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Two Decades Constructed Wetland Experience in Treating Municipal Effluent for Power Plant Cooling at the Shand Power Station, SaskPower Part VI: Multivariate (Quadratic) Function Model(s) for o-PO_4^{3-}-P Removal

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ABSTRACT

This paper is sixth in publication series on 20-year period constructed wetland operating experience at SaskPower's Shand Power Station and describes multivariate regression models for o-PO_4^{3-}-P (OP) removal efficiency during two main plant growth cycle periods: the plant growing season of May to September (R^2 = 0.84-0.95, p <0.001) and during the die-off period of October to November. For the growing season, the best most meaning model to describe the OP removal efficiency was a quadratic function as follows: $-4.81\ (OP)^2 - 4.53\ T + 0.39\ OP{*}BOD + 4.25\ OP{*}pH + 58.88\ TAN - 6.91\ pH{*}TAN + 9.36$; where p for each coefficient is <0.05. Aging effect of the CW on OP removal efficiency during the plant growing period was somehow also revealed but it was statistically weak (p = 0.15) and effect OP release of only ~0.45% per year. Of particular note, the results here suggest pH as an important variable during the plant growing season showing up in TAN, o-PO_4^{3-} speciation and in some other ill-defined forms, whose proper control and optimization could lead to more efficient CW performance. HPO_4^{2-} (and not the commonly purported $H_2PO_4^-$) was implicated as the dominant target species for biological uptake of OP, as high pH interactions with influent OP concentration favored OP removal within the operating pH range of 8.0 to 9.7. Unlike the growing season, the best model fits for the plant senescing period were non-polynomial, but multivariate functions. With exception of temperature, the derived regression coefficients (β_is) and constant (intercept) were vastly different in magnitude and in some cases by the direction of influence; being especially marked by: net background release of OP and no significant effect by pH on OP removal. The consistent negative temperature effect shown for both periods is likely associated with microbial activities on detritus materials either as suspended solids in the overlying and/or in the sediments.

Keywords: Wetlands; temperature; phosphate-phosphorus; quadratic regression model; pH; BOD; TAN

1. INTRODUCTION

The paper is the sixth in series of publications assessing the performance of a constructed wetland (CW) as a tertiary treatment technology of municipal wastewater (MWW) for condenser cooling at the Shand Power Station of SaskPower (Quagraine, 2017a, b; Quagraine and Duncan, 2017). In the third of the series (Quagraine et al., 2017b) we focused on the annual performances of the SaskPower CW in removing various contaminants including total phosphorus (TP) and orthophosphate (o-PO_4^{3-})-P (OP) in MWW for condenser cooling application.

Although there are various phosphorus (P)

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species or forms in MWWs including particulate and organic P, the P fraction of interest as far as the SaskPower CW operation and for that matter this manuscript is concern is OP. o- PO_4^{3-} is a composite term for the four inorganic monomeric phosphate species of general formula ($H_{(3-n)}PO_4^{n-}$; n = 0-3), which are interchangeable simply by pH variations. OP (o-PO_4^{3-}-P) is of interest because it dominates the P fractions in the MWW going into the SaskPower CW; constituting an annual average of 90% TP with standard deviation of only 6.6% (Quagraine et al., 2017b). o-PO_4^{3-} is in relatively high but variable levels in treated MWW effluents (e.g. 0.6-51.0 mg/L in secondary treated MWW (SMWW) effluents as observed from different USA locations (Vidic et al., 2009). It is a critical constituent in dictating scale formation and bio-fouling tendencies in industrial cooling applications; whilst in contrast inhibiting corrosion due to the protective layer of scales it forms on the metal surfaces. o-PO_4^{3-} content is indeed of concern in cooling water systems for which the effluent of this CW serve; it can form the tenacious calcium phosphate ($Ca_3(PO_4)_2$) scale, and its presence has the potential to nucleate or "seed" other mineral scales.

Considering that nutrient removals by CWs commonly follow seasonal patterns, which may not necessarily reflect annual patterns, the fifth paper investigated the seasonal performance of the CW in removing OP (Quagraine, 2017b). Multiple linear regression (MLR) analysis was performed on the monthly average data for the various years within the 20-year study period and showed temperature and inlet OP as statistically significant explainable or predictor variables (at least at the 80% confidence level: i.e. $p \leq 0.2$) in describing the OP removal efficiencies for some years. However, but for the temperature effect, the derived models were inconsistent amongst these years. Although influent OP concentration effect was consistently shown as net removals, it varied substantially in magnitude between the years. What is responsible for the variability in the derived models between the years? Could it relate to age or maturation of the CW; or simply the influence of other operational, environmental and climatological co-factors? Answers to questions such as these would help to maximize long-term high efficiency OP removal by CWs. Yet, lack of understanding of the most efficient pathways or the key process variables which can remove OP from the water column or soil pore water into permanent sinks as well as the inability to predict desorption or release of P from unavailable forms to OP in the environment has hampered such achievements (Lamb III, 1984; Vymazal et al., 1998).

