1}- 630 µg L^{-1}), (240 µg L^{-1} - 650 µg L^{-1}) and (240 µg L^{-1} -810 µg L^{-1}) for Pb, Cr and Cd, respectively.

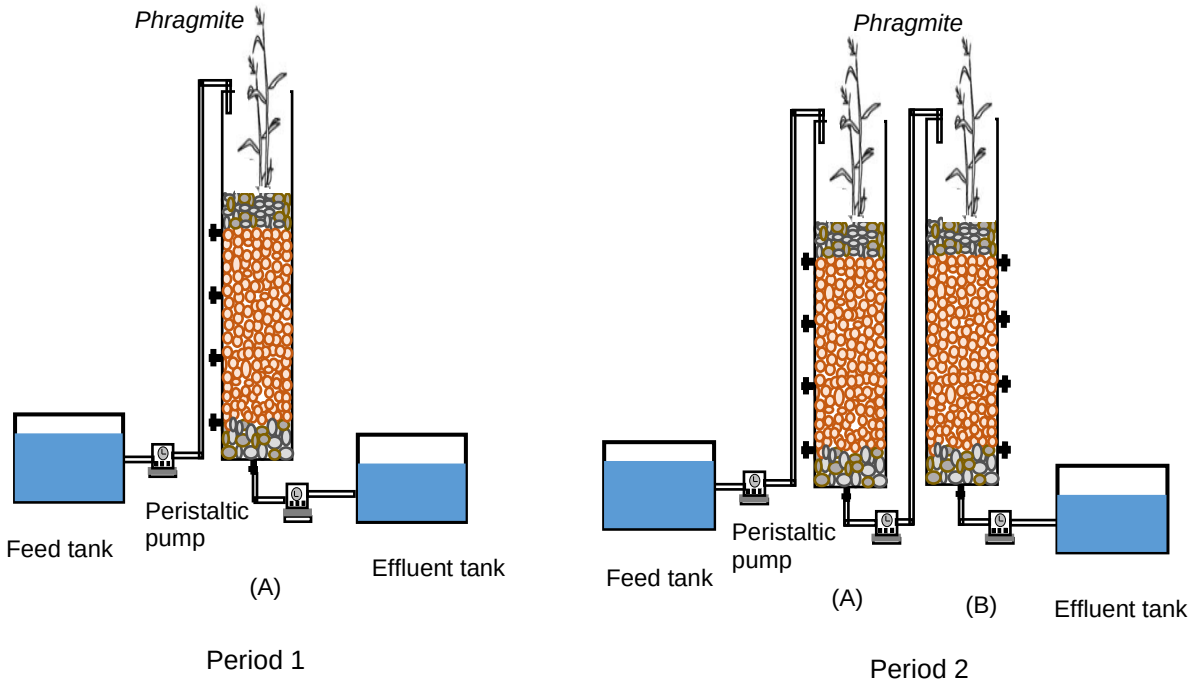

Figure 1. Schematic description of the constructed wetland system in Period 1 (left) and Period 2 (right).

2.2. Batch analysis

Batch experiments were used to investigate the kinetic of the adsorption process and examine the kinetics of heavy metal adsorption by the ferric dewatered sludge. To investigate the effects of sludge dosage and equilibration time, different masses of the sludge sample (0.1, 0.5 and 1.0 g) were equilibrated with 100 ml each of heavy metal solutions (0.5 mg L^{-1} for Pb, 1 mg L^{-1} for Cr and 5 mg L^{-1} for Cd), which were contained in 250 ml polyethylene bottles for 1–96 h using a rotary shaker. At specified time points, the mixture was withdrawn, filtered and analysed for each heavy metal using an Optima 210 DV ICP OES, and the uptake of those metals was determined using Eq. (1).

$$q_e = \frac{(c_o - c_e)}{m} v \quad \text{.....(1)}$$

Here, C_o and C_e (both in mg L^{-1}) are the initial (t=0) and final heavy metals concentrations at equilibrium (q_e), respectively; q_e is the mass of heavy metal adsorbed on the adsorbent (sludge) at equilibrium (mg g^{-1}); v is the volume of the solution (L); and m is the mass of ferric dewatered sludge used (g).

2.3. Description of the STELLA model

According to Jay Forrester's systems dynamics language, STELLA is a software for graphic and dynamic simulation. The use of iconographic modelling techniques makes the model a flexible simulation tool with an easy user interface for making change and calibrate. The user can immediately view the effects of the changes, which reduces the time required to develop the model (Jørgensen and Fath, 2011).

Conceptual diagrams of the adsorption processes, plant uptake and plant growth for Pb, Cr and Cd are shown in the STELLA diagrams below (Figures 2-4). The major mechanisms for HM dynamics in CWS considered in this study were adsorption and plant uptake. The removal of heavy metals in CWs is widely attributed to adsorption and plant uptake (Kosolapov et al., 2004; Marchand et al., 2010). The developed models have five state

variables including dissolved HM (DISHM), plant HM (PLHM), which means the heavy metals that are available for plant uptake are those that are present as soluble components in the soil solution or those that are easily solubilized by root exudates, Although plants require certain heavy metals for their growth and upkeep so that the third state is plant biomass (PLBHM), detritus HM (DETHM) and adsorption (ADSHM), all expressed in mg of HM per day. Adsorbent HM concentration and contact time are considered to be major forcing functions in the model, since the adsorption process is highly related to the retention capacity of substrates over time (Marchand et al., 2010). The state variables, processes, parameters and auxiliary variables used in the model are shown in Table 1. Detailed descriptions of each mechanism responsible for removal and HM dynamics are presented below.

