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Modeling BOD removal in free water-surface constructed wetlands with variable residence time-based methods

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Abstract

Constructed wetlands (CWs) have been applied for several years in the removal process pollutants from secondary treatment plants and stormwater. In this paper, the Variable Residence Time (VART) model for solute transport in streams was extended to simulate the BOD removal process in free water surface flow constructed wetlands (FWS CWs). The double layer concept of the basic VART model was extended to FWS CWs, contemplating the wetland as a similar layer system with water column (WC) and root zone (RZ). The RZ was further divided into advection dominated upper root layer, and diffusion dominated the lower root zone. Two distinctive models were developed based on this, namely VART-BOD-F model that incorporates the first-order decay of BOD and VART-BOD-M model that combines multiple Monod kinetics in the wetland system. Unlike conventional wetland methods, both models involve dynamic root zone concept with changing reactive depth. The application of mass exchange between the water column and dynamic diffusion root zone was the distinct feature of the models. From time series data based simulation test results, coefficient of determination (r^2) and root mean square error (RMSE) values for the VART-BOD-F model ranges from 0.79 to 0.91 and 0.69 to 1.84, respectively, while for VART-BOD-M model varies from 0.83 to 0.96 and 0.63 to 1.77 respectively. Furthermore, the performance of the second model (VART-BOD-M model) was tested later with another data obtained from Manzala Wetland, Egypt (Deng et al., 2016). When the two models compared, including with the exiting DND model, the VART-BOD-M model, which involved various mechanisms showed better values of r2 and RMSE, and capable of following reasonably best fit concerning observed effluent concentration. Although the VART-BOD-M model has better efficiency than the VART-BOD-F model, it involved several parameters and certain assumptions that might have compromised the results and analysis. Hence, the VART-BOD-M model can be a better tool for simulating the BOD removal process in FWS CWs when there is data available for defined parameters.

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Modeling BOD removal in free water-surface constructed wetlands with variable residence time-based methods

1 Introduction

In this section, the background information on modeling organic matter removal process in free-water surface wetlands is presented. The primary and specific objectives of this paper are discussed following the background information. The end of this section contains some of the limitations.

1.1 Background

Constructed wetlands (CWs) have been applied for several years in the removal process of BOD and other pollutants from the effluent of secondary treatment plants and stormwater. The effluent coming from biological wastewater treatment plants mainly contains complex and soluble organic compounds, biodegradable substrates, and soluble microbial products (Duncan and David, 1999). The decomposition of litter in vegetated wetlands has a significant contribution to the increasing concentration of organic matter in the wetlands (Brix, 1997). BOD removal process in free -water surface (FWS) CWs is supported by various physical and biogeochemical transformations of soluble organic matter.

Free-water surface CWs have shallow water depth opened to the atmosphere with floating and emergent macrophytes where organic matter is removed by sedimentation, filtration, oxidation, reduction, adsorption, precipitation, and biological degradation with microbially stimulated processes (Hemond and Benoit, 1988, Brix, 1997, Mitchell and McNevin, 2001, Kadlec and Wallace, 2009 a). Investigation of King et al. (1990) and Edenborn (2004) show, sedimentation and aerobic BOD degradation of BOD is limited to water column and interface of soil and water surface of the wetlands, except during high organic loading. But other studies show, organic matter in the rhizosphere is microbially degraded both aerobically near the live root system and anaerobically beneath the root of macrophytes (Kadlec and Wallace, 2009 b, Vymazal, 2011).

Extensive efforts have been made in developing numerical models to increase the removal efficiency of the wetlands, to introduce improved design techniques, and to get a better understanding of complex processes and interactions between water, soil matrix, vegetation, and microorganism in the wetland system. Some the models developed are based on assumption of classic first-order organic matter degradation with constant initial concentration and with plug-flow analysis primarily approximating hydraulic conditions, and on “black-box” approaches overlooking various processes mechanisms undertaking in the wetland system (Chen et al., 2006, EPA, 1999, Naz et al., 2009, Tomenko et al., 2007). The black-box modeling approach has no distinct chemical kinetic consideration and theoretical substantiation concerning the molecularity of organic matter reactions taking place (ReVelle et al., 1965). Various investigations have been carried out in developing processed based numerical modeling of BOD removal in FWS CWs (Kumar and Zhao, 2011, Meyer et al., 2015). But the majority of them didn’t consider advective-dispersive exchange, the difference in concentration and chemical kinetics of organic matter. The constructed wetlands model-based review of several authors showed the linear regression models developed various times that make use of the influent-effluent dynamics of constructed wetlands failed to reflect the complex processes taking place in the wetlands (Rousseau et al., 2004, Langergraber, 2008).

To address the limitation of the numerical models that are based on the first-order kinetic and linear regression models relating to 2-3 variables, processes-based models were recommended to contemplate the various reactions and individual processes taking place in the wetlands (Kumar and Zhao, 2011). The model developed by (Hantush et al., 2013) simulated the removal of nitrogen and phosphorous in the flooded wetlands considering the multifaceted reactions and dynamics of the various process. Aboukila and Deng (2018) developed a variable residence time- based tool to simulate the removal process of total phosphorous and ammonium in free water surface wetlands. The simulation result of their model demonstrates the efficiency of a process-based modeling approach to predict various pollutants and to design constructed wetlands. The carbon cycling simulation model developed by (Sharifi et al., 2013) reflects multifaceted biogeochemical interactions that affect carbon cycling in flooded wetlands. One of the models developed during this study period was called the VART-BOD model published by Deng et al. (2016) and developed by integrated Monod kinetics of microbial activities with other mechanisms that involve in BOD removal process in FWS CWS.

1.2 Objectives of the Project

The primary goal of this thesis work is to present two distinct models developed during the study that simulates BOD removal in FWS CWs. The first one was named the VART-BOD-F model, and the second one, already published by Deng et al. (2016), was called VART-BOD-M. Intending to produce that, the two models were developed by extending the mass exchange simulation concept of basic Variable Residence Time model (VART) developed by Zahraeifard and Deng (2011) that incorporates the first order BOD decay rate to VART-BOD-F and Monod Kinetics to VART-BOD-M in water column and root zone of the FWS wetland.

The specific purposes of this paper are:

- To describe the conceptual model for BOD removal process in FWS CWs,
- To show the competence of the numerical models based on first-order reaction rate and double Monod Kinetics for BOD removal process in FWS CWs
- To show the capability of the two VART-BOD-F and VART-BOD-M to DND model of unsteady-state condition applied in 12 months' water quality data of Gustine city FWS constructed wetland.

1.3 Limitations

One of the main constraints during the study period was the availability of limited data and information for the existing wetland parameters in the study location to simulate and test the model. But, some of the parameter values were transposed from other experimental works of literature and books that have similar wetland characteristics. Later in 2016, the performance of one of the two models (VART-BOD-M) was tested with additional data from a constructed wetland in Egypt (Deng at el., 2016). Furthermore, the presentation of this thesis work after completion was delayed due to personal problems and now became a challenge in re-writing the report differently due to the earlier publication by of a portion from this thesis work by (Deng at el., 2016).

2 Methodolgy

This section covers the methods used to develop the BOD removal models, including Literature Review, Study Area and Location, Conceptual Model, Mathematics of the Modeling, Model Parameter Estimation, and Sensitivity Analysis. The location of the study area and the data collected for simulation of the models were comprised under the Study Area. The conceptual model included in this section illustrates the layers of the wetland system and the various processes involve in organic matter removal. Then, the mathematics of the modeling was described in detail under this section. At the end of the section, the model parameter estimations and the sensitivity analysis were covered.

2.1 Litrature Review

An extensive and critical literature review was done during this paperwork to understand various processes involved in pollutant removal and the different numerical methods developed to simulate organic matter and other contaminants removal process in FWS constructed wetlands. From the review of the literature, the groundwork was established for the development of variable time-based models to simulate the BOD removal in FWS CWs.

2.1.1 *Types of constructed Wetlands*

Constructed wetlands (CWs) are engineered secondary wastewater treatment systems commonly designed to remove pollutants by mimicking a natural process in wetland soil, microbial activities, an assemblage of various vegetation (Babatunde et al., 2009, Haberl et al., 2003). Based on different criteria, government agencies, books, and authors classify constructed wetlands into several classes such as restored wetlands, created wetlands, treatment wetlands, recreation, mitigation, and habitat for wildlife wetlands (EPA, 1993, Keefe et al., 2004). From the hydraulic aspect (flow directions and water surface level), they can also be classified as free-water surface flow (FWSF), and sub-surface flow (SSF) CWs (Kadlec and Knight, 1996b, Shutes, 2001). The SSF wetlands, commonly adopted in Europe, Australia, and South Africa, can be further divided into a vertical flow and floating raft constructed wetlands (Brix, 1994). Horizontal free surface flow (HSF) CWs, dominant in North America (Vymazal, 2005), have a shallow water depth of low flow velocity over substrates and contain rooted macrophytes submerged partially in the water (Shutes, 2001).

Constructed Wetlands are essential for aquatic environment protection, social and economic development (Bergstrom et al., 1990). The primary functions of constructed wetlands are flood and coastal protection, groundwater recharge, sediment trapping, contaminant removal, global geochemical cycling, and increased agricultural yield (Kennedy and Mayer, 2002). Furthermore, Wetlands can be places for recreation (hunting, fishing, and bird watching), habitat for wildlife (EPA, 1993), and have a considerable role in a hydrologic cycle (Bullock and Acreman, 2003). Though numerous functions and importance are evident, constructed wetlands are mainly implemented for secondary wastewater treatment purpose due to their economic feasibility, ease and flexibility to control (Solano et al., 2004), reliability on natural processes and low impact on environmental than conventional wastewater treatment methods (Siracusa and La Rosa, 2006).

Nonetheless, the focus of this study will be on free surface horizontal flow constructed wetlands.