Although regression analyses were performed in the fifth paper on a ~2-decade span of observatory data, the adopted approach which limited analysis of the monthly variations to individual years or monthly averages within a period of years, did not provide adequate data sets for rigorous analysis to accurately capture the key predictor variables accounting for the variations in OP removal or release. Therefore, despite numerous potential factors of influence on OP removal or release in CW treatment systems, the paper dwelt only on the effect of three main seasonal related factors: inlet OP concentration, temperature, and rainfall. Ignoring significant independent variables potentially creates biases in model predictions and hence consideration needs to be given to other significant variables including polynomial and interaction terms. Also, multicollinearity, a phenomenon indicating existence of moderate to strong correlations between two or more of the predictor variables in a multiple regression analysis and highly expected in an observational study such as this current one was overlooked. For complex treatment systems with multiple predictor variables such as in free water surface (FWS) CW, the presence of multicollinearity is indeed most likely. Ignoring multicollinearity in the regression analyses inherently implied ignoring potential additional influence that any one particular variable could impose apart from its common (per se) influence together with the other predictor variables on the dependent variable. Poor handling the presence of multicollinearity in MLR analyses may create unstable parameter (regression coefficient) estimates, render them less precise or useful, create larger standard errors and may result in "intuitively wrong" signs for the estimated parameters even though the R^2 statistic may be high (van der Kruk, 2005). The challenge therefore is with the selection of best subset of variables (including their interaction and/or polynomial terms) in ensuring irrelevant predictor variables are excluded and important ones maintained to yield the most statistically reliable outcome.

The present paper evaluates the regression outcomes of the monthly average data for the entire study period and therefore looks into quantifying the effect not only of the climatological factors in rainfall and temperature on OP removal efficiency, but also the effect of the CW age and the influent wastewater quality; which includes parameters such as inlet OP, biochemical oxygen demand (BOD), total ammonia nitrogen (TAN), NO_3^--N and pH and their interaction terms. It is anticipated that theresults in this paper would prove useful in understanding OP removal by CWs and provide basis for more reliable design and consistent performance of CWs to remove OP, which is still so much desired. But to set the stage for the discussion, a brief review of the literature in terms of the current high state of variability or unreliability in OP removal by CWs (as background information and basis for the relevance of this present manuscript) is outlined in the next section.

2. BACKGROUND

This section briefly reviews the literature on the problem of high variability in OP removal by CWs. With no or little recognition of the key process and environmental variables which influence o-PO_4^{3-} removal or release, the literature reports on CW efficiency or capability to remove o-PO_4^{3-} from MWW seem confusing and at times even controversial (USEPA, 1999). At the core of this confusion is the general lack of specificity in the wetland literature as to the actual form(s) of P being referenced in the removal or release by the CW; i.e. whether it is o-PO_4^{3-}, organic P, polyphosphate or particulate P. To maintain focus of the discussion on o-PO_4^{3-} or o-PO_4^{3-}-P (herein abbreviated as OP), any generic citations of P or soluble P as referenced in this present manuscript is hereafter purposely replaced by o-PO_4^{3-}-P (i.e. OP), except where clear evidence exists to suggest these processes occur via different P form(s) or as total P (TP). The following are the basis for this assumption: a) The naturally occurring form of the element P is o-PO_4^{3-} and it is the dominant form also in most natural water and wastewater (Nejad et al., 2013; Vidic et al., 2009); b) It is more commonly in the form of o-PO_4^{3-} that biological and chemical uptake or release of P occurs (Cotner and Wetzel, 1992; Liu et al., 2012); c) Compounds of P in wastewaters, after hydrolysis and biodegradation, change to soluble o-PO_4^{3-} (Nejad et al., 2013); and lastly d) o-PO_4^{3-} is the usual common measure of P. In fact, some fraction of polyphosphates and organic P may be readily hydrolyzed and hence reactive to the molybdate analytical test (Kadlec and Wallace, 2009), which is the typical measure of o-PO_4^{3-}; these fractions may therefore be inclusive in reported o-PO_4^{3-} concentrations.

2.1 Reversibility in OP removal

Accumulation (the main means of CW removal) of OP can occur biologically, chemically or physically, but many of the accumulation mechanisms are reversible and may result in OP release at particular times of the year and under different operating conditions (Calder, 2001). For instance, biologically, newly CWs may exhibit less OP release until equilibrium of growth and die-back is established. On annual basis, CWs generally show a net removal of OP by biological mechanisms (Calder, 2001), but after plants are fully matured, there is, on average no net year-to-year increase in plant storage (Calder, 2001; Kadlec and Wallace, 2009) or in some cases, net annual OP releases occur (Quagraine et al., 2017b). Yet, these contrasting annual performances at different maturation stages of a CW may not necessarily reflect on seasonal uptake trends over time.

While equilibrium exists to regulate the storage and release of OP, climatological factors (e.g. temperature and rainfall) and influent quality variability prevent a stationary equilibrium (Kadlec, 1989); i.e. a dynamic equilibrium instead exists. Therefore, during the course of a year, uptake and return may occur at different times, thus influencing removal differently in different seasons (Kadlec and Wallace, 2009; Quagraine, 2017b). For instance, compared to OP loads in MWWs, biological uptake (by plants and microbes) is usually minor overall (Calder, 2001; Lamb III, 1984; USEPA, 1999), yet on seasonal basis, plant uptake can be a very large part of OP removal or release, where plant storage follows typically the pattern of a growing season (spring and early summer) increase to a maximum, followed by a senescence-season decrease to a minimum, with the cycle repeating each year (Kadlec and Wallace, 2009).