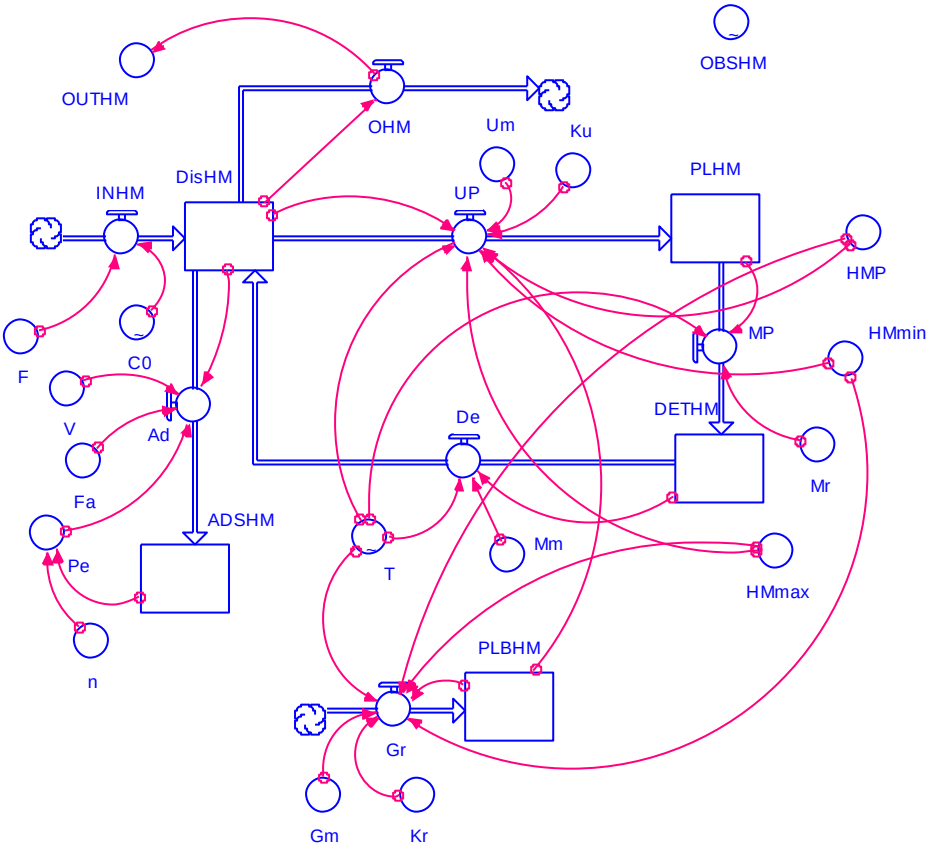

Figure 2. A STELLA diagram of the HM model.

146 2.3.1. Process equations

147 The adsorption process was described by the equilibrium between HM in water and HM in
148 the adsorbent. Unlike other processes, this process is fast and reaches equilibrium in hours,
149 based on the batch results (Figure 9). Therefore, 0.02 delta time (DT) was selected as the
150 time step. DT refers to the time interval between calculations in STELLA software. In addi-
151 tion, the adsorption process was multiplied by a factor (*Fa*) of 2.5, 5 and 3, respectively for
152 Pb, Cr and Cd for column A, and 3.5, 14 and 5, respectively for Pb, Cr and Cd for column B.
153 These factors were based on experimental results, and it is expected that they will vary ac-
154 cording to the type of media, HM concentrations, type of pollutant, type of CWs, etc.
155 Adsorption process can be describe using equation 2, where, *Fa* is a factor, *DISHM* is
156 dissolve HM (either Pb, Cr or Cd) (mg day^{-1}), P_e is the equilibrium concentration (mg L^{-1} day^{-1}) and *V* is the volume of wastewater (L).
157
158

159 $$Ad = Fa\left(DISHM - P_e \times V\right) \quad (2)$$
160

161 P_e can be calculated by using equation 3, where *ADSHM* is adsorption of HM (either Pb, Cr
162 or Cd) (mg day^{-1}), T_A is the total amount of adsorbent (g), K_F is the Freundlich constant (L g^{-1}) and *n* is the heterogeneity factor.
163
164 $$P_e = \left(\frac{ADSHM}{T_A \times K_F}\right)^n \quad (3)$$
165

166 Mohammed et al. (2016) found that the Freundlich adsorption model was well fit to describe
167 the adsorption behaviour of Pb, Cr and Cd, with correlation coefficients of 0.97, 0.98 and
168 0.98 for Pb, Cr and Cd, respectively.
169 The growth of the plant, *phragmites australis* depends on the amount of HM in the plant and
170 can be described as a function of maximum growth rate at the optimum temperature.

Furthermore, the plant's growth can be expressed by Michaelis-Menton equation of dissolved HM. The following equation was used to describe plant growth:

$$Gr = \frac{G_m \times PLB \times \left(HM_p - HM_{\min}\right) \times 1.05^{(T-20)}}{K_r \times \left(HM_{\max} - HM_{\min}\right)} \quad \text{.....(4)}$$

Here, G_m and K_r are maximum HM growth rate of the plant and the plant's growth rate (Michaelis-Menton half saturated constant for growth); *PLB* is plant biomass; HM_P, HM_{min} and HM_{max} are heavy metal in the plant, minimum heavy metal in the plant and maximum heavy metal in the plant, respectively; and *T* is temperature. Plant uptake (*phragmites australis*) is defined as a function of maximum uptake rate at the optimum temperature as explained in equation 5, where U_m and K_u are the maximum uptake rates of plants and the uptake rate of HM (Michaelis-Menton half saturated constant for uptake), respectively.

$$Up = \frac{U_{\max} \times PLB \times \left(HM_{\max} - HM_p\right) \times DISHM \times 1.05^{(T-20)}}{\left(DISHM - K_u\right) \times \left(HM_{\max} - HM_{\min}\right)} \quad \text{.....(5)}$$

The first order reaction with Arrhenius function of temperature was used to express the plant mortality and the detritus and as shown below.

$$MHM = PLHM \times M_r \times 1.07^{(T-20)} \quad \text{.....(6)}$$

$$De = DETHM \times M_m \times 1.07^{(T-20)} \quad \text{.....(7)}$$

$$KT = K_{20}\theta^{(T-20)} \quad \text{.....(8)}$$

Here, M_r and M_m are the mortality rate and maximum HM mineralization, respectively; KT is the removal rate constant at T°C; K_{20} is the removal rate constant at 20◦C; θ is

197 dimensionless; and T is the water temperature (◦C). The value of θ is 1.05 for plant growth
198 and plant uptake, whereas the plant's mortality decomposition is more sensitive to
199 temperature changes. Therefore, the θ value ranges from 1.07 to 1.08 (Kumar et al., 2011).

200 2.4. Calibration and sensitivity analysis

201 Before applying the resulting STELLA model to estimate the removal of heavy metals, the
202 model was calibrated and validated using a standard trial and error procedure. In general,
203 model calibration is a process adjusting the selected parameter values to obtain the best fit
204 between the observed data and simulated results. In practical modelling, sensitivity analysis
205 is carried out to aid in model calibration. This is done by changing the parameters and
206 observing the corresponding response on the selected parameter. Thus, the sensitivity (S) of
207 a parameter (P) is defined as follows:

208 $$S = \frac{\delta X / X}{\delta P / P} \quad \text{.....(9)}$$

209

210 Here, X is the model output. The higher the value of S, the more important the parameter
211 (Jørgensen and Fath, 2011). The relative change in the parameter is chosen based on
212 experimental knowledge as to the certainty of the parameters.

213 Table 1. Summary of the state variables, processes, parameters and their associated units in the model development for Pb, Cr and Cd.