2.1.2 *Wetland mechanisms involve in BOD removal*

Modeling of organic matter removal process in treatment wetlands has substantial support in predicting the level of biodegradable organic matters transported from municipal wastewater treatment plants (WWTPs), which lead to degradation of dissolved oxygen in an aquatic ecosystem. Generally, treatment wetlands are combined with biological WWTPs to reduce the level of BOD in the effluent. Typically, the effluent of biological wastewater treatment plants is rich in several complex and soluble organic compounds, biodegradable substrates, and soluble microbial products (Duncan and David, 1999).

Wetland vegetations are one of the most substantial components in FWS wetlands design. The most common types of wetland plants found in free-water surface wetlands include submergent, emergent, floating, and rooted macrophytes. Several investigations carried out to identify the role of wetland vegetations in organic matter removal process in wetland system in terms absorbing and accumulating organic matter in their tissues, providing medium and habitat for growth and microbial activity , and act as the channel of oxygen transmission for rhizosphere to carry out aerobic biodegradation (Akratos et al., 2008, Naz et al., 2009, Vymazal, 2001). The research conducted by Langergraber (2005) showed the role plant uptake of organic matter and other nutrients in sub-surface flow wetlands in the simulation study. But other several researchers later controverted this conclusion and showed their role in indirect BOD removal by providing an essential environment for microbial activities (Baldizón et al., 2002, Brix, 1994, Brix, 1997, Scholz and Xu, 2002).

The investigation of Sankararajan et al. (2017) presented the influence of relative humidity in the BOD removal process in the CWs. Furthermore, the presence of oxygen in constructed wetlands is significant for aerobic bacteria to grow and, ultimately, for the removal of pollutants. Kadlec and Knight (1996b) discussed the oxygen demanding process to remove BOD in constructed wetlands. Microorganisms play a vital role in the BOD removal process in constructed wetlands. The experiment supported-research carried out by Polprasert et al. (1998) showed the critical role of bacteria in the removal process of organic matter in CWs by incorporating the kinetic model with biofilm kinetics.

Various physical and biogeochemical processes affect the organic matter removal in FWS wetlands, including sorption, volatilization, sedimentation, filtration, dispersion, advection, diffusion, exchange and mixing, and oxidation (Kadlec and Wallace, 2009). The wetland models developed various times, which reflected a combination of these processes in their model parameters showed better capability in predicting the pollutants removed by the wetlands (Giraldi et al., 2010, Kumar and Zhao, 2011).

2.1.3 *Review of BOD removal models in FWS wetlands*

The design and operation method of CWs in performing organic matter removal process effectively depends on complex interactions undergoing in the wetlands. For this reason, several CWs models have been developed to increase the removal efficiency of wetlands. The models developed range from simple simulation or black-box models (empirical, numerical, and statistical) to dynamic and complex process-based models (Nabizadeh and Mesdaghinia, 2006, Giraldi et al., 2010, Kumar and Zhao, 2011). Many research studies have been done in developing several ecological models to simulate various contaminants in CWs including rules of thumb and regression equations (Rousseau et al., 2004), first-order models, time-dependent retention models, tank-in-series or plug inflow models, multiple regression and neural networks model (Akratos et al., 2008, Tomenko et al., 2007) and one-dimensional transport with inflow and storage (OTIS) numerical solute transport models (Chen et al., 2006, Kadlec, 2000, Keefe et al., 2004, Kumar and Zhao, 2011). Therefore, the excessive effort made to develop several models to acquire better understanding of the convoluted physical, chemical and biological interdependent processes taking over at a time in constructed treatment wetlands shows the importance of alternative process-based numerical models in treatment wetlands as optimum designing criteria and in treatment efficiency improvement (Richardson et al., 1996, Tomenko et al., 2007, Langergraber, 2008, Kumar and Zhao, 2011).

Hijosa-Valsero et al. (2010) used four statistical models to predict the removal level of organic matters and other pollutants in CWs with respect to wetland plants and other various Physico-chemical parameters. The data used for the modeling process was secondary data obtained from past study and contains different Physico-chemical parameters, including temperature, varying PH, conductivity, the concentration of dissolved oxygen, and redox potential. Different statistical operations, like stepwise regression, clustering tree diagrams, classification and regression trees, and redundancy analysis, were carried out using various software. The findings of the four statistical models are different from non-contradicting outputs, which illustrate Physico-chemical parameters, dissolved oxygen amount, and the presence of macrophytes in the wetlands affect the level of organic and other pollutants removal considerably.

Polprasert et al. (1998) evaluated the role suspended and biofilm bacteria in the removal process of organic matter in HFWS CWs by incorporating the kinetic model with biofilm kinetics based on the experimental data of three laboratories and one pilot-scale FWS constructed wetland at the same climatic condition. The HRT considered in the study was calculated by averaging the inlet and outlet rate, neglecting the effect of evaporation for the pilot-scale wetland. Subsequently, the biofilm kinetics was done in the root matrix of laboratory-scale wetland. All the model parameters used in this method, including temperature Coefficient, dispersion Number, and reaction rates for the suspended biomass, reaction rates for biofilm biomass, and biofilm thickness, were from laboratory experiments and literature. The result of the biofilm kinetic model simulation clearly shows the increase in the efficiency of organic matter removal due to the consideration of biofilm bacteria in HFS CWs.

Damk ohler number Distribution" (DND) modeling approach was extended and applied by Carleton and Montas (2007) to non-steady state flow conditions on Gustine Wetlands in Gustine, California. The model presumes a physical process of mixing and transport of pollutants as stochastic-convective flow (ratio between the velocities in any pair of stream tubes is persistent with mean velocity variation with respect to flow alteration), and neglects diffusive, transverse and mixing with dispersion. At a steady-state condition, the flow was considered as two dimensional with variation in vegetation density transverse to the flow direction. Another presumption of the model is that a group of local stream tubes with different velocities and removal coefficient is a function of vegetation surface area density transverse to the flow. The concept of extending the model to unsteady flow contains few presumptions like a constant stream- tube (reaction rate coefficient) and volume of flow, and variation of flow velocity with a change in gradient but not with the normal depth of flow.

The evaluation of the DND model for the application was conducted on a series of five correspondingly sized, rectangularly shaped, vegetated cells of Gustine wetland using BOD_5 removal data of 13 months. The simulation result indicates the same RTD shape parameter with a previous analysis of Carleton and Montas (2007) during the steady-state condition. Overall, a good correlation between measured and effluent BOD_5 concentration was observed. But the model generally has limitations in considering constant RTD with respect to time, neglecting depth of flowing water, consideration of stochastic-convective flow, and consideration of vegetation density or depth only along transverse flow direction ignoring several relevant parameters and processes in the wetland. To fully understand the significance of modeling in multipart processes of pollutants removal in treatment constructed wetlands, further investigation of different modeling processes is crucial.

2.2 Study Area

The City of Gustine, located approximately 29 miles west of Merced in California, is a small town with an approximate area of 1.6 square miles dominated by agriculture (EPA, 1999). The 2010 US Census shows, the population of the city was 5,520. The master plan of the city updated in March 2003 indicates the wastewater treatment plant of the city has been receiving an average of 1.8 million gallons of wastewater per day (City of Gustine, 2003). The highest portion (two-third) of organic load received by the treatment plant comes from diary processing industries and the rest from other sources. Out of the total wastewater received, two-third of the organic (EPA, 1993). In the beginning, the wastewater system was designed with 14 aeration ponds working in series. The EPA (1999) report indicates the average BOD_5 concentration of wastewater treatment was 1,200mg/l. This concentration is beyond the average standard of 30 BOD/30TSS requirements of USEPA (EPA, 1993).

To improve the effluent treatment system efficiency, FWS CW was implemented from 1986 to 1987 with five parallel and identical rectangular vegetated cells (1A, 1B, 1C, 1D, and 2A) following the pilot wetland cell study (EPA, 1993). But, the most current documentation from City of Gustine, the "Wastewater Treatment Facilities Master Plan Update, (2005)", indicates the wetland system has six cells operating in parallel. The data in this report reflected the study prior to the enlargement of the system when it contained only five cells. According to the EPA (1999) report, the wetland has approximately $42055ft^2$ free water area. Figure 1 shows the location and visibility map of the wastewater treatment facility and wetland location in the city of Gustine. The schematic drawing in Figure 2 shows how the wetland cells operate in parallel.

The influent and effluent BOD_5 data were extracted for all the five cells carefully by digitizing from unsteady state DND modeling publication of Carleton and Montas (2007) to apply for VART-BOD modeling approach in this paper. The average water flow velocity for Cells 1A, 1D and 2A were in the range of 30-35 m/d, but for the two other cells (1C and 1B) were in the range of 10-17m/d (Carleton and Montas, 2007). The mean flow velocity was considered for testing the VART-BOD model.