2.2 Variability in OP removal

Various types and sizes of CWs have demonstrated capability to remove P from treated MWW effluents of different grades (i.e. primary, secondary-both conventional and lagoon/stabilizing ponds, and tertiary) but to different degrees (Quagraine, 2017a). Studies on CWs performance in removing P is commonly monitored as TP, occasionally as OP (Quagraine, 2017a), but rarely as the other forms of P. Based on reviewed TP data (Quagraine, 2017a), P (or OP) removal is somewhat more consistently displayed for raw/primary MWW treatment, but less consistently for secondary and tertiary MWW treatment (ranging from 0 or negative removal (Beutel, 2012; Greenway, 2005) to >98% removal efficiency (Anderson et al., 2013) by FWS-CWs and ~16% (Steinman et al., 2003) to ~82% (Shi et al., 2004) by HSSF-CW). The removal efficiency also appears to be very dependent on site specificity and/or the operation of the CW (Quagraine, 2017a).

Different parameters, including compositional ones such as pH, cation concentration, chemical oxygen demand (COD) content and P load and operational ones such as temperature and dissolved oxygen (DO) can affect biological OP removal from wastewaters (Mulkerrins et al., 2004) and may play significant roles in the dynamic equilibrium associated with uptake and release of OP. In the next sections, some critical influencing factors of relevance in evaluating the results from the current investigation are discussed.

2.2.1 pH effect

As mentioned earlier, phosphate as loosely used in most reports in the wetland literature and also commonly called "orthophosphate (o-PO_4^{3-})" or "reactive P" is actually a composite measure of four inorganic monomeric phosphate species of general formula ($H_{(3-n)}PO_4^{n-}$; n = 0-3), which are interchangeable simply by pH variations. Because of charge and available proton differences in the various species of o-PO_4^{3-} (herein used more strictly as the composite term to distinguish from the trivalent PO_4^{3-} species), these species may demonstrate different biological (plant and microbe) absorption, chemical and biological adsorption/desorption, metal coordination and anion exchange tendencies. Therefore, at different wastewater pH, o-PO_4^{3-} removal may vary significantly.

2.2.2 Maturation (Age) effect

As noted earlier, the performance of various types and sizes of CWs at various maturation stages were recently reviewed (Quagraine, 2017a) and they demonstrate different levels of efficiency to remove o-PO_4^{3-} (or TP) from treated MWW effluents of different grades (i.e. primary, secondary-both conventional and lagoon/stabilizing ponds, and tertiary). From a laboratory scale vertical subsurface flow CW (VSSF) study, Martín et al. (2013) reported 76% removal of o-PO_4^{3-} from a tertiary MWW (3^o-MWW), with an outflow concentration of 0.13 mg/L. Cameron et al. (2003) reported ~82% removal of o-PO_4^{3-} from a lagoon treated MWW by a surface flow (FWS) CW to produce an outflow concentration of only 0.03 mg/L. Even from a primary treated MWW effluent, o-PO_4^{3-} removal of ~98% to produce an effluent concentration of only 0.09 mg/L was demonstrated by a small scale horizontal subsurface flow CW (HSSF) (Wu et al., 2008). These examples are however all data reported for newly CWs (within the first few years of operation) and may not characterize long-term performance. In fact, the reviewed data (Quagraine, 2017a) generally shows more TP removal for CWs that have been in operation for only ≤2 years than those that have operated longer, Nevertheless, other CWs even in their first two years of operation were reported to remove OP meagerly ≤7% (Beutel, 2012; TWDB, 2000) or even the release of it (Beutel, 2012).

Indeed most reported studies on o-PO_4^{3-} or OP have been on small pilot scale demonstrations and even for the fewer commercial scale demos, data collection are usually consistent only for the early (1-5) years of operation (Quagraine, 2017a); being more sporadic in later years. It should be noted that new plants growing in a freshly planted CW will uptake more OP than a mature CW, which will have OP leaching from dying (senescent) plants as well as uptake by growing plants (USEPA, 1999). Likewise, newly placed soils or media will have a greater OP sorption capacity than a mature system which will have most sorption sites already saturated (USEPA, 1999).

2.2.3 Size effect

Despite the known decline in OP removal with wetland maturation (Section 2.2.2), some large natural wetlands were shown to remove OP even after 50 years with percentage concentration reductions ranging, for example, from 13 to 33% (Fetter et al., 1978; Mudroch and Capobianco, 1979; Spangler et al., 1977). These observations led to the consideration of wetland size effect on OP removal and subsequently the construction of large wetlands for the purposes of P control.

In a recent article by Kadlec (2016), the performance of large (>40 ha) CWs with operation years ranging from 4 to 41 years was reviewed. On the average, lesser TP consistently departs than enters such large CWs. It is worth noting however, that apart from two (Columbia and Lakeland) CWs with respective inlet TP of 2.55 mg/L and 5.08 mg/L, the inlet TP for these large CWs were generally very low (<0.9 mg/L) with a median of only 0.11 mg/L. Some of the large CWs displayed start-up trends (either as short-term OP releases or greater OP removal), ranging to several years, which likely resulted from antecedent soil and vegetation conditions (Kadlec, 2016).