Symbol	Description	Value			Unit	Source
State variables						
ADSHM	Amount of HM adsorbed in ferric dewatered sludge	-			mg HM day^{-1}	Calculated
DISHM	Dissolved amount of HM in ferric dewatered sludge	-			mg HM day^{-1}	Observed data
PLHM	Amount of HM found in plants	-			mg HM day^{-1}	Estimated
PLBHM	Amount of HM found in plants biomass	-			mg HM day^{-1}	Estimated
DETHM	Amount of HM found in detritus and used by bacteria	-			mg HM day^{-1}	Estimated
Processes						
Gr	HM requirement for growth	Eq.(4)			mg HM day^{-1}	-
Up	HM through plants	Eq.(5)			mg HM day^{-1}	-
Mp	Mortality of plant	Eq.(6)			mg HM day^{-1}	-
De	Decomposition of detritus	Eq.(7)			mg HM day^{-1}	-
Ad	HM adsorption	Eq.(2)			mg HM day^{-1}	-
Parameters		Pb	Cr	Cd		
HMmax	Maximum HM in plants	0.11	1	1.5	g $(100g)^{-1}$	Estímated
HMmin	Minimum HM in plants	0.001	0.195	0.016	g $(100g)^{-1}$	Estímated
Um	Maximum uptake of HM from plants	0.26	0.114	0.09	mg HM (L $day)^{-1}$	Calculated
Ku	Michaelis Menton for uptake	5.24	2.18	2	day^{-1}	Calculated
Mm	Maximum mineralization	0.2	0.2	0.2	day^{-1}	(Kumar et al., 2011)
Pe	HM equilibrium concentration				mgHM (L $day)^{-1}$	Calculated

HMp	HM in plant	-	-	-	mg mg^{-1}	Calculated
		0.000024	0.00052	0.00002		Kumar et al.,
Mr	Mortality rate				mg HM $(L\ day)^{-1}$	2011)
		0.001	0.001	0.001		Calculated
Gm	Maximum growth of plant				mg day^{-1}	Calculated
Kr	Michaelis Menton plant growth rate	5.8	4.3	2	mg HM $(L\ day)^{-1}$	
		3.8	2.6	0.45		
Others						
INHM	Inflow of HM	TF			mgHM day^{-1}	Observed data
C_0	HM concentration of inflow	TF			mgHM L^{-1}	Observed data
T	Temperature requirement of plant growth	TF			°C	Observed data
V	Volume of wastewater	12			L	Experiment
F	Flow rate of wastewater into the CW	12			L day^{-1}	Experiment
TA	Amount of adsorbent	2500			g	Calculated

214 TF is a Table function which is incorporated into the model.

3. Result and discussion

3.1. Simulation of heavy metals using STELLA software

Experiments were carried out for two periods using column A (215 days) for Period 1 and columns A and B (185 days) for Period 2. A comparison of the measured and modelled data was undertaken using Period 1 for calibration and Period 2 for validation. During the calibration, the input parameters were obtained from experimental measurements, theoretical calculations or existing literature (Table 1). The model was calibrated by trial and error adjustment of the key parameters (within a reasonable range) until predictions under similar conditions had good agreement with the observed data. The measured HM concentrations ranged from 54 µg L^{-1}- 264 µg L^{-1}, 21 µg L^{-1}- 190 µg L^{-1} and 87 µg L^{-1}- 342 µg L^{-1}, respectively, for Pb, Cr and Cd. Whereas the simulation ranged from 92 µg L^{-1}- 255 µg L^{-1}, 38 µg L^{-1}- 262 µg L^{-1} and 80 µg L^{-1}-324 µg L^{-1}, respectively, for Pb, Cr and Cd during the calibration period. The maximum value of the measured effluent concentration (OBS) for all of the HM was very close to the value simulated by the STELLA model. However, the predicted data were slightly higher than the measured data for all of the HM, with the exception of a few data points. In addition, the model did not simulate very low values for all of the HM. Figure 4 shows the entire trend of model calibration and validation for column A. The mean percent error (MPE = (OBS - OUT)/OBS × 100) equals 38%, 33% and 30%, respectively, for Pb, Cr and Cd during the calibration period, and 15%, 20% and 10%, respectively, for Pb, Cr and Cd during the validation period. It is worth noting that the validated data for the HM was quite close to the observed data, despite the fact that the simulation data was higher than the observation data for the period of 320- 400 days (during validation between 105 and 185 days in period 2) in the case of Cr. This slight fluctuation in the model simulation and the experimental data could be due to experimental error or accumulation of biomass within the CWs (growth of microorganism). This could also be attributed to the fact that the plants were not harvested during the experimental period. The uptake of HM by plant is a step function during the growing season and zero after harvest

until the next growing season start (Jørgensen and Fath, 2011). However, the contribution of plant harvesting is a small percent to the total HM removal in CWs, so that it is ignore in this study (Cheng et al., 2002; Kosolapov et al., 2004; Marchand et al., 2010).

. Another possible reason may be that apart from the adsorption process, the HM in CW can be removed by other processes, such as precipitation, oxidation, ion exchange and redux reaction (Galletti et al., 2010). However, the system was operated to be fully saturated for 3:50 hours and unsaturated for 10 minute and due to a limitation of DO diffusion within HH sludge (Wang et al., 2008), there is aerobic and anaerobic condition along the height of the column as shown in figure (3). Therefore, the co-precipitation of HM with Fe oxide is very dependent on DO variations so that the binding of metals with Fe oxide cannot be a long-term removal mechanism, and then metals may be released back to the system. Moreover, Fe oxide high affinity to metals that have similar size of Fe such as Cd, however the co-precipitate is limited when there is sufficient amount of SO_4 which reducing the potential of metal removal (Marchand et al., 2010). In addition, under anaerobic condition and because of there is no sufficient carbon source required by sulphate- reducing bacteria to sulphides, precipitation metals as metal sulphide cannot occur (Stefanakis et al., 2014).

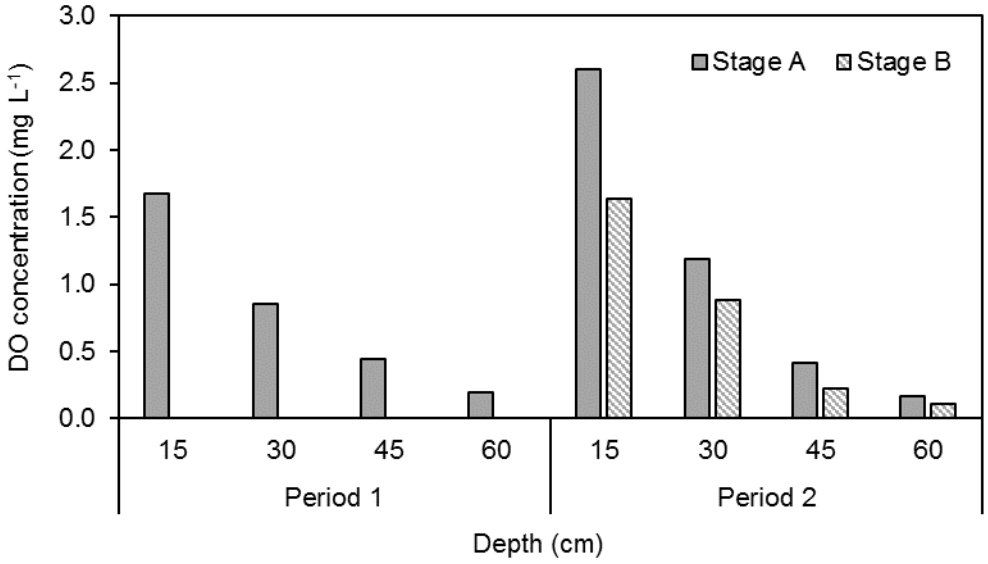

Figure 3 Vertical initial DO distribution at different depth (from top layer to bottom) in four stages of constructed wetland system.