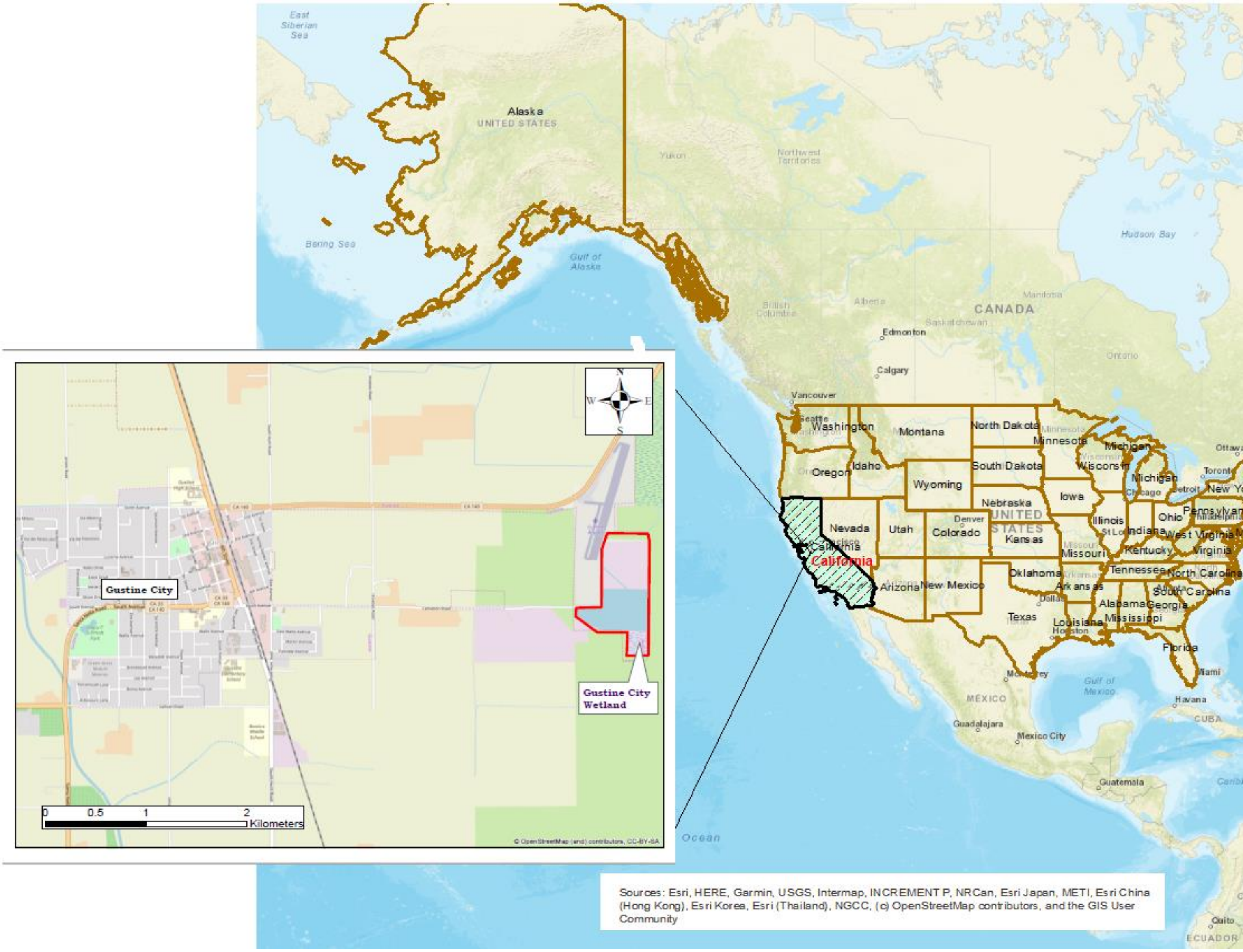

Figure 1. Gustine City wastewater treatment facility visibility and location map (Not-to-Scale)

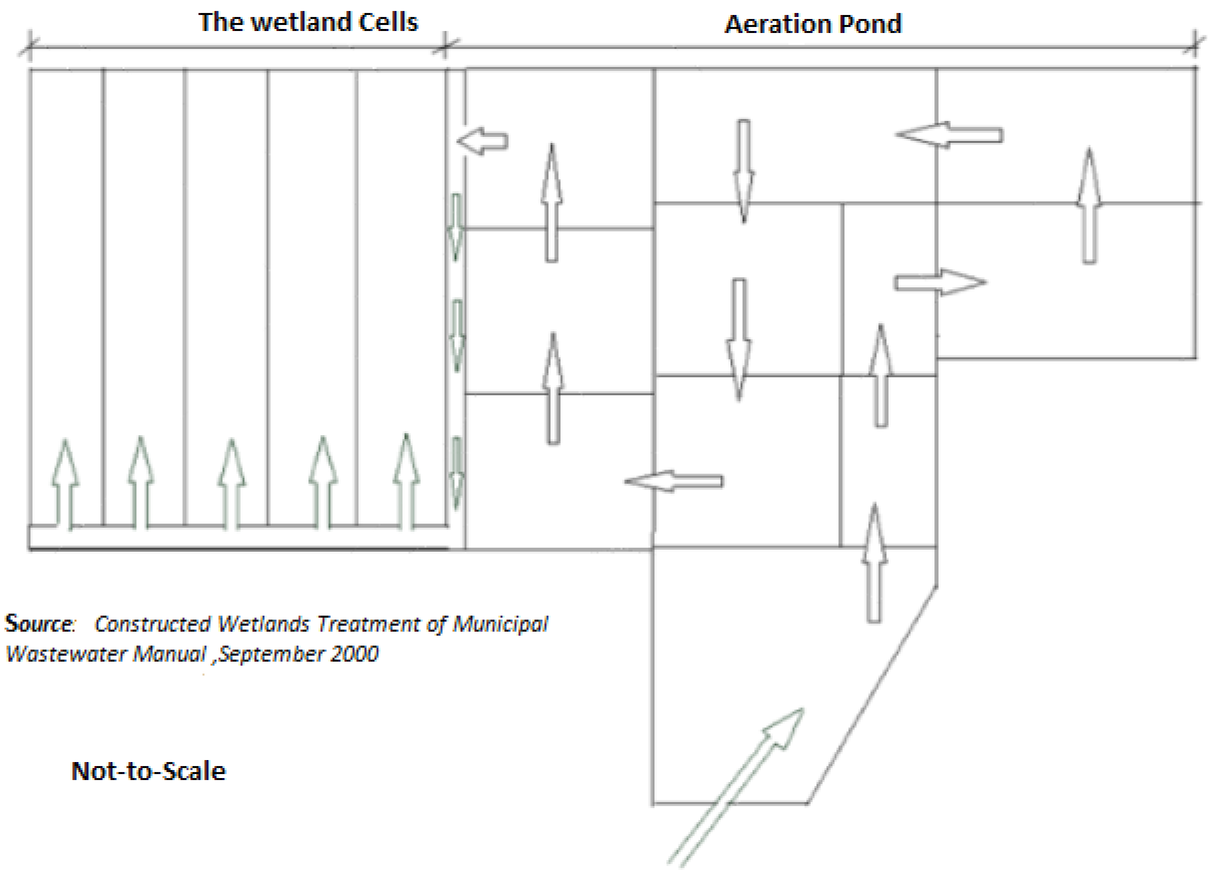

Figure 2. Schematic representation of Gustine City wastewater treatment facility and the Constructed wetland system.

2.3 Coceptual Model Development

Free water-surface wetlands are fundamentally characterized by a large suite of microbials and various biogeochemical processes that influence the removal of organic matter in the water column and root zone of the wetland system (Duncan and David, 1999, Kadlec and Wallace, 2009). The development of BOD removal methods in this paper is based on these mechanisms that influence the organic matter decay in the wetland system, including microbial degradation, advection, dispersion, diffusion, and exchange in between water column and root zone. The following basic assumptions were employed during the extension of the conventional VART model Zahraeifard and Deng (2011) to BOD removal process mechanisms. To apply the two transient storage zones concept of the conventional VART model to BOD simulation methods, FWS CWs were considered as a double-layered system that consists of the water column and root zone.

The water column is the upper vegetated layer exposed to the atmosphere where organic matter is degraded by aerobic microbial activities. Whereas, the root zone of the wetland is the soil-based system of wetland that supports emergent macrophytes and provide food for their life. The root-zone of FWS CWs was further divided into two sub-zones based on the type of microbial activities, including the aerobic upper sub-root zone dominated by advection process and anaerobic lower sub-root zone dominated by diffusion (Deng et al., 2016).

2.3.1 *The Water Column (WC)*

The water column of FWS CWs is part of the wetland system exposed to the atmosphere and mainly aerobic except during the high loaded BOD inflow condition (Kadlec and Wallace, 2009 a). The organic matter that comes from the effluent of wastewater treatment systems, stormwater, and decomposition of detritus inside the wetlands is principally degraded through aerobic bacterial activities in the water column (Hammer, 1989).

Among several biogeochemical processes that take place in the water column, advection, dispersion, aerobic decay, and exchange of organic matter between the water column and the root zone will be considered to model the BOD removal process in FWS CWs. The most common chemical expression presented by Kadlec and Wallace (2009) for aerobic BOD decay can be re-written for the water column of FWS CW as:

$$\mathrm{CH_2O}_W + \mathrm{O_2} \xrightarrow{\textit{Aerobic Bacteria}} \mathrm{CO_2} + \mathrm{H_2O} + Biomas_{groth} \quad (1)$$

Where $\mathrm{CH_2O}_W$ -represents BOD at water column

The aerobic microbes decompose the BOD for their life, and as a result new biomass will be formed. The increase in biomass concentration has an essential role in the modeling of organic matter removal and considered in Monod Kinetics.

2.3.2 *The Rhizosphere (Root Zone/RZ)*

The root zone of the FWS CWs is the subsurface layer below the water column that provides a substrate for the life of emergent plants and habitat for micro-organisms. The dynamic root zone was further divided into advection dominated the upper sub-root zone, and diffusion dominated the lower root zone (Deng et al., 2016). The upper root zone is aerobic due to the presence of released oxygen from macrophytes through their roots. Though, several publications show that BOD in reduced area of oxidized upper root zone is degraded by multi-step reaction of anaerobic process (Cooper and Centre, 1996, Kadlec and Wallace, 2009 b) , aerobic microorganisms found in soil layer are the main agents in decaying BOD in the oxidative layer of the wetland soil (Brix, 1987). The primary mechanisms of BOD removal in the upper sub-root zone include advection, the mixing, and exchange between the water column and the lower diffusion dominated the root zone.