For these large scale CWs with established vegetation and proven lasting TP removal abilities, seasonality was generally found to be weak for steady flow systems. Differences between wet and dry seasons were shown, but they were suggested to be flow-driven. It is to be noted that most of these large CWs are in warm (not temperate) climates and hence do not experience the plant dormancy induced by winter conditions. Climatic conditions impact on the speed and seasonality related with the processes of growth, death, litter fall and decomposition, which operate year-round (Kadlec and Wallace, 2009). In temperate zones, plant uptake can be a significant portion of seasonal OP removal or release (Kadlec and Wallace, 2009). But the question asked in the introduction section still stands; would CW maturation have any effect on seasonal performance in removing OP?

2.3 Data limitations in OP removal CW design models

To answer the question in the preceding section requires a long-term consistent acquisition of OP removal data by CWs across seasons. In fact, part of the confusion with respect to CW long-term capability to remove OP has to do with the lack of quality data of sufficient details-both temporally and spatially on full-scale CW (USEPA, 1999). Shorter term and sporadic monitoring, as commonly found in the literature, can give deceptive prediction of the long-term seasonal performance and the longevity of a CW as treatment technology. Even for the long-term operating large CWs (Kadlec, 2016), the most number of years of data records collected was 16; with the oldest CW having only 11 years of data records.

In lieu of long-term consistent research studies to obtain adequate data sets of rigorous quality control (QC) for reliable regression analyses, wetland design models have typically only been built on data combination from (a) research studies of more rigorous QC with those of field studies of randomly collected data and of little QC; and (b) from small CW with minimal pre-treatment with those from large CW used for polishing SMWW (USEPA, 1999).

With data availability spanning through a 20-year period and involving different seasons of operation where variations in OP load in the MWW effluent to the medium sized (23.5 ha) CW is expected-both temporally and spatially, long-lasting seasonal trends in OP removal from MWW effluents could be established. Furthermore, the main factors of influence on the seasonal variation in OP removal and release within the CW could be determined to enable their manipulation both in designing and operating stages for optimum performance. Lastly, seasonal influences on the CW performance and the effluent quality (in terms of OP) could likewise be ascertained with reference to the CW maturation to determine the longevity of CWs as OP treatment technology for power plant cooling application.

3. MATERIALS AND METHODS

3.1 CW site, design and operation

The details of the CW features (location, design and operations) were reported in the earlier papers (Quagraine et al., 2017a, b; Quagraine and Duncan, 2017). The CW is a FWS CW of total surface area of 235,000 m^2 consisting of two major identical cells with each divided into three sub-cells and mostly consisting of planted bulrush and cattails and emergence of a variety of natural sedges and marsh. The site (49.12^o N, 103.04^o W) is located in a temperate region where monthly temperature and rainfall averages from April to November are 5.0, 12.1, 16.8, 19.5, 18.6, 12.4, 5.6, and -4.3^{o}C, and 17.2, 52.1, 76.2, 65.0, 49.5, 43.0, 18.6 and 3.2 mm, respectively (El Dorado Weather, 2016).

The CW feed comes from storage ponds of treated MWW (City of Estevan). The CW operation usually begins in May and cease in October, although various logistical factors sometimes led to extending the operation to November. Outside the operating periods (i.e. colder months), the city's treated MWW is fully stored in the ponds. Earlier in the CW operation (1994-1995), the MWW effluent from the city's wastewater treatment plant (WWTP) was of a facultative lagoon (FL) quality, but was upgraded to conventional secondary (CS) treatment in early 1996 and continues to date, although this report extends only to the end of 2014 CW operating period.

3.2 Sampling and testing

Sampling for CW influent and effluent quality was done typically once or twice in a week. Sampling and testing details for OP were outlined earlier (Quagraine, 2017b) and hence are omitted here for brevity. A total of 1,739 individual OP data (including ~670 inflow/outflow storage pond pairs of samples) in the span of three seasons (spring to fall) per year were collected within the twenty year period of investigation and analyzed. These individual data were further analyzed as monthly averages within individual years for the study period.

3.3 Statistical and mathematical analysis of data

3.3.1 Correlation analysis

Correlation analyses were conducted with the removal efficiency of OP as the dependent and climatic factors such as temperature and rainfall and wastewater composition parameters such as inlet o-PO_4^{3-}-P, BOD, TAN, NO_3^--N and pH as independent variables as previously described (Quagraine, 2017b; Quagraine and Duncan, 2017).