A comparison of the observed and predicted Pb, Cr and Cd concentration values in the effluent during the model calibration process obtained using linear regression is shown in Figure 5. The R^2 values for Pb, Cr and Cd outlet concentration values were 0.75, 0.69 and 0.62, respectively. The R^2 values for comparisons of the observed and predicted Pb, Cr and Cd outlet concentration values during the model validation process (Figure 6) were 0.78, 0.65 and 0.74, respectively for Pb, Cr and Cd concentration. These values represent good correlations between the model predictions and the experimental measurements.

Based on these results, the mathematical model developed in this study could be used to describe the HM removal process in the VFCW using ferric dewatered sludge as the primary media. The model was run using STELLA software for a period of 185 days for column B. Since the results of the validation data in column A displayed a good match between simulated and experimental data, the calibration for column B was performed with the column A data. The experimental effluent HM concentrations ranged from 25 µg L^{-1} to 76 µg L^{-1}, 8 µg L^{-1} to 22 µg L^{-1} and 24 µg L^{-1} to 76 µg L^{-1}, respectively for Pb, Cr and Cd. On the other hand, the simulation data for Pb, Cr and Cd ranged, respectively, from 23 µg L^{-1} to 63 µg L^{-1}, 11 µg L^{-1} to 24 µg L^{-1} and 27 µg L^{-1} to 68 µg L^{-1}, as shown in Figure 7. This figure shows that the mean concentration values of HM for the measured and simulated values were very close and, therefore, the overall simulation is acceptable for column B. The MPEs for this column were 17% for Pb, 17% for Cr and 17% for Cd. A comparison between the observed and predicted Pb, Cr and Cd concentrations in effluent during the model validation process for column B showed good correlations between the model predictions and the experimental measurements, with R^2 being 0.82, 0.71 and 0.76, respectively, for the Pb, Cr and Cd outlet concentrations (Figure 8).

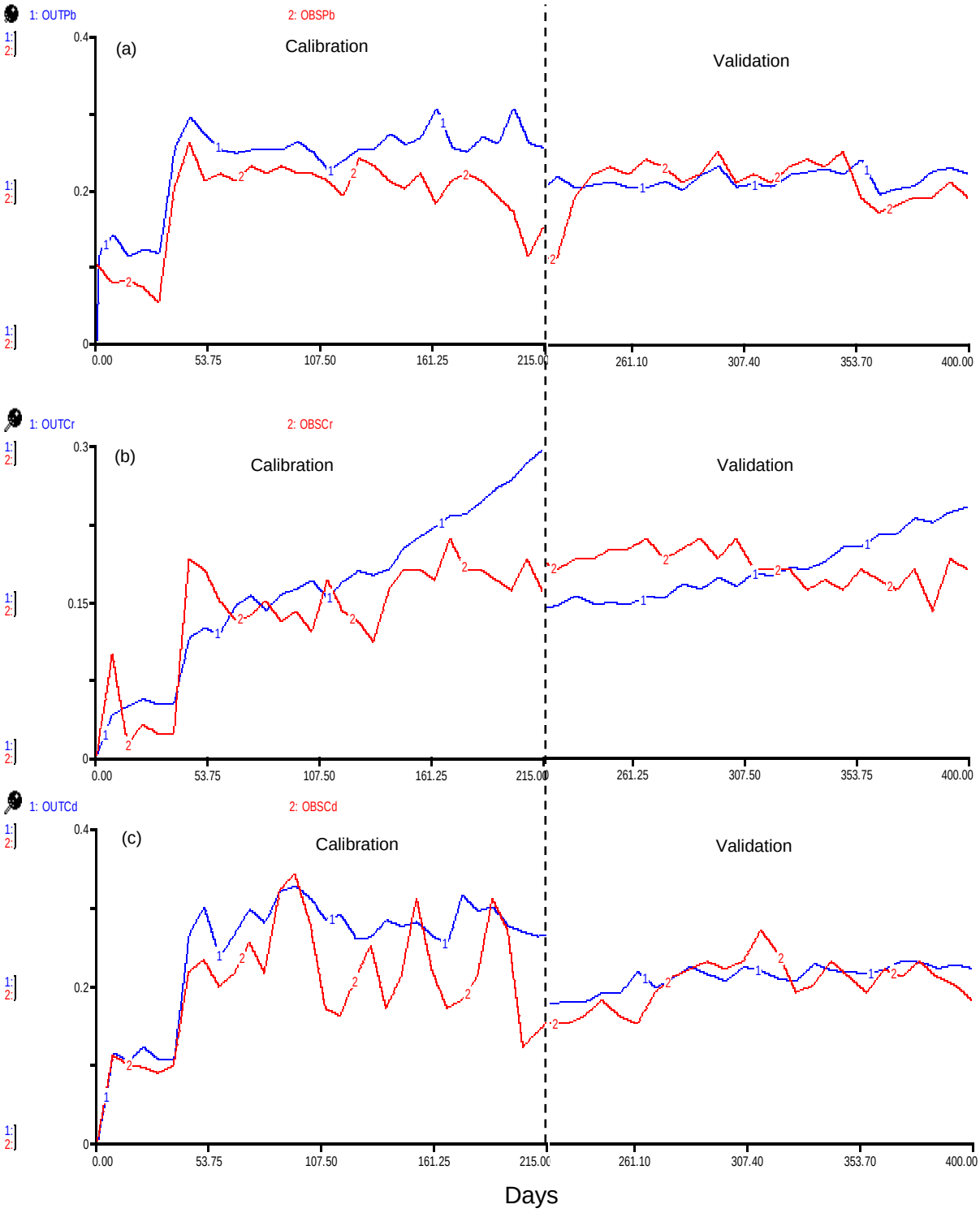

Figure 4. Model calibration and validation for (a) Pb, (b) Cr and (c) Cd removal in mg L^{-1} in VFCW for column A.