The lower sub-root zone is a deeper part of the root zone below the layer exposed to the oxygen released by the macrophytes root system. The BOD removal in this sub-root zone is supported by anaerobic microbial processes, diffusion and the BOD exchange with the advection dominated upper sub-root zone. The sizes of the two layers of the root zone are not constant due to the nature of diffusion processes that change with time about the BOD concentration gradient (Deng et al., 2016). Anaerobic BOD decay in diffusion dominated root zone follows various steps to convert organic matter into methane and carbon dioxide (Jinadasa et al., 2019). Initially, the organic matter will be hydrolyzed into a soluble form of compounds ready for fermentation bacteria consumption (EPA, 1999). The fermentation of hydrolyzed organic matter yields volatile fatty acids of various types. Among several volatile fatty acids produced during the fermentation, lactic acid is produced in soil sediment of an extremely reduced condition in conjunction with heavy metal removal (Edenborn, 2004). Making an allowance for this and considering the limited amount of anaerobic BOD degradation in FWS CWs, application of the VART-BOD modeling process ponders only acetic acid metabolic pathway for the anaerobic reaction of the wetlands root zone as shown in Figure 3. Jinadasa et al. (2019) and Kadlec and Wallace (2009 c), fermentation of hydrolyzed organic matter to acetic acid can be expressed by the chemical reaction presented in Eq (3).

$$C_6H_{12}O_6 \quad \rightarrow \quad 3\ CH_3COOH + H_2 \qquad (2)$$

The main product formed during the anaerobic reaction in flooded soils and sediments is acetic acid (Vymazal, 1999). Strictly Anaerobic sulphate-reducing and methanogen bacteria then use the end-products of fermentation. Therefore, the two types of bacteria play an essential role in organic matter decomposition and carbon cycling predominantly in shallow depth of wetland root system (Kadlec and Wallace, 2009 b, Vymazal, 1999). The final stage of the anaerobic process is methanogenesis, which is carried out by several species of methanogenic bacteria producing methane as the major product from acetic acids (Kadlec and Wallace, 2009 c). The chemical reaction for methanogenesis process most commonly written as:

$$CH_3COOH + 4\,H_2 \rightarrow CH_4 + 2\,H_2O \qquad (3)$$

The above chemical reaction expressions of the organic matter and other biogeochemical mechanisms displayed on conceptual model on Fig.3 were used to define VART-BOD model parameters.

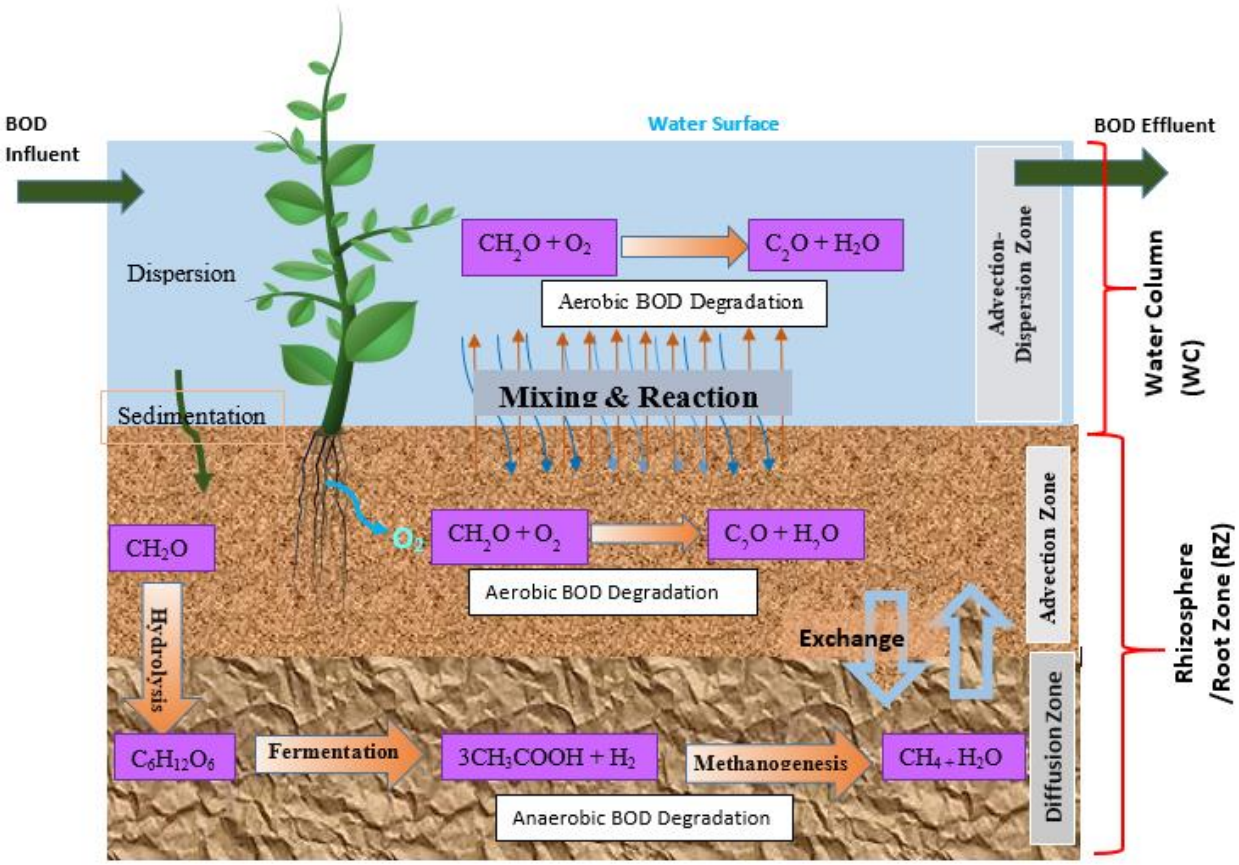

Figure 3. Conceptual model demonstrating biogeochemical mechanisms for BOD removal in FWS constructed wetlands

2.4 Mathematics of modeling BOD removal process in FWS CWs

The BOD removal in FWS CWs involves various mechanisms. Based on the processes in the conceptual model shown in Figure 3 and using the proven VART model equations (Deng and Jung, 2009) for longitudinal dispersion and transport of solutes in streams, two distinct models were extended for the BOD removal process in FWS CWs. Both models involve mixing and reactions between the water column and the root zone. Aerobic and anaerobic BOD degeneration processes were considered using Multiple Monod kinetics of microbial activities.

To distinguish the competence and advantages between the “process-based” and “black box” modeling approach, new modeling techniques were employed for the typical first-order reaction and the process-based double Monod reactions in both models (VART-BOD-F and VART-BOD-M) respectively. In the same manner as that of the basic VART model, the new BOD removal process models were based on MATLAB code that incorporates advection-dispersion dominated water column (WC), and advection-diffusion dominated root zone (RZ).

2.4.1 ***VART-BOD modeling involving first order decay (VART-BOD-F)***

A first-order modeling approach was a common application in constructed wetland design and pollutant removal processes, including organic matters, nitrogen, phosphorus and suspended solids (Kadlec and Knight, 1996a, Mitchell and McNevin, 2001). But some researches showed later the limitations of the first-order kinetic method in simulating the removal of pollutants in wetlands (Kadlec, 2000). One of the main constraints of first order model is merging and oversimplifying complex reactions undertaking in the wetlands system. However, the first-order model models are still applicable in constructed wetland design where there is data constraint to define multiple parameters of most process-based models. In this paper, the first order reaction of organic matter decay in FWS CWs was incorporated with the basic VART model developed by Zahraeifard and Deng (2011) and extended to apply for the BOD removal process in the wetlands.

From Eq (1), the rate of concentration of CH_2O (BOD) removed at a time t considering the first order reaction rate:

$$\frac{\Delta B}{\Delta t} = -KB \tag{4}$$

Where K-the first order rate constant

B- BOD concentration at time t

$\frac{\Delta B}{\Delta t}$ - Change of BOD concentration with time

The negative sign in Eq (4) indicates the decreasing rate of BOD concentration at the effluent.

The development of the VART-BOD-F model is based on a single substrate concentration-dependent reaction rate in both the water column and the root zone of the wetland system. The sink terms of the model were adopted from the rate of first-order BOD decay in Eq (4) and applied for the water column and the root zone BOD concentration. The longitudinal dispersion of BOD concentration was considered by employing the Fickian dispersion coefficient in the water column, and the diffusion in the root zone was represented by the effective diffusion coefficient.

Therefore, the VART-BOD-F model incorporating first order BOD decay can be presented as:

$$\frac{\partial B_W}{\partial t} + U\frac{\partial B_W}{\partial x} = K_s\frac{\partial^2 B_W}{\partial x^2} + \frac{A_{diff}+A_{adv}}{A}\frac{1}{Tv}(B_R - B_W) - KB_W \tag{5}$$

$$\frac{\partial B_R}{\partial t} = \frac{1}{Tv}(B_W - B_R) - KB_R, Tv = \begin{cases} T\,min\,For t \leq Tmin \\ t for t \geq Tmin \end{cases} \quad (T\,min > 0) \tag{6}$$

$$A_{diff} = 4\pi D_R t_R \;, \; t_R = \begin{cases} 0 for t \leq Tmin \\ t - T\,min\,For t \geq Tmin \end{cases} \tag{7}$$

Notation of terms:

B_W and B_R are Concentrations of BOD_5 in water column and root zone respectively(mg/l) ; A is the cross-sectional flow area of water column [m^2] ; A_{adv} and A_{diff} are the areas [m^2] of water advection and diffusion dominated zones respectively; K is the first order rate constant [day^{-1}]; T_{min} is the minimum mean residence time [s] for BOD to travel through the water column; T_v is the actual varying residence time of BOD [s]; K_s is the longitudinal Fickian dispersion coefficient [m^2/s]; D_R denote the effective diffusion coefficient [m^2/s] in the root zone and t_R represents the time [s] since the BOD release from root zones to the water column.

Eq (4) to (7) make up a new model called VART-BOD-F, for predicting the BOD removal process in FWS wetlands. The BOD removal process in the water column is defined in Eq (5), while in the root zone is described in Eq (6). The two terms, KB_W and KB_R , in Eq (5) and (6) were comprehended from the first order BOD decay rate and applied to water column and root zone system. The spacing used between grid cells was 5m, and the time step length was 360s. Incorporating influent concentration as upper boundary conditions and setting zero initial BOD concentrations for water column and root zone, programming of the model was performed by Semi Lagrange approach MATLAB Code to work out numerical analysis and to simulate the model.