3.3.2 Multivariate quadratic polynomial regression models

In the fifth paper (Quagraine, 2017b) the dependence of the inlet OP coefficient (k_1) on OP, BOD and pH on annual stages prompted the idea that OP removal efficiency is potentially a quadratic polynomial function of at least these independent variables. As discussed above, CW maturation may also influence OP removal efficiency. Furthermore, based on the annual data of the SaskPower CW (Quagraine et al., 2017b), relations between OP and NH_4^+ (the dominant speciation form of TAN for the operating pH range) and/or NO_3^--N uptakes were implied. Thus, influent TAN and NO_3^--N may potentially also influence the OP removal efficiency. To verify, a quadratic polynomial model containing these five compositional parameter terms and/or their interactions as well as the CW age and the climatological parameters of temperature and rainfall, as shown in Eq. 1, was to be tested to fit the monthly (May to November) observed data sets for the entire study period.

$$Y = \beta_1 z_1^2 + \beta_2 z_2 + \beta_3 z_3 + \beta_{14} z_1 z_4 + \beta_{15} z_1 z_5 + \beta_6 z_6 + \beta_7 z_7 + \beta_8 z_8 + C^* \quad (1)$$

where Y represents the OP removal efficiency (%); β_1, β_2, β_3, β_6, β_7 and β_8 represent the principal effects (regression coefficients) associated with inlet OP concentration (z_1), temperature (z_2), rainfall (z_3), CW age (z_6), inlet TAN concentration (z_7) and inlet NO_3^--N concentration (z_8); β_{14} and β_{15} represent the interaction effect between OP (z_1) and BOD (z_4) and OP (z_1) and pH (z_5) on OP removal efficiency; and C* as all other contributions to OP removal. The interaction terms, z_1z_4 and z_1z_5, are included based on the initial results from the annual data as discussed earlier (Quagraine, 2017b). Some researchers (e.g. Ozer-Balli and Sorensen, 2010) however advocate that regression models with interaction terms (e.g. X_1X_2) should always be accompanied by the main corresponding terms (i.e. X_1 and X_2), as the interaction effect may be significant only due to left-out variable bias. Further, effect of pH on TAN speciation may make the interaction term for these two variations also relevant. Hence, a more general quadratic polynomial function represented by Eq. 2 was tested to fit the observatory data.

$$Y = \beta_1 z_1^2 + \beta_2 z_2 + \beta_3 z_3 + \beta_4 z_4 + \beta_{14} z_1 z_4 + \beta_5 z_5 + \beta_{15} z_1 z_5 + \beta_6 z_6 + \beta_7 z_7 + \beta_{57} z_5 z_7 + \beta_8 z_8 + C^* \quad (2)$$

In total, only 92 of the monthly data for the entire study period qualified to be used in the regression analyses as some data were missing either due to omissions or errors in the sampling and/or the measurement processes. The regression analysis tool of Excel® was used in the multi-linear regression analysis, but they were performed by stepwise variable selection approach and considering all possible permutations at each step for any particular total predictor terms. Unlike the preliminary models in the fifth paper (Quagraine, 2017b); the popularly adopted *p* value of 0.05 was used to determine the statistical significance of the quadratic polynomial models (to validate that the OP removal efficiency was more reliably to be described by polynomial functions rather than linear functions). Depending on the number of independent variables accepted in a model, any combination of the coefficients β_1, β_2, β_3, β_4, β_5, β_6, β_7, β_8, β_{14}, β_{15}, β_{57} and C* were estimated and their statistical significance determined based on the *p* values from t-test statistics. Thus, in general, the suitability of a model was based on the combination of the following criteria: *p* value ≤ 0.05 for significance of F in the analysis of variance (ANOVA); *p* value ≤ 0.05 of t-tests for all included predicator variables, except an arbitrary accommodation of a maximum of only one predictor to exceed this value but which should be ≤ 0.2; high correlation coefficient of determination (i.e. $R^2 \geq 0.65$ (Prairie, 1996)); absolute standard residual errors of <2; and a good distribution of residuals. For fair selection from models with different number of independent variables (k), the adjusted coefficient of determination ($\bar{R}^2$), rather than R^2, was used as basis. Both $\bar{R}^2$ and R^2 were Excel® multiple regression analysis outputs.

Attempts were initially made to develop a general model to account for OP removal based on all the 92 datasets, but yielded several inconsistent models with not much statistical differences to offer preference of any one over another (i.e. based on the R^2 and *p*-statistics information). The data were therefore subdivided into 3 seasonal groups to develop separate model(s) to account for the respective seasonal treatment performance: 12 in May for spring, 61 in June to September for summer/early fall, and 19 in October and November for late fall. From these, the data set that deviated significantly from the model prediction (i.e. those with absolute standard residual errors >2) were deemed discordant and excluded from the model determination. In addition to the CW age, the monthly average data of the various variables for the selected data used in predicting the main models are shown in Table 1.

4. RESULTS AND DISCUSSION

Initially, attempts were made to develop a general regression model between OP removal efficiency and the operating conditions (including climatological and composition influences) over the entire study period using the 92 selected monthly (May to November) datasets, but yielded several inconsistent and meaningless models. MLR analyses based on seasonal sub-groupings of the datasets produced more reliable outcomes as shown in Table 2 and are discussed in details below.

4.1 Model(s) describing OP removal efficiency during spring operation

The monthly average data for the variables considered during spring (May) operation of the CW are shown in Table 1. Despite the limited amount of data for the spring period (N = 12), by excluding 3 observations as discordant (i.e. with absolute standardized errors of >2.0), Model A (a quadratic polynomial function of inlet OP, pH and temperature) was derived to account for the OP removal efficiency by the CW in spring. The square of OP and the interaction term of pH and OP showed the most significant (consistent) influence on OP removal efficiency. Temperature also demonstrated some influence, but was only weakly shown (p = 0.18). There were indications of the potential for pH (alone) to also show some influence but was found not to be of statistical significance (p = 0.4); likely due to the limited number of data sets employed in the regression analysis. The smaller a sample size the less likely a difference to be detected (Dahiru, 2008).