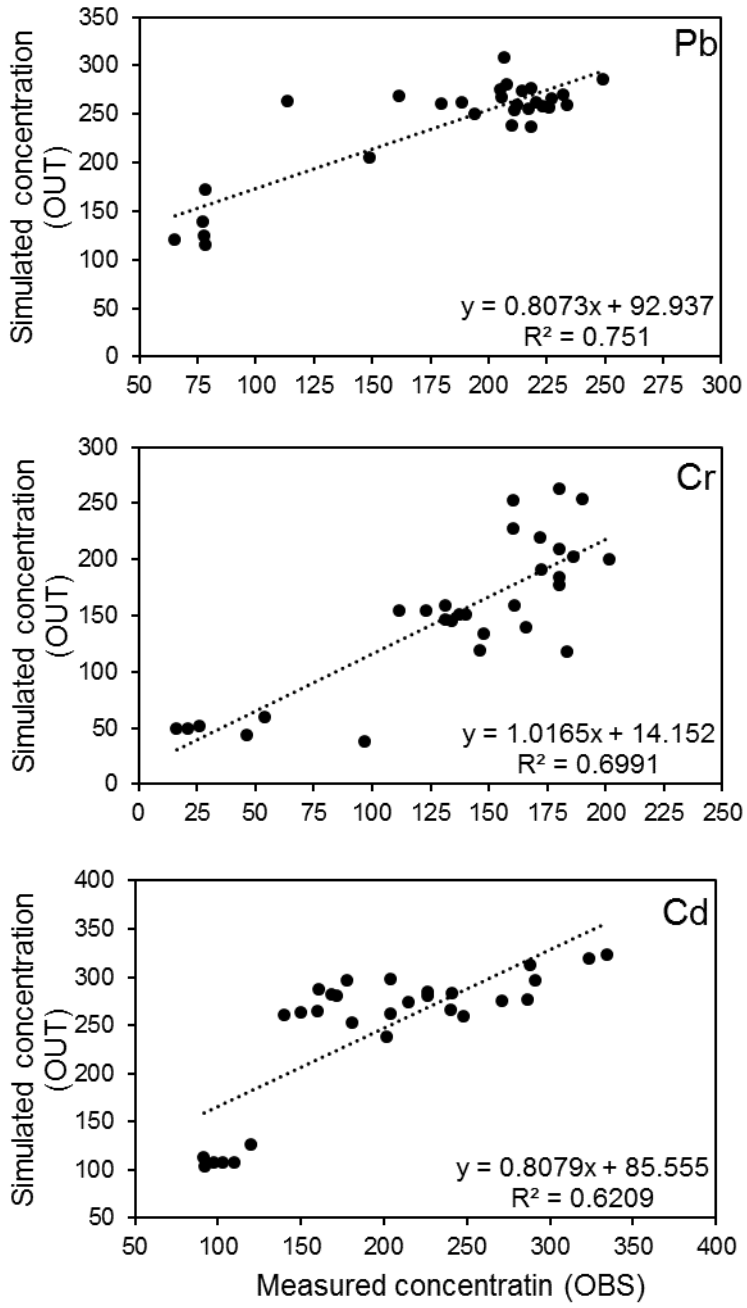

Figure 5. Comparison of model predicted and field measured of Pb, Cr and Cd removal in µg L^{-1} in VFCW for column A during model calibration.

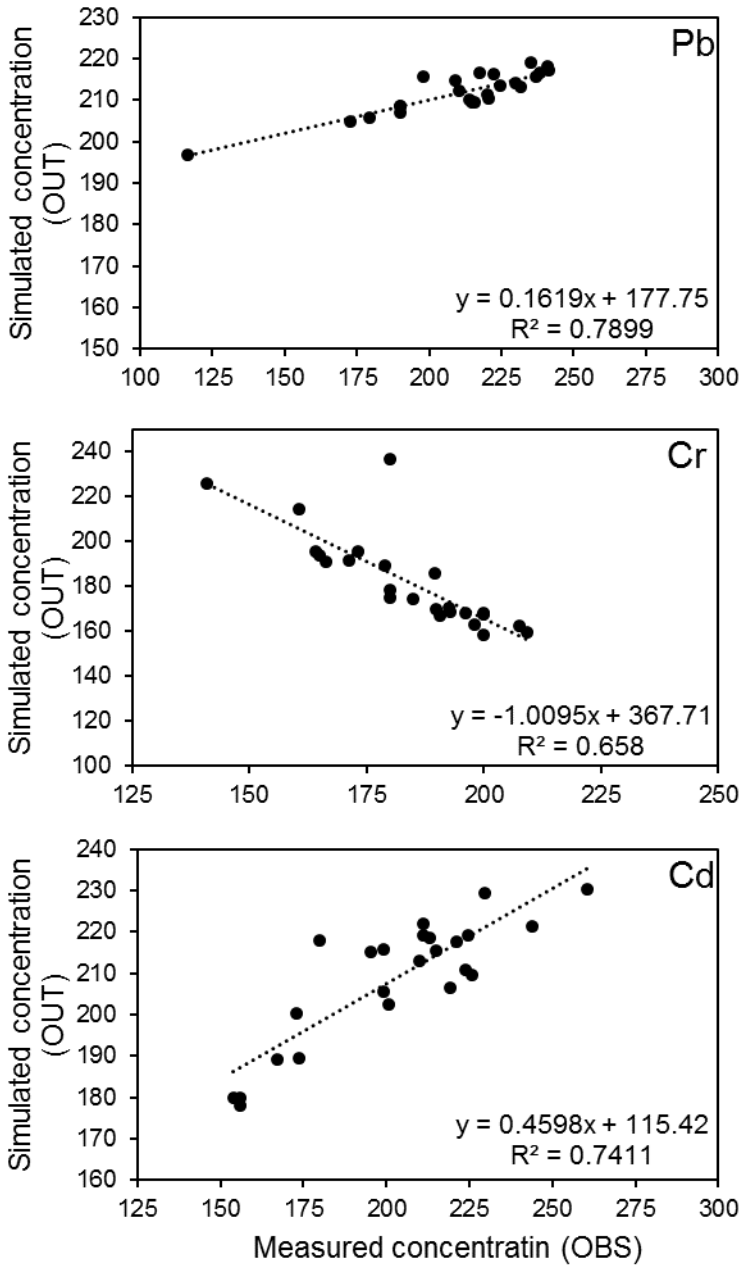

Figure 6. Comparison of model predicted and field measured of Pb, Cr and Cd removal in µg L^{-1} in VFCW for column A during model validation.