2.4.2 *VART-BOD modeling involving Monod Kinetics (VART-BOD-M)*

The basic VART model was also extended to incorporate the various biochemical reactions involved in the BOD removal process in FWS wetlands. Monod (1949) defined the association of microbial growth to organic matter decay in wetland using Monod Kinetics. The basic concept of biodegradation kinetics is to consider the microorganisms as the main decomposers of the substrate (organic matter). Based on the research done by ReVelle et al. (1965), the second-order reaction mechanism for organic matter degradation, aerobic, or anaerobic degradation of organic matter with microbial activity is functionally dependent on the concentration of substrate (organic matter) and increased concentration of bacteria). Increased rate of bacterial growth and oxidized-reduced products during aerobic and anaerobic reactions are related to the rate of organic matter decay to the concentration of biomass and substrate Monod (1949).

Among several specific microbial growth rate equations developed, double Monod Kinetic equation was widely applied in BOD removal processes (Monod, 1949, Yassine et al., 2013). Therefore, the net biomass growth rate of double Monod kinetics is:

$$\frac{dX}{dt} = \mu X - K_D X \tag{8}$$

Where X- biomass concentration, μ-specific growth rate & K_D bacterial death rate constant.

The specific growth rate for substrate- S and half saturation constant-K is commonly expressed as:

$$\mu = \mu_{max}\left(\frac{S}{K+S}\right) \tag{9}$$

Where μ_{max} - maximum specific growth rate

From Eq (10) and (11), the net growth rate of bacteria can be expressed as:

$$\frac{dX}{dt} = \mu_{max}\left(\frac{S}{K+S}\right)X - K_D X \tag{10}$$

Where μ_{max} - maximum specific growth rate, S-substrate, K-Half saturation constant, X- biomass concentration and K_D bacterial death rate constant.

For aerobic bacterial growth limited by multiple substrates (S_1 and S_2) with half saturation constant K_{s1} and K_{s2} respectively, the double Monod Kinetics Eq (10) for aerobic bacteria growth rate, neglecting the death rate can be described as:

$$\frac{dX_{(Aero)}}{dt} = \mu_{\max(Aero)} \left(\frac{S_1}{K_{s1}+S_1} \right) \left(\frac{S_2}{K_{s2}+S_2} \right) . X_{(Aero)} \qquad (11)$$

Where $\mu_{\max(Aero)}$ -maximum specific aerobic growth rate and $X_{(Aero)}$- aerobic bacteria concentration.

Redefining variables in Eq (11) for the limiting substrates and half saturation constants for aerobic BOD decay condition, the rate of aerobic bacterial growth for water column can be described as:

$$\frac{dX_{Aero}}{dt} = \mu_{\max(Aero)} \left(\frac{C_{oc}}{C_{oc} + K\, s_{oc}} \right) \left(\frac{C_{DO}}{C_{DO} + K\, s_{DO}} \right) . X_{(Aero)} \qquad (12)$$

Where X_{Aero}- is aerobic bacteria concentration(mg/l); $\mu_{max\, aero}$-Maximum growth rate of aerobic bacteria (day^{-1}) ; $Ks_{\ OC}$ - Half saturation constant for organic carbon; C_{DO} - Concentration of dissolved oxygen (mg/l), ; $K\, s_{DO}$- Half saturation constant for dissolved oxygen (mg/l); C_{OC} - Concentration of dissolved carbon (mg/l); $K\, s_{DC}$-Half saturation of dissolved carbon (mg/l); $K_{\ D1}$- death rate constant of aerobic bacteria (day^{-1}).

The BOD decay in the upper root zone is aerobic due to oxygen released through the roots of the wetland plants. Beneath the live plant root system of the root zone, organic matter mainly decays anaerobically. The anaerobic degradation of soluble organic matter is a multi-step process of fermentation followed by methanogenesis to produce volatile fatty acids and methane, respectively (Vymazal, 1999, Cooper and Centre, 1996, Kadlec and Wallace, 2009). The amount of organic matter converted to volatile fatty acid in soil sediment is usually combined with mineralization (Segers and Kengen, 1998). Therefore, hydrolysis and fermentation processes associated with volatile fatty acid converting- bacteria were not considered explicitly in anaerobic BOD degradation process to simplify the complexity of the chain reaction rate order. From this presumption, methanogenic bacteria use the converted amount of acetic acid from organic matter as a sole substrate during the methane production process, excluding hydrogen and formats. The reason behind this is evidence from publications that indicate most of the methane (70%) production is from acetate in wetland soil sediment (Drake et al., 1996, Goodwin and Zeikus, 1987, Segers and Kengen, 1998). The investigation of Husain (1998) pointed out that anaerobic bacteria (methanogenic bacteria) growth rate is mainly determined by the inhibition of acetic acid concentration.

Therefore, inhibition of the acetic acid on the methanogenic process is taken into account in methane-producing bacterial growth rate. Hence, the fermented acetic acid and methane forming bacteria yields methane as a product and increased the concentration of methanogenic bacteria. Therefore, the rate of anaerobic bacteria growth is proportional to the amount of acetate removed with respect to acetic acid inhibition coefficient. From this basic idea, the amount of acetic acid converted during the fermentation process can be assumed to be equivalent to the concentration of BOD used as a substrate for methane forming bacteria during methanogenesis.

Based on Monod Kinetic equation described on Eq (8), the growth rate of anaerobic bacteria in diffusion dominant lower root zone of the wetland system can be written as:

$$\frac{dX_{(Anaero)}}{dt} = \mu_{(Anero)} X_{(Anaero)} - K_{D2}. X_{(Anaero)} \quad (13)$$

Where μ_{Anero} is the specific growth of anaerobic bacteria.; $X_{(Anaero)}$- Concentration of anaerobic (methanogenic) bacteria in root zone (mg/l) and K_{D2} -death rate constant for anaerobic bacteria (day^{-1})

The specific growth rate of anaerobic bacteria with inhibition coefficient and half saturation constant of acetic acid is generally written as:

$$\mu_{Anero} = \mu_{\max(Anero)} \left\{ \frac{C_{Ac}}{K_{Ac} + C_{Ac} + \frac{{C_{Ac}}^2}{K_i}} \right\} \tag{14}$$

Where $\mu_{max(\,Anaero)}$-Maximum growth rate of anaerobic bacteria (day^{-1}); K_i -Inhibition coefficient for acetic acid (mg/l); K_{Ac}-Half saturation constant for acetic acid (mg/l); C_{Ac}-Concentration of acetic acid (mg/l)

Depending on concentration of methanogenic bacteria, the acetic acid inhibition and the death rate term for specific maintenance rate (Haberl et al., 2003), the growth rate of anaerobic bacteria concentration in diffusion dominant root zone can be written as:

$$\frac{dX_{(Anaero)}}{dt} = \mu_{\max(Anero)} \left\{ \frac{C_{Ac}}{K_{Ac}+C_{Ac}+\frac{{C_{Ac}}^2}{K_i}} \right\} X_{(Anaero)} - K_{D2}.X_{(Anaero)} \tag{15}$$

Incorporating the Monod Kinetic expressions shown on Eq (14) and (17) to the basic VART model (Deng and Jung, 2009) and maintaining the remaining terms of advection-diffusion as defined for VART-BOD-F model, another model for simulation of BOD removal in FWS wetlands was developed and presented as:

$$\frac{\partial B_W}{\partial t} + U\frac{\partial B_W}{\partial x} = K_s\frac{\partial^2 B_W}{\partial x^2} + \frac{A_{diff}+A_{Adv}}{A}\frac{1}{Tv}(B_R - B_W) - K_W X_{Aero} B_W \quad (16)$$

$$\frac{\partial B_R}{\partial t} = \frac{1}{Tv}(B_W - B_R) - K_R X_{Anaero} B_R\ , Tv = \begin{cases} T\min Fort \le Tmin \\ tfort \ge Tmin \end{cases} , (T\min > 0) \quad (17)$$

$$A_{diff} = 4\pi D_R t_R\ , t_R = \begin{cases} 0 fort \le Tmin \\ t - T\min Fort \ge Tmin \end{cases} \quad (18)$$

Eq (14) to (12) describe the new model called VART-BOD-M to simulate the BOD removal process in FWS wetlands. Eq (18) represents the water column process of BOD removal, whereas Eq (19) represents the root zone process. The solution for the equations can be obtained by a numerical method of split operator scheme (Deng et al., 2016, Deng et al., 2010) and the MATLAB programming with the Semi-Lagrange approach. The influent concentration was considered as the upper boundary condition and zero initial concentrations in the water column and root zone. The step lengths of time and the grid cells size in the MATLAB code programming were 360s and 5m, respectively based on the basic VART model approach (Deng and Jung, 2009). The Monod Kinetics was applied to reflect the aerobic and anaerobic BOD decay illustrated in the conceptual model. In a similar manner of the VART-BOD-F model, the depth ratio for advection and diffusion zone was considered in terms of the area ratio.

2.5 Models parameters estimation

The parameter values used to simulate the two models were collected from the existing wetland data. The flow velocities in each cell, as shown in Carleton and Montas (2007), were used in computing the average velocity in each cell. The length of each cell considered during the simulation was 337.42m and had a cross-sectional area of 3908m^2 (EPA, 1993). The average flow velocities were considered in each cell to simulate the BOD_5 transport. Hence, it is assumed that the flow velocities occurring in each cell were constant. The computed average velocities for each cell are displayed in Table 1. For cells 1A, 1D, and 2A, the flow velocity fluctuations were very scattered, and the ranges were too wide. The variation of flow velocity ranges from 13 to 37 m/d in Cell 1A, 22 m/d to 36 m/d in Cell 1D, and 19 to 51 m/d Cell 2A. Cell 1B and Cell 1C had fairly constant flow velocities of 15m/d and 10m/d, respectively (Carleton and Montas, 2007). Initially, varying residence time T_v was carried out by dividing the length of wetland to the average velocity in each cell.