4.2 Model(s) describing OP removal efficiency during summer/early fall season

For the June-September (summer/early fall) monthly datasets (N = 61), three subgroups were identified: (a). A first (SG-1) subgroup (N = 37) dominated by June and July datasets (~68%) and characterized (see Table 1) by heaviest monthly rainfall (65.2 ± 34.9 mm), highest average monthly inlet OP (2.4 ± 1.2 mg/L) and BOD (9.6 ± 5.2 mg/L) ([OP]*[BOD] = 26.7 ± 21.6 (mg/L)^2), and highest monthly average pH and OP product value (i.e. [OP]*pH = 20.4 ± 9.8 mg/L. pH units); (b). A second (SG-2) subgroup (N = 13) dominated by August and September monthly datasets (~77%) and characterized by the lowest mean monthly rainfall (41.9 ± 34.7 mm) and of moderately lower mean monthly inlet OP and BOD ([OP]*[BOD] = 20.1 ± 42.9 (mg/L)^2) and inlet pH and OP product value (i.e. [OP]*pH = 15.6 ± 11.1 (mg/L) as compared to the SG-1 subgroup); and (c) A third (SG-3) subgroup (N = 11) dominated by July and August monthly datasets (~73%) and marked by least inlet OP (1.4 ± 0.8 mg/L) and BOD (4.0 ± 2.7 mg/L) ([OP]*[BOD] = 7.3 ± 7.2 (mg/L)^2) and the lowest monthly average pH and OP product value (i.e. [OP]*pH = 12.3 ± 6.4 mg/L. pH units). The average rainfall for the SG-3 subgroup (61.4 ± 27.8 mm) was only moderately less than that for the SG-1 subgroup (65.2 ± 34.9 mm).

Table 1 The monthly average data of the considered variables in spring (May), summer/early fall (June to September) and late fall (October and November) used in predicting the main model(s) in the study

Variables	Spring		Summer/Early Fall (SG-1[a])		Late Fall	
	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD
OP (mg/L)	1.1 - 7.4	2.3 ± 1.9	0.5 - 5.7	2.4 ± 1.2	0.5 - 3.6	1.4 ± 0.8
BOD (mg/L)	4.8 - 23.0	12.1 ± 5.7	1.9 - 20.4	9.6 ± 5.2	3.0 - 25.0	11.9 ± 6.3
TAN (m/L)	0.4 - 22.5	3.4 ± 7.2	0.1 - 16.2	2.3 ± 3.3	0.2 - 7.5	1.7 ± 1.9
NO_3^--N (mg/L)	0.0 - 8.3	1.2 ± 2.7	0.1 - 13.8	1.8 ± 3.2	0.1 - 6.8	1.4 ± 1.6
pH	8.1 - 9.0	8.7 ± 0.3	8.0 - 9.7	8.7 ± 0.5	8.0 - 9.0	8.6 ± 0.3
Temp (^{o}C)	8.0 - 12.7	10.6 ± 1.7	11.9 - 20.7	16.8 ± 2.4	-3.7 - 7.0	2.7 ± 3.7
Rainfall (mm)	9.6 - 108.4	64.1 ± 36.5	5.2 - 134.6	65.2 ± 34.9	0.0 - 80.6	15.7 ± 21.0
OP Removal (%)	-25.0 - 98.8	19.9 ± 36.5	-77.9 - 37.0	-3.6 ± 28.4	-90.2 - 60.6	12.5 ± 24.3

Note: [a]See results and discussion section for details

Table 2 Polynomial regression models describing relations between OP removal efficiency by the CW and changes in inlet OP (z_1), BOD (z_4), pH (z_5), TAN (z_7) and NO_3^--N (z_8), temperature (z_2), rainfall (z_3), age of the CW (z_6) and some interaction terms