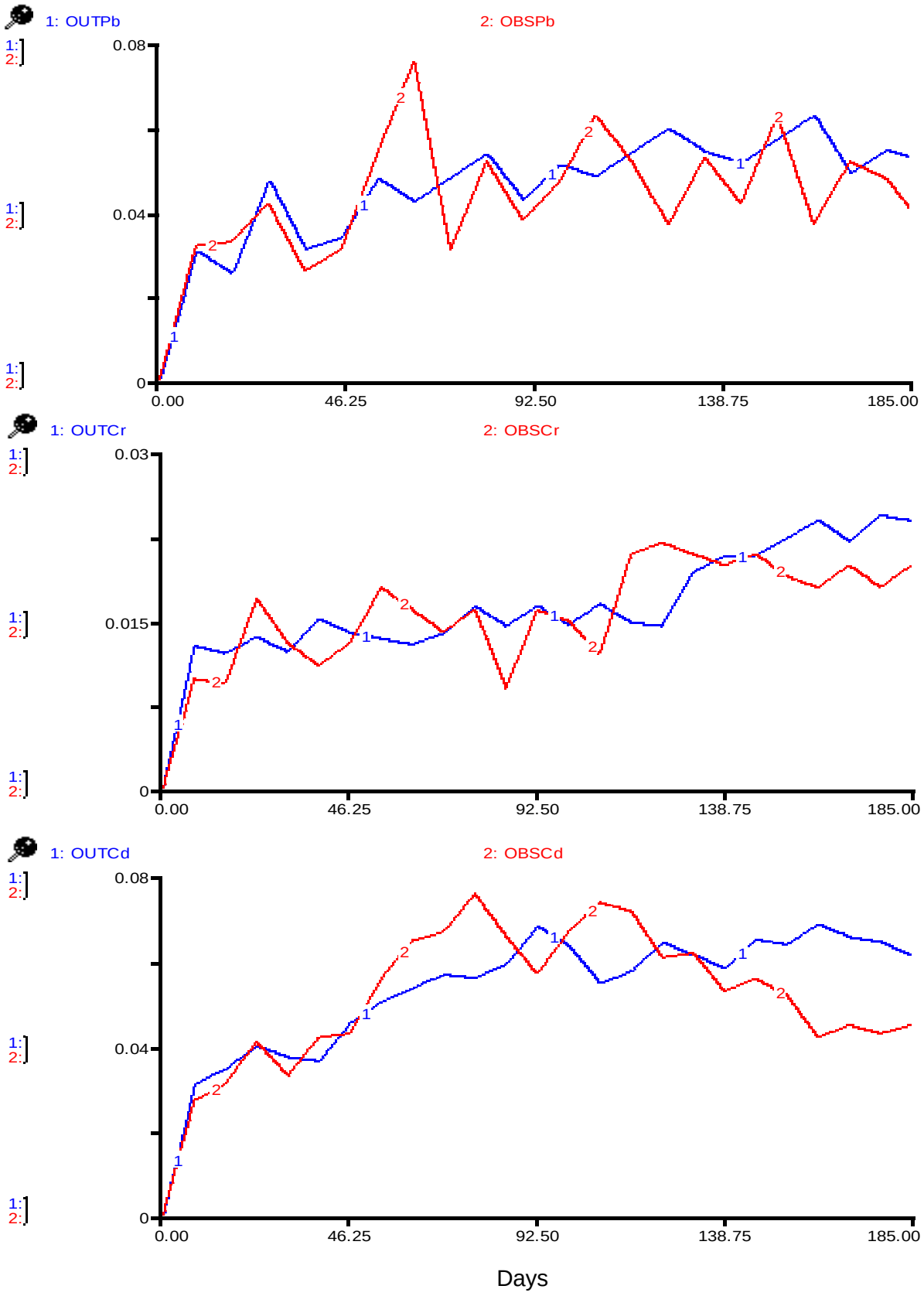

Figure 7. Model validation for (a) Pb, (b) Cr and (c) Cd removal in mg L^{-1} in VFCW for column B.

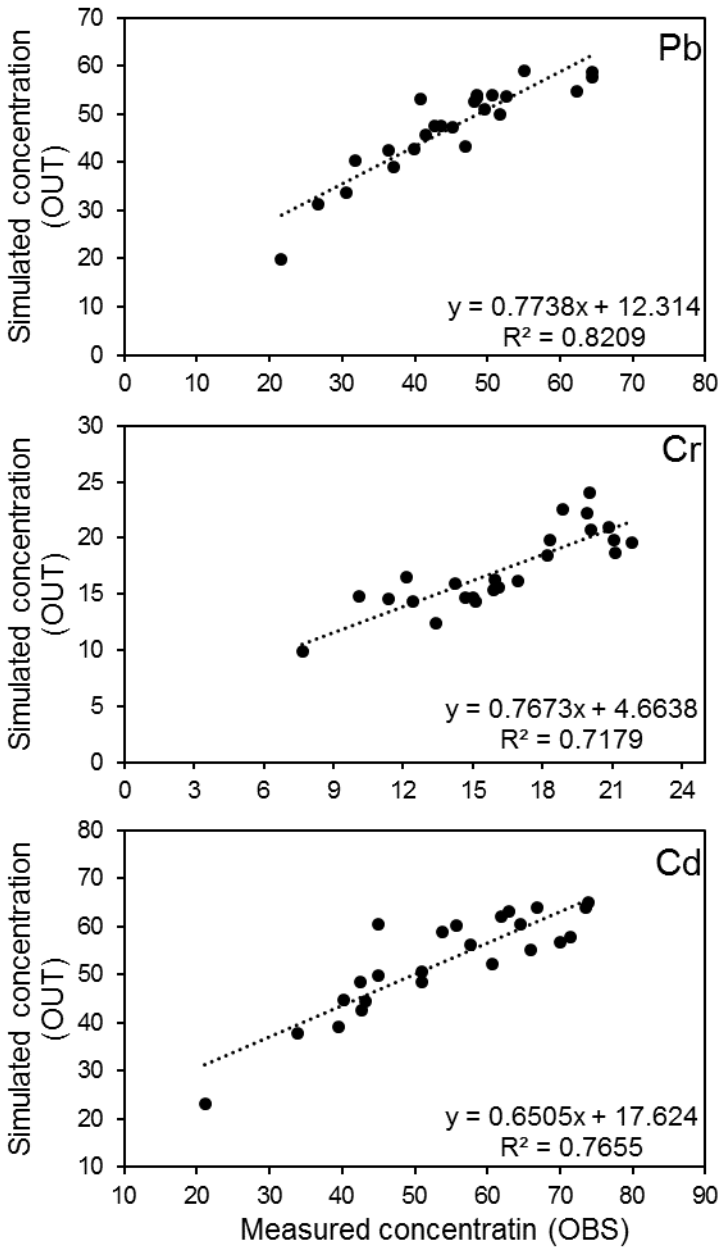

Figure 8. Comparison of model predicted and field measured of Pb, Cr and Cd removal in μgL^{-1} in VFCW for column B during model validation.