Table 1.Average flow velocities considered to simulate each wetland cell

Cell 1A (m/d)	Cell 1B (m/d)	Cell 1C (m/d)	Cell 1D (m/d)	Cell 2A (m/d)
33	17	10	28	31

Throughout the simulation period, the individual wetland cell was considered as an independent wetland. Hence, different values of hydraulic conductivities were assumed in each cell considering probable variation in size of soil sediment particles, the presence of plants and hydraulic conditions in each cell. Fetter (2014) investigated ranges of hydraulic conductivities for different particle sizes of soils. The parameter value for K_S (longitudinal dispersion coefficient) was considered based on the recommendation by (Deng et al., 2001). For lack of information on the project site during this investigation, some of the initial parameter values were selected based on other literatures experimental results which are relevant and consistent with exiting information of the Gustine wetland (Carleton and Montas, 2007, Deng et al., 2011, Deng and Jung, 2009, Eljamal et al., 2008, EPA, 1993, Kadlec and Wallace, 2009, Klass, 1984, Pavlostathis and Giraldo-Gomez, 1991, Soto et al., 1993). Complete detail of the input parameters used on the entire simulation of the two models is found in Appendix C.

2.6 Sensitivity analysis

The sensitivity and performance of the two models were evaluated based on a variation of coefficient of determination (r^2) and mean root square error (MRSE) values for a 20% decrease in each parameter of the model. Furthermore, a comparison of the r^2 values for the two models was also carried out with respect to the DND model of the unsteady-state condition and is illustrated in Table 2. Table B-1 and B-2 in Appendix B present the results of sensitivity analysis. The values of the models for r^2 and RMSE by 20% decrease in each parameter of the two models were displayed in the Appendix. To avoid the repetition of information for all cells, the analysis was illustrated only for the first cell (cell 1A). However, all cells were evaluated similarly to validate the percentage change, and no significant change was observed. The percentage increase in parameter values was also tested, but the difference in change of RMSE and r^2 values was in reverse direction to that of percentage decrease. Therefore, the percentage decreases values were chosen and illustrated in Appendix B for cell 1A.

It can be seen from Table B-1 and B-2 that the magnitude of variations on RMSE and r^2 value is different for all parameters. Even some parameters don't have a significant effect on RMSE and r^2 values for a 20% change to their original model value. For the VART-BOD-F model in Table B-1, the model was sensitive for parameters such as D_s, Tv, K, U, and Ks, successively while the rest parameters have minimal effect to a 20 percent change. But for the VART-BOD-M model, a 20% reduction in each parameter implies more than 5% change on RMSE values on $\mu_{max(anaero)}$, K_i, K_W, K_R, K_{Ac}, U, K_{D2}, X_{Aero}, C_{AC}, and X_{Anaero} parameters in decreasing order. The effect on r^2

values was almost in a similar sequence, except the magnitude of percentage change to the original r^2 values. The full sensitivity analysis report for both models is located in Appendix B in detail.

3 Results and Discussions

The simulation results indicate the models are efficient in predicting the BOD removal process. The results of the models are very close to the observed data than the Damkohler number distribution (DND) model result. Appendix-A presents the comparison of the combined simulation of effluent concentration for the two models concerning the observed data.VART-BOD-F and VART-BOD-M models were able to simulate efficiently and show reasonable agreement between observed and simulated data curves. The simulation results in each cell and the sensitivity of the two models for various parameters used are discussed in section 3.1 and 3.2 in detail.

3.1 VART-BOD-F model

The classic first-order modeling approach applied to the corresponding variable residence time-based model was capable of predicting the effluent concentration of BOD_5 in all Gustine wetland cells. Figure A1, A2, A3, A4, and A5 in Appendix A demonstrates the simulated results of the effluent concentration of BOD_5 for 360 days in cells 1A, 1B, 1C, 1D and 2A respectively. The VART-BOD-F model simulation result labeled by green color in each cell attained sound fitness between the observed and simulated effluent concentration over the entire period. As can be seen from the simulation results, the peaks of simulated values were reasonably closer to that of the observed BOD_5 effluent concentration in all cells.

To evaluate the performance indicator of the model, coefficient of determination(r^2), and root mean square error (RMSE) was calculated for each wetland cell and displayed in Table 2. The overall values of r^2 for VART-BOD-F were reasonable than the existing DND model in almost all cells except in 1D where slight difference occurred.

3.2 VART-BOD-M model

Incorporation of multiple Monod kinetics into basic VART model shows better improvement on the prediction of observed-effluent concentration for the BOD removal process. The simulation results of VART-BOD-M, labeled by the solid black line in Appendix A, followed the line of the best fit of the actual effluent data more closely than the VART-BOD-F and the existing DND models. Comparing all the models, the remarkable difference of plotting can be obtained from 9/28/1989 and 3/27/1990 due to the pick observed concentrations during the period.

Despite the limitation of experimental data for all the model parameters at the existing condition, consideration of different processes by introducing various parameters in both the water column and root zone of the wetland system significantly improved the result of the model. Unlike the VART-BOD-F model, the involvement of multiple numbers of parameters enhanced the pointed calibration process of the model. The result of sensity analysis also clearly indicated the effect of reaction kinetics with respect to biomass concentrations in the BOD decay process. The result of sensitivity analysis displayed in Tables B-1 and B-2 in Appendix-B illustrates the variation in RMSE and r^2 value for a 10% decrease in various model parameters of cell 1A. The sensitivity of acetic acid inhibition constant value epitomizes the effect of volatile fatty acids on Ph value and anaerobic microbial activity.

Table 2 demonstrates a comparison of RMSE and r^2 values for VART-BOD-F, VART-BOD-M, and DND models. In all the wetland cells, the values of r^2 for the VART-BOD-M model has reasonably exceeded the two model values. Compared to the VART-BOD-F, the RMSE value of the VART-BOD-M model was closer to unity. The test result of the VART-BOD-M model on Manzala wetland, Egypt (Deng et al., 2016), further proved the performance of the model in simulating the BOD removal. Therefore, the VART-BOD-M model, developed by incorporating multiple Monod Kinetics in FWS wetlands, was able to predict the effluent concentration of the BOD competently in all cells.

Table 2. Comparison of performance indicator for the three models

Wetland Cell	**DND model**	**VART-BOD models**			
		VART-BOD-F		**VART-BOD-M**	
	r^2	**r^2**	***RMSE***	**r^2**	***RMSE***
1A	0.77	0.91	1.42	0.96	1.05
1B	0.59	0.93	0.69	0.97	0.63
1C	0.43	0.77	1.23	0.85	1.19
1D	0.62	0.8	0.89	0.93	0.82
2A	0.7	0.79	1.84	0.83	1.77

Figures displayed in Appendix-A show a comparison between VART-BOD-F, VART-BOD-M models, and the observed concentration of BOD in all cells of the Gustine wetland. As indicated on the legend of each cell, the observed BOD_5 influent was labeled with red circles, observed effluent is marked with blue stars, effluent VART-BOD-F is colored with solid green and effluent VART-BOD-M is marked with solid black color.

4 Conclusions and Recommendation

In this paper, two new modeling approaches, VART-BOD-F, and VART-BOD-M (Deng et al., 2016), are presented for the BOD removal process in FWS CWs. The two models considered the FWS wetlands as a double-layered system consists of the water column and the root zone. Based on the microbial activities, the root zone of the wetland system was further divided into aerobic advection dominated, and anaerobic diffusion dominated layers. VART-BOD-F model considered a first-order decay rate of organic matter in addition to advection, dispersion, diffusion, and mass exchange of organic matter in between the layers. While VART-BOD-M predicts the removal of BOD by incorporating multiple Monod kinetics of microbial activities with other geochemical processes including advection, dispersion, diffusion, and mass exchange of BOD_5. The VART-based BOD removal models simulate the BOD removal in FWS CWs uniquely by incorporating the dynamics of diffusion dominated root zone. The two models were tested and compared with the existing model and observed data of one year. Based on the comparison and simulation result, the following conclusion is drawn

The first model (VART-BOD-F) was based on the theory of the typical first-order modeling approach that considers the BOD decay independent of the substrate. The sink term of the model considered limited dependency on the rate of organic matter decay substrate. The applicability of the model is evaluated from the reasonable fit of simulations curves with respect to the observed effluent data from Gustine Wetland, California. The predicted root-mean-square error (RMSE) values are 1.42,0.69,1.23,0.89 and 1.84 for cell numbers 1A, 1B, 1C, 1D and 2A respectively. The coefficeints of determination(r^2) produced in cells 1A, 1B, 1C, 1D and 2A are 0.91, 0.93, 0.77, 0.80 and 0.79 respectively. These r^2 values are consistently higher than the existing DND model.

The VART-BOD-M model formulation of the BOD removal process has been extended based on the reliance of the multiple Monod kinetic reaction on multiple substrates. The model validity is evaluated on one-year time series data of Gustine wetland BOD_5 concentration. The model was further tested with wetland data from Manzala lake located in Egypt and capable of simulating the BOD removal effectively (Deng et al., 2016). The determined values of r^2 and RMSE for the model are 096,0.97,0.85,0.93 and 083, and 1.05,0.63,1.19,0.82, and 1.77 in wetland cells 1A, 1B, 1C, 1D and 2A respectively.

As can be seen from Table 2 and Appendix A, the VART-BOD-M model can show better effluent predicting capability and ability to produce more reliable performance indicator values (RMSE and r^2) than the VART-BOD-F model and the exiting DND model. Even though the VART-BOD-M model produced a better result than the VART-BOD-F model, it involved various parameters and certain assumptions that might have compromised the results and analysis. Therefore, it can be concluded that VART-BOD-M model is a great tool to predict the removal of BOD in FWS CWs when there is the required data available.

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Appendix-A: Simulation results

Figure A-1, A-2, A3, A-4, and A-5 shows the simulation result of BOD_5 concentrations in Gustine Wetland for cells 1A, 1B, 1C, 1D and 2A respectively.