Models		Regression Equation	N, k	$\bar{R}^{2b}$	p^c
		May (Spring)			
A		^{S}-3.68$(z_1)^2$ – ^{WS}3.53z_2 + ^{S}6.23z_1z_5 – ^{NS}34.38	9, 3	0.93	0.0009
		June to September (Summer/Early Fall)			
B	SG-1	^{HS}–4.33$(z_1)^2$ – ^{HS}3.68z_2 – ^{HS}24.74z_5 + ^{HS}4.43z_1z_5 + ^{HS}213.74	37, 4	0.87	0.0000
C		^{S}–3.59$(z_1)^2$ – ^{HS}4.54z_2 + ^{S}1.43z_4 + ^{S}4.20z_1z_5 – ^{NS}0.61	37, 4	0.82	0.0000
D		^{HS}–5.16$(z_1)^2$ – ^{HS}3.89z_2 – ^{HS}24.85z_5 + ^{HS}4.48z_1z_5 + ^{S}2.07z_7 + ^{HS}218.51	37, 5	0.90	0.0000
D*		^{HS}–5.10$(z_1)^2$ – ^{HS}3.88z_2 – ^{HS}25.29z_5 + ^{HS}4.42z_1z_5 + ^{HS}0.25z_5z_7 + ^{HS}222.92	37, 5	0.90	0.0000
D$^{@}$		^{HS}–3.83$(z_1)^2$ – ^{HS}3.78z_2 + ^{WS}0.68z_4 – ^{HS}21.59z_5 + ^{S}3.96z_1z_5 + ^{HS}187.71	37, 5	0.88	0.0000
D$^{@2}$		^{HS}–4.45$(z_1)^2$ – ^{HS}3.69z_2 – ^{HS}28.52z_5 + ^{HS}3.93z_1z_5 + ^{S}1.90z_7 + ^{MS}1.00z_8 + ^{HS}251.65	37, 6	0.90	0.0000
D$^{(?)}$		^{HS}–4.79$(z_1)^2$ – ^{HS}3.93z_2 + ^{NS}0.41z_4 – ^{HS}22.97z_5 + ^{HS}4.19z_1z_5 + ^{S}1.89z_7 + ^{HS}202.60	37, 6	0.89	0.0000
E$^{(?)}$	SG-2	^{MS}–5.98$(z_1)^2$ – ^{WS}3.16z_2 – ^{HS}0.80z_3 + ^{S}6.99z_1z_5 + ^{NS}13.21	13, 4	0.87	0.0003
		May to September (Plant Growing Season)			
F		^{HS}–2.78$(z_1)^2$ – ^{HS}4.38z_2 + ^{S}0.29z_1z_4 – ^{S}16.39z_5 + ^{HS}2.63z_1z_5 + ^{S}1.87z_7 + ^{S}168.51	49, 6	0.86	0.0000
F*		^{HS}–2.71$(z_1)^2$ – ^{HS}4.38z_2 +^{S}0.28z_1z_4 – ^{S}16.80z_5 + ^{HS}2.58z_1z_5 + ^{S}0.22z_5z_7 + ^{S}172.49	49, 6	0.86	0.0000
F**		^{HS}–4.81$(z_1)^2$ – ^{HS}4.53z_2 + ^{S}0.39z_1z_4 + ^{HS}4.25z_1z_5 + ^{S}58.88z_7 – ^{S}6.91z_5z_7 + ^{NS}9.36	49, 6	0.86	0.0000
G		^{HS}–3.24$(z_1)^2$ – ^{HS}4.56z_2 + ^{S}0.32z_1z_4 – ^{S}15.89z_5 + ^{HS}2.85z_1z_5 – ^{WS}0.47z_6 + ^{S}1.97z_7 + ^{HS}168.64	47, 7	0.87	0.0000
G*		^{HS}–3.17$(z_1)^2$ – ^{HS}4.56z_2 + ^{S}0.32z_1z_4 – ^{S}16.32z_5 + ^{HS}2.80z_1z_5 – ^{WS}0.47z_6 + ^{S}0.24z_5z_7 + ^{HS}172.86	47, 7	0.87	0.0000
G**		^{HS}–5.21$(z_1)^2$ – ^{HS}4.67z_2 + ^{HS}0.42z_1z_4 + ^{HS}4.43z_1z_5 – ^{WS}0.43z_6 + ^{S}59.23z_7 – ^{S}6.94z_5z_7 + ^{NS}13.61	47, 7	0.86	0.0000
		October to November (Plant Senescing Season)			
H		^{HS}45.60z_1 – ^{S}2.80z_2 + ^{HS}3.14z_4 – ^{S}1.77z_6 – ^{HS}24.18z_7 – ^{MS}24.91	17, 5	0.82	0.0001
I		^{HS}46.15z_1 – ^{S}3.91z_2 + ^{WS}0.32z_3 + ^{HS}3.41z_4 – ^{MS}1.42z_6 – ^{HS}24.17z_7 – ^{S}33.61	17, 6	0.84	0.0002

Note: ^{HS}Highly significant - $p \leq 0.001$; ^{S}Significant - $0.001 < p \leq 0.05$; ^{MS}moderately significant - $0.05 < p \leq 0.1$; ^{WS}weakly significant - $0.1 < p \leq 0.2$; ^{NS}Non-significant - $p > 0.2$; $^{b}\bar{R}^2$ is the adjusted R^2 (R^2 for models A, B, C, D, D*, D$^{@}$, D$^{@2}$, D$^{(?)}$, E$^{(?)}$, F, F*, F**, G,G*, G**, H and I are respectively 0.95, 0.89, 0.84, 0.91, 0.91, 0.90, 0.92, 0.91, 0.91, 0.88, 0.88, 0.88, 0.89, 0.89, 0.89, 0.87 and 0.90); ^{c}Model significance (by ANOVA). Note! Models D$^{(?)}$ and E$^{(?)}$ do not meet the model acceptance criteria as outlined in the manuscript