3.2. Sensitivity analysis

A sensitivity analysis provides a good overview of the most sensitive components in the model. This type of analysis attempts to provide a measure of the sensitivity of the parameters by forcing functions, initial values of the state variables of the sub models, to the state variables of greatest interest in the model (Jørgensen and Fath, 2011). The sensitivity of the model was tested using the 10 parameters which were most likely to be important: Gm, Kr, Um, Ku, Mm, Mr, HMmax, HMmin, n and Kf (Table 2). This was done by examining the relative change in the model output and dividing it by the relative change in the value of the tested parameter. The magnitude of the changes in the parameter values may be proportional to the value of the parameter; this also depended on the possible range of the parameter. Most changes were made between -50% and +50% (van der Peiji and Verhoeven, 1999). In this study, changes were made at ±40%. Table 2 shows that the increase and decrease of n caused a significant change in the corresponding state variable of the model. Similarly, the change in Kf also caused changes in the model output and the corresponding state variables. This is primarily because the adsorption process supposes that the main process for the removal of HM by ferric dewatered sludge in the CWs. The rigid structure and fixed set of parameters do not accurately reflect the changes in the output of VFCW.

Table 2. Sensitivity analysis for the selected parameters included in the model.

Change of	Parameter value			S (+40%)			S (-40%)		
	Pb	Cr	Cd	Pb	Cr	Cd	Pb	Cr	Cd
Gm	2.08	3	0.82	1.08×10^{-8}-1.33×10^{-7}	2.18×10^{-8}-1.43×10^{-7}	1.64×10^{-7}-3.22×10^{-7}	2.10×10^{-8}-1.32×10^{-7}	2.18×10^{-7}-6.23×10^{-7}	7.08×10^{-8}-2.47×10^{-7}
Kr	2.8	3	1.26	1.43×10^{-8}-2.1×10^{-8}	1.98×10^{-7}-2.13×10^{-6}	1.08×10^{-8}-2.33×10^{-8}	1.08×10^{-8}-1.33×10^{-7}	1.11×10^{-7}-5.01×10^{-6}	2.08×10^{-7}-4.91×10^{-7}
Um	0.26	0.114	0.09	1.48×10^{-5}-3.69×10^{-5}	0.41×10^{-5}-0.55×10^{-3}	6.63×10^{-6}-2.02×10^{-5}	1.56×10^{-5}-3.92×10^{-5}	0.41×10^{-3}-0.55×10^{-3}	6.63×10^{-6}-2.02×10^{-5}
Ku	5.24	2.18	2	3.91×10^{-6}-2.38×10^{-5}	0.19×10^{-3}-0.33×10^{-3}	2.14×10^{-6}-1.00×10^{-5}	1.41×10^{-5}-4.72×10^{-5}	0.31×10^{-3}-0.63×10^{-3}	2.71×10^{-6}-1.47×10^{-5}
HMmax	0.11	1	1.5	2.01×10^{-5}-8.75×10^{-5}	6.67×10^{-5}-8.93×10^{-5}	5.08×10^{-8}-1.55×10^{-7}	1.45×10^{-5}-6.33×10^{-5}	0.19×10^{-3}-0.26×10^{-3}	1.19×10^{-7}-3.65×10^{-7}
HMmin	0.001	0.195	0.016	2.32×10^{-5}-0.11×10^{-3}	0.11×10^{-3}-0.15×10^{-3}	7.17×10^{-8}-2.18×10^{-7}	8.83×10^{-9}-3.51×10^{-7}	0.15×10^{-5}-0.12×10^{-3}	7.12×10^{-8}-2.16×10^{-7}
Mr	0.001	0.001	0.001	2.48×10^{-6}-8.48×10^{-6}	7.73×10^{-5}-0.18×10^{-3}	1.32×10^{-6}-5.97×10^{-6}	2.67×10^{-6}-8.61×10^{-6}	8.03×10^{-5}-0.18×10^{-3}	1.41×10^{-6}-6.09×10^{-6}
Mm	0.2	0.2	0.2	1.16×10^{-5}-9.86×10^{-5}	1.82×10^{-6}-4.72×10^{-5}	5.84×10^{-8}-8.68×10^{-6}	1.09×10^{-7}-1.16×10^{-5}	5.05×10^{-6}-0.10×10^{-3}	1.41×10^{-6}-6.09×10^{-6}
n	0.53	1.52	0.5	0.60×10^{-1}-2.00×10^{-1}	2.72×10^{-3}-3.36×10^{-1}	1.32×10^{-1}-3.20×10^{-1}	3.10×10^{-1}-6.41×10^{-1}	4.70×10^{-3}-5.91×10^{-1}	2.03×10^{-1}-6.70×10^{-1}
Kf	43	1.7	0.43	0.12×10^{-1}-0.54×10^{-1}	1.4×10^{-3}-4.44×10^{-1}	0.3×10^{-1}-1.43×10^{-1}	0.23×10^{-1}-1.03×10^{-1}	7.50×10^{-3}-22.70×10^{-1}	5.00×10^{-1}-2.60×10^{-1}

3.3. Fate of heavy metals in VFCW

To assess the performance of the VFCW for the removal of HM from landfill leachate, a simulation scenario investigated the HM dynamics for the anoxic condition using ferric dewatered sludge as the primary media in the VFCW. The input data of the HMs were inserted into the STELLA software during model calibration and integrated by using the second order Runge-Kutta method with a time step of 0.02 day. Once the model finished its run (i.e., at the end of 215 days), the amount of HM that accumulates into the state variables, and the processes of the model show how much HM is removed by the individual pathways. Therefore, it is possible to calculate the efficiency of the individual processes, such as Ad (Eq. 2), Up (Eq. 5) and Mp (Eq. 6) and De (Eq. 7). A mass balance for all state variables, as simulated by the model, revealed that approximately 89%, 91% and 91% for Ad; 6%, 5.1% and 5.2% for Up; and 1%, 1.15% and 1% for Mp and De for respectively Pb, Cr and Cd. The results from the mass balance show that the major HM transformation routes in this study were adsorption, with a small amount of uptake by the plant. The effect of various parameters on adsorption was studied via batch experiments (Mohammed et al., 2016). The adsorption results of Pb, Cr and Cd ions by ferric dewatered sludge showed a slightly better fit with the Freundlich compared to Langmuir. The Langmuir isotherms data found that ferric dewatered sludge had 40 µg g^{-1}, 130 µg g^{-1} and 30 µg g_{-1} adsorption capacity for Pb, Cr and Cd, respectively. On the other hand, the Freundlich isotherm results showed that a precipitation reaction may occur for Pb and Cd removal where n values > 1 (Mohammed et al., 2016). Lead and cadmium could precipitate to form insoluble compounds with sulphide in anaerobic zones of CWs (Kadlec and Wallace, 2008). Figure 9 indicates, as per the laboratory batch experiment, a sharp rise in the Pb and Cr removal within the first hour, indicating the instant at which the removal of these HM takes place. This can be adduced to the excess of binding sites on highly accessible surfaces, like particles and macropores. Over time, the curve starts to plateau because the rate of removal is much slower. This is due to the accumulation

of metal ions on the binding sites until it reaches equilibrium; and thereafter, sorption would be via intraparticle diffusion in meso- and micropores and/or sorption by the organic matter (Zhou and Haynes, 2011).