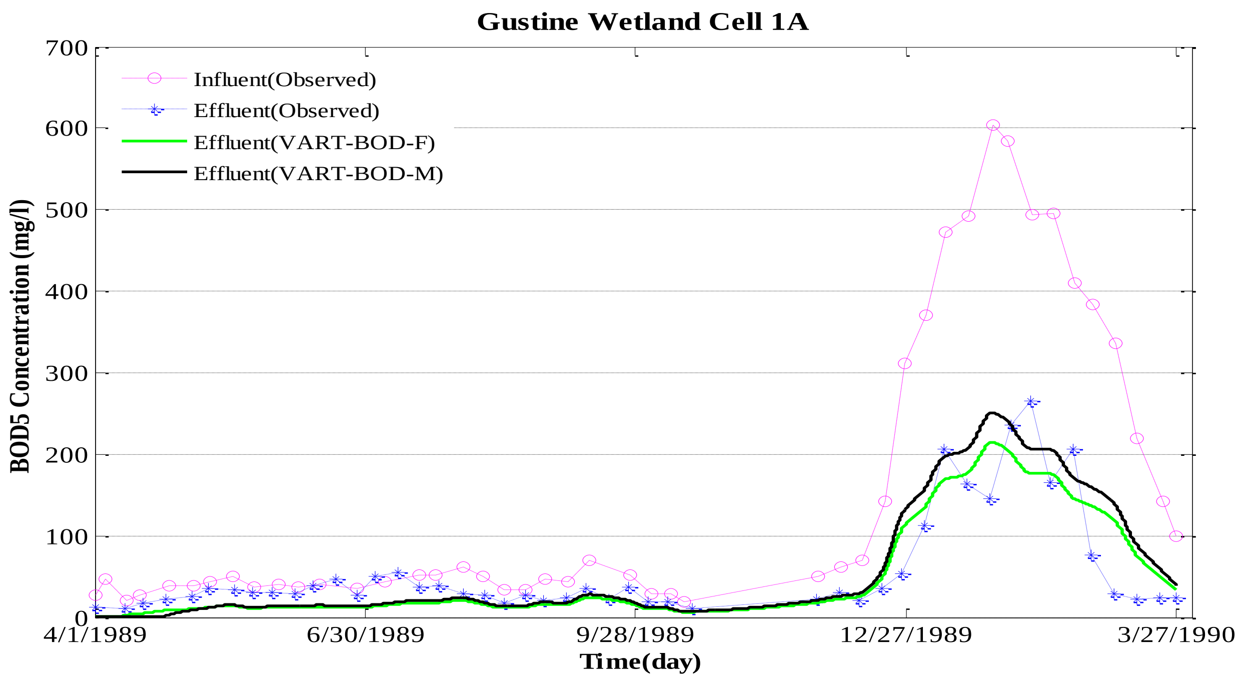

Figure A-1. Cell 1 A

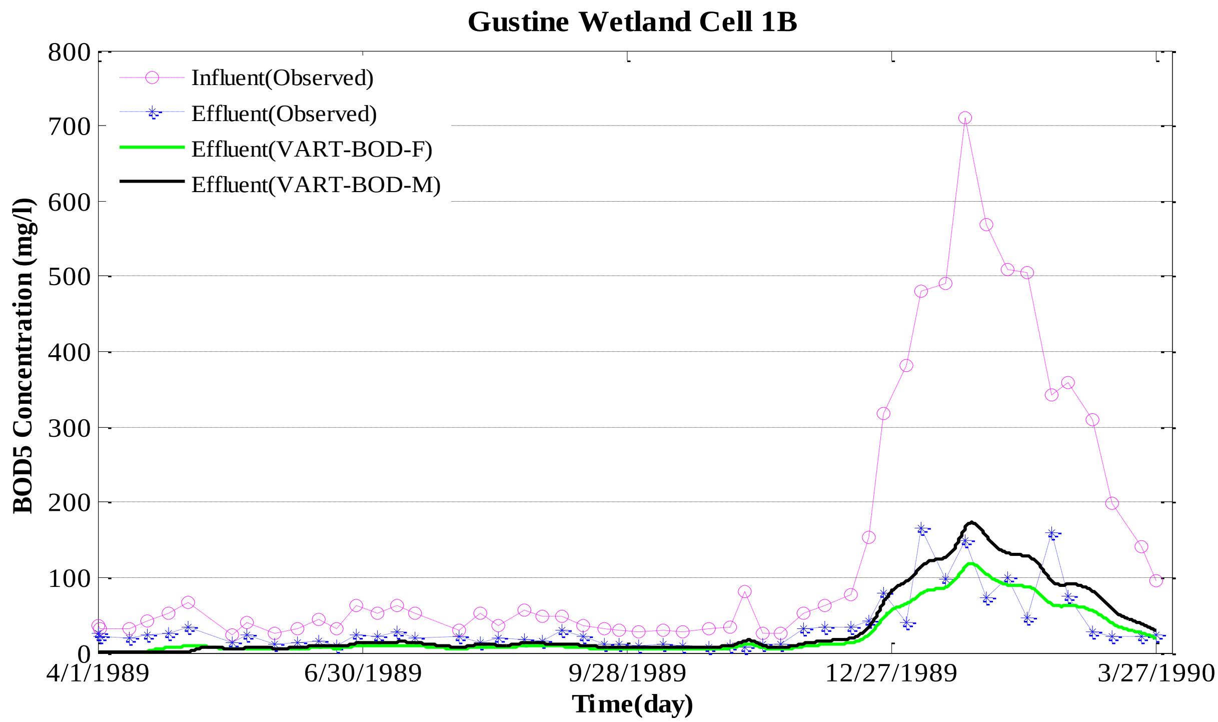

Figure A-2. Cell 1B

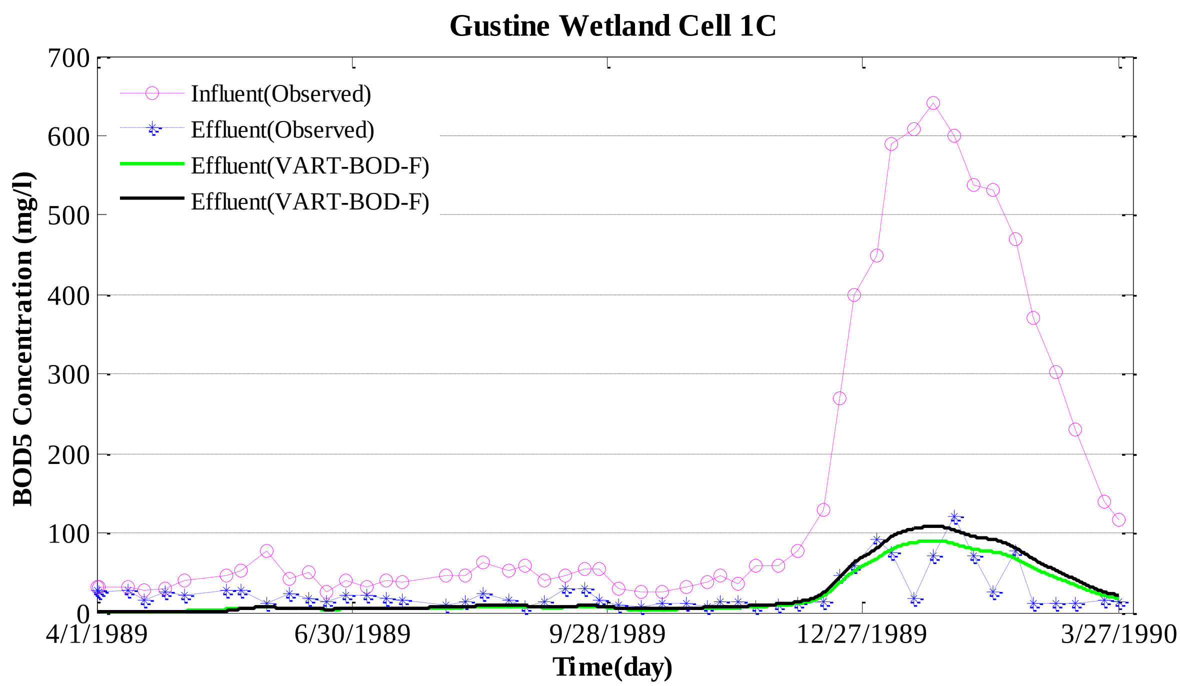

Figure A- 3. Cell 1C

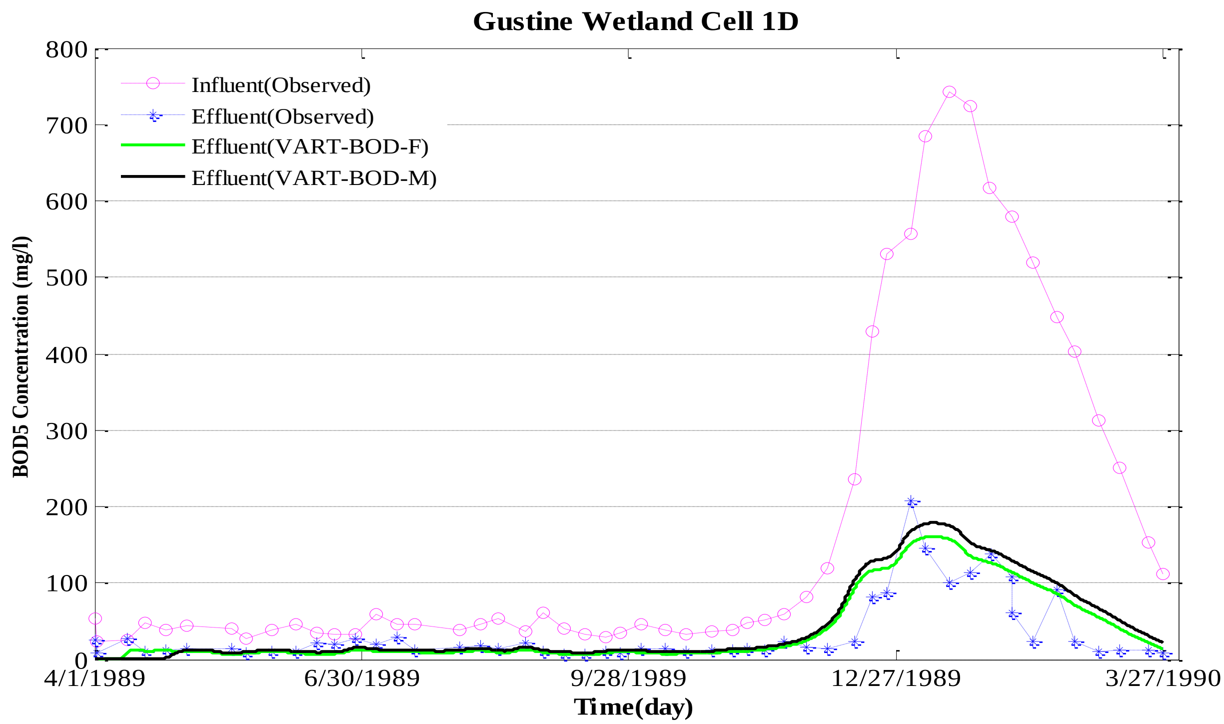

Figure A- 4. Cell 2D

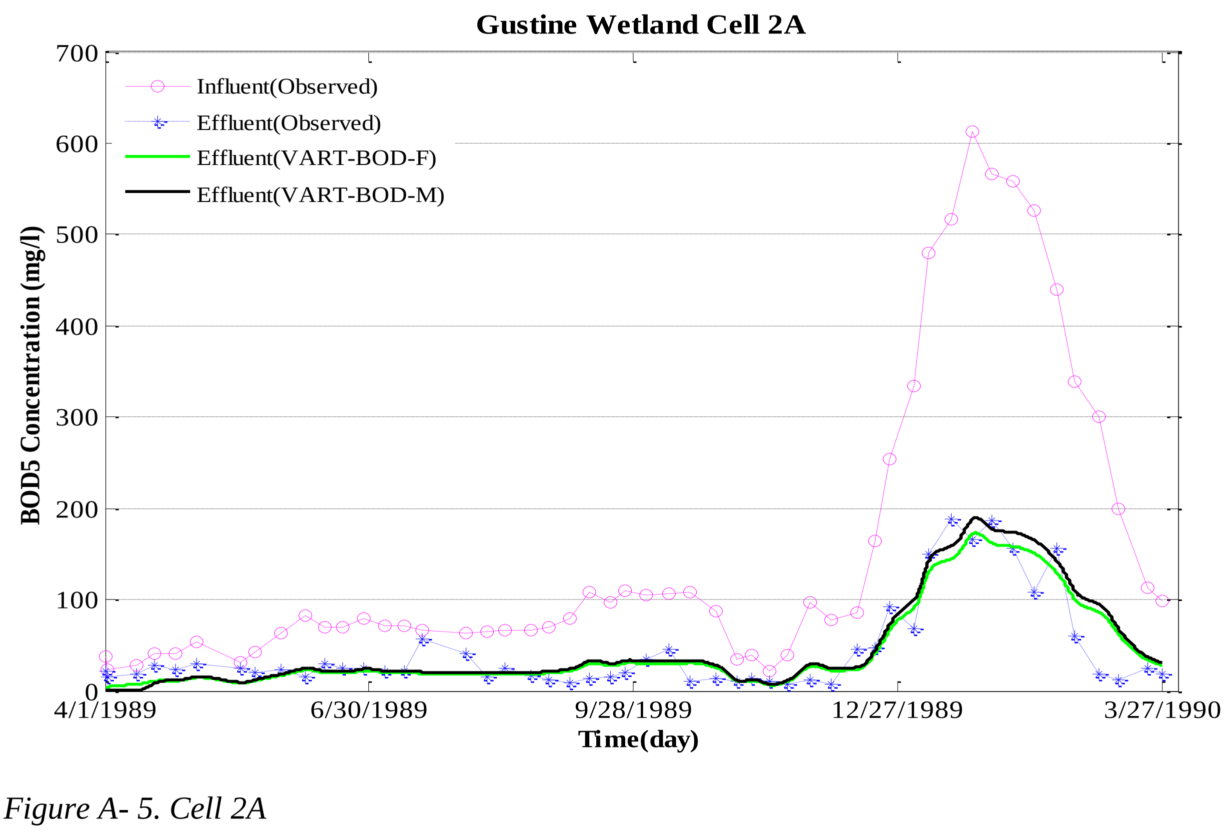

Figure A- 5. Cell 2A

Appendix B: Results of Sensitivity analysis

Table B 1. Sensitivity analysis of the VART-BOD-F model in Gustine Cell A

Model Parameters	Unit	Original value	20% decrease	Original RMSE value	Original r^2 value	RMSE value after 20 %	r^2 value after 20% decrease	% change in RMSE value	% change in r2 value
U	m/s	33	24.6	1.42	0.91	1.03	0.95	27.46	-4.4
Ks	m/s	5E-08	8E-06	1.42	0.91	1.34	0.58	5.63	36.26
$\frac{A_{Adv}}{A}$	-	0.99	0.792	1.42	0.91	1.45	0.82	-2.11	9.89
Ds	m^2/s	1E-05	4E-09	1.42	0.91	0.87	0.88	38.73	3.3
Tv	s	70.5	56.4	1.42	0.91	0.89	0.9	37.32	1.1
K	day-1	0.23	0.18	1.42	0.91	0.98	0.88	30.99	3.3

Table B 2. Sensitivity analysis of the VART-BOD-M model in Gustine Cell A.

Model Parameters	Unit	Original values of model parameters	20% decrease	Original RMSE value	Original r^2 value	RMSE value after 20 % decrease	r^2 value after 20% decrease		
U	m/s	33	24.6	1.05	0.96	0.92	0.97	12.38	-1.04
K_s	m/s	5e-8	4e8	1.05	0.96	1.07	0.96	-1.90	0.00
$\frac{A_{Adv}}{A}$	-	0.99	0.79	1.05	0.96	1.08	0.95	-2.86	1.04
D_s	m^2/s	1e-5	8e-6	1.05	0.96	1.09	0.97	-3.81	-1.04
T_v	hr	245.4	196.32	1.05	0.96	1.06	0.96	-0.95	0.00

K_W	l/mg/day	1.28e-2	1.02e-2	1.05	0.96	2.08	0.90	-98.10	6.25
$\boldsymbol{X_{Aero}}$	mg/l	0.1	$8.00e^{-2}$	1.05	0.96	1.17	0.89	-11.43	7.29
$\boldsymbol{K_{DO}}$	mg/l	0.5	4.00e-1	1.05	0.96	1.06	0.93	-0.95	3.12
$\boldsymbol{K_{OC}}$	mg/l	4.125	3.30	1.05	0.96	1.06	0.94	-0.95	2.08
C_{DO}	mg/l	0.687	5.50e-1	1.05	0.96	1.06	0.93	-0.95	3.12
$\boldsymbol{C_{OC}}$	mg/l	15	1.20e-1	1.05	0.96	1.04	0.92	0.95	4.17
$\mu_{\max(Aero)}$	day^{-1}	0.4	3.20e-1	1.05	0.96	1.07	0.90	-1.90	6.25
K_{D1}	day^{-1}	0.15	1.20e-1	1.05	0.96	1.06	0.93	-0.95	3.12
$\boldsymbol{X_{Anaero}}$	mg/l	0.04	3.20e-2	1.05	0.96	1.12	0.85	-6.67	11.46
$\mu_{\max(Anero)}$	day-1	0.49	3.92e-1	1.05	0.96	2.27	0.82	-116.19	14.58
K_i	mg/l	1.015	8.12e-1	1.05	0.96	2.11	0.67	-100.95	30.21
$\boldsymbol{K_{D2}}$	day^{-1}	0.019	1.52e-2	1.05	0.96	1.17	0.86	-11.43	10.42
$\boldsymbol{K_{Ac}}$	mg/l	$4.02e^{-3}$	3.22e-3	1.05	0.96	0.91	0.99	13.33	-3.13
$\boldsymbol{C_{Ac}}$	mg/l	0.871	0.696	1.05	0.96	1.13	0.93	-7.62	3.12

Appendix C: Parameter Estimation

Table C. VART-BOD-F and VART-BOD-M models parameters used for Simulation of BOD removal in Gustine wetland

Model Parameters	Description	Unit	Value of parameter used
TL	Length of cell	m	337.42
TT	Total simulation period	d	360
DX	spacing between grid cells	m	5
Δt	Time step size	s	360
A	Cross sectional area	m^2	3908
$\frac{A_{Adv}}{A}$	Constant for ratio of root zone and water column area to that of wetland cross-sectional area	-	0.99
K_S	Longitudinal dispersion coefficient	m^2/s	5E-08
Ds	Effective diffusion coefficient in root zone	m/s	1E-05
Tv	Initial varying residence time	s	8.8E5 to 2.9E6
K	First order decay constant of BOD in the wetland	day-1	0.23
X_{Aero}	Aerobic bacteria concentration in water column and root zone	mg/l	0.1
K_{sDO}	Half saturation constant for dissolved oxygen	mg/l	0.5
K_{sDC}	Half saturation constant for organic carbon	mg/l	4.125
C_{DO}	Concentration of dissolved oxygen	mg/l	0.687
C_{DC}	Concentration of dissolved carbon	mg/l	15
$\mu_{max(aero)}$	Maximum growth rate of aerobic bacteria	day-1	0.4
K_{D1}	Death rate constant of aerobic bacteria	day-1	0.15
X_{Anaero}	Anaerobic bacteria concentration	mg/l	0.04
$\mu_{max(anaero)}$	Maximum growth rate of anaerobic bacteria	day-1	0.49

K_i	Inhibition coefficient for acetic acid	mg/l	1.015
K_{D2}	Death rate constant for methanogenic bacteria	day-1	0.019
K_w	BOD decay rate in water column	l/mg/day	1.28E-2
K_R	BOD decay rate in root zone	l/mg/day	8E-7
K_{AC}	Half saturation constant for acetic acid	mg/l	4.02E-3
C_{AC}	Concentration of acetic acid	mg/l	0.8761