The adsorption process in STELLA was described in such a way to calculate the P_e concentration using the Freundlich isotherm. From the model simulation, approximately 526 µg, 518 µg and 640 µg of Pb, Cr and Cd, respectively, adsorbed during the calibration stage of the model run and the corresponding inflow of these heavy metals amounts were 591 µg, 570 µg and 712 µg for Pb, Cr and Cd, respectively. The high amount of HM adsorbed by the media was a result of using ferric dewatered sludge as the main substance and an anoxic condition to elongate the contact time between the media and HM. The overall simulation of Ad is reasonably good in the STELLA model, especially for the adsorption process.

Unfortunately, no data from the use of ferric dewatered sludge as a substrate in CWs for HM removal were found in the literature. Therefore, there is no comparison data. However, several authors used the STELLA program to describe the adsorption process in CWSs and used different kinds of substrate and pollutants. Pimpan and Jindal (2009) show that the maximum cadmium removal simulated by the STELLA software occurred through the accumulation in the soil with mass fraction values of 33.6–76.6% at different hydraulic retention times. Kumar et al. (2011) revealed that 72% of phosphorus removed through the adsorption process simulated by the STELLA software using alum sludge and vertical flow constructed wetland. Accordingly, adsorption seems to be the main process to remove Cd and phosphorous in CWS.

The uptake of HM by plants in this study was low. This primarily because the CWs plants can be contribute to HM removal through substrate stabilization, rhizosphere oxidation, the supply of organic matter for microorganism and the transportation of water to wetland soil, rather than through the direct uptake of metals (Kosolapov et al., 2004).

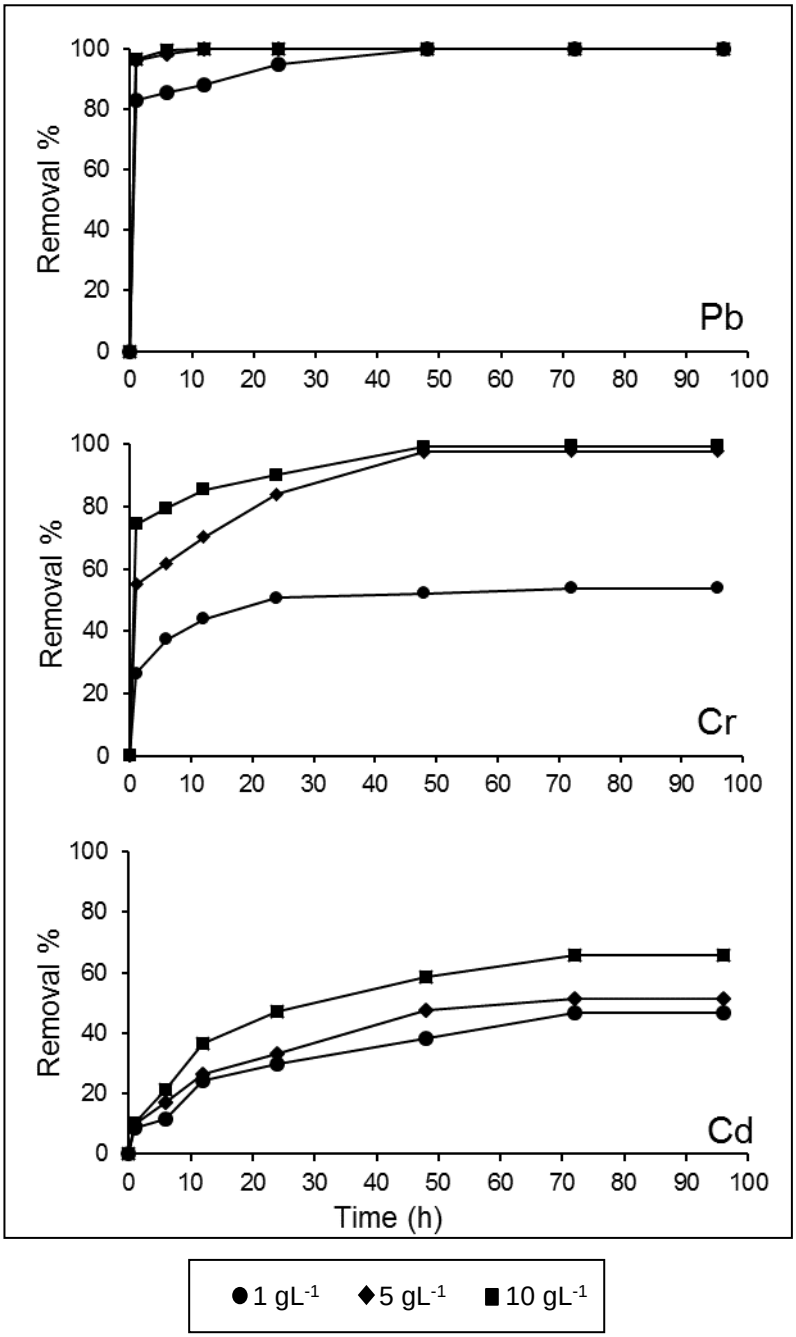

Figure 9. Removal efficiency of heavy metals by ferric dewatered sludge at different sludge dosage and contact time.

4. Conclusion

In this study, a dynamic model for HM transformation in a vertical flow constructed wetland and using ferric dewatered sludge as main substance was developed using STELLA. The mechanisms used in this modelling process included adsorption, uptake by the plant and

plant growth. The most significant pathway of heavy HM retention was adsorption. In terms of the model's sensitivity, the adsorption parameter was the most important factor. The model was calibrated in order to achieve predictions that were close to the experimental data. A reasonable agreement was obtained between the measured and predicted results. A mass balance showed that up to 89%, 91% and 91% of the removal of HM was through adsorption, which is highly significant, whereas removal through the plants is about 6%, 5.1% and 5.2% for Pb, Cr and Cd, respectively. This study demonstrates that the developed mathematical model could be used to describe the Pb, Cr and Cd removal process from landfill leachate in the VFCW using ferric sludge.

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