MLR analyses of the datasets for the SG-1 subgroup, which on average was moderate in the removal or release of OP (removal efficiency: -3.6 ± 28.4%), ultimately yielded a 5-predictor quadratic polynomial function (Model D or D* in Table 2) to best describe the OP removal efficiency for those prevailing conditions in summer and early fall (Fig. 1 illustrates the goodness of the predictive model (D) fit to the observed data). The MLR analysis results showed the following order of certainty on the independent variables to predict OP removal efficiency: pH and OP interaction (pH*OP) (p = 3.5 × 10^{-8}) >$(OP)^2$ (p = 1.4 × 10^{-6}) >Temperature (p = 2.4 × 10^{-6}) >pH (p = 6.0 × 10^{-6}) >TAN (p = 0.01) for Model D; and pH and OP interaction (pH*OP) (p = 4.3 × 10^{-8}) >$(OP)^2$ (p = 1.4 × 10^{-6}) >Temperature (p = 2.3 x 10^{-6}) >pH (p = 4.4 × 10^{-6}) >pH*TAN (p = 0.01). As can be seen from Table 2 and the p values on the predictor variables, there is not much to choose from between the regression outputs of Models D and D*. Hence, the one with the simpler composition is preferred; i.e. the one containing TAN (Model D) over the one with the interaction term pH*TAN (Model D*).

Despite the apparent weak statistical significance (p = 0.15) of BOD in the other 5-predictor model for dataset SG-1 (Model $D^{@}$), there were reasons to consider it also as a relevant model. First, with the exclusion of pH, the estimated BOD coefficient in the 4-predictor Model C derived from the same monthly datasets is statistically significant (p = 0.009) (See Table 2). Second, its (BOD) inclusion to the 4-predictor Model B to derive Model $D^{@}$ (See Table 2), though meager, not only improves R^2 but also the adjusted R^2 and standard error. Nonetheless, a more critical evaluation of the data suggests that the instability of BOD as a predictor variable is only due to multicollinearity. Multicollinearity may create unstable parameter (regression coefficient) estimates, render them less precise or useful, create larger standard errors and may result in "intuitively wrong" signs for the estimated parameters even though the R^2 statistic may be high (van der Kruk, 2005). Influent BOD correlates fairly well with pH (R^2 = 0.38; n = 37 or R^2 = 0.54; n = 35) and TAN (R^2 = 0.24; n = 37 or R^2 = 0.61; n = 34). Consequently, inclusion of pH (Model $D^{@}$) and TAN (Models $D^{(?)}$) together with BOD somehow weakens the model's $\bar{R}^2$ and its dependence on BOD; statistically rendering it as weakly significant or non-significant predictor variable, respectively (Table 2). In fact, Model $D^{(?)}$ does not even meet the model acceptance criteria. Model D (without BOD) is therefore the preferred 5-predictor model for the SG-1 dataset and fits the observed data closely (Fig. 1).

It is worth noting that the magnitudes and direction of impact of the predictor coefficients of Model D did not follow the same order of statistical significance or reliability of these predictors as shown above. Nevertheless, the interaction between pH and OP was both the principal statistical (dependable) and practical (actual impact) term responsible for OP removal for the monthly SG-1 subgroup conditions in summer/early fall (as well as in spring-See Models A and D). As an interaction term, the positive effect of pH*OP on OP removal is explainable either chemically - by adsorption and/or precipitation (Freeman and Rowell, 1981; Gunawan et al., 2010; House and Donaldson, 1986) or biologically - by uptake (Akpor et al., 2008) associated with pH-speciation of o-PO_4^{3-} (sum of H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}) towards HPO_4^{2-} and PO_4^{3-} at higher pH conditions. As pk_2 and pk_3 of H_3PO_4 is ~ 7.2 and 12.3, respectively (Hagen and Hopkins, 1955), and with pH in this monthly group ranging from 8.0 to 9.7, HPO_4^{2-} is expected to be the dominant target species for OP removal. The influence of TAN, though seemingly weak (by the magnitude of its impact), is of practical importance as the only other identified predictor variable in the model to effect OP removal. It may be explained by biological (likely algae-bacteria) uptake of TAN and OP (Delgadilo-Mirquez and Pareau, 2016). As in May (Model A), increasing temperature and influent OP (as a square in the regression equation) negatively impacted the removal efficiency of OP, contributing rather to its release. Based on the average temperature of 16.84°C, temperature alone could result in a mean release of ~65% OP over the inlet OP concentration for the prevailing conditions for the SG-1 monthly subgroup. The temperature effect is likely associated with microbial activities on detritus materials either as suspended solids in the overlying and/or in the sediments. Despite the positive interaction effect of pH and OP on removing OP, on their own as individual predictor variables, they presented the most negative impact to OP removal.

It is noteworthy that inclusion of NO_3^--N to Model D indicates it as moderately significant (p = 0.08) in a 6-predictor model (Model $D^{@2}$) with R^2 and $\bar{R}^2$ as only marginally better and the p value for significance of F in the ANOVA as only marginally worse than that of Model D. Also, apart from pH, there was some worsening of the statistical significance of the other predictor variables (i.e. greater p values were observed) when NO_3^--N is included in the model. Therefore, although the predictive power of Model $D^{@2}$ is strong enough to suggest NO_3^--N as a relevant predictor variable, the reduction in the statistical significance of the overall model and the other predictor variables creates some doubts on the precision of the estimated coefficients in the 6-predictor model as compared to Model D. The estimated coefficients in Model D are expected to be more reliable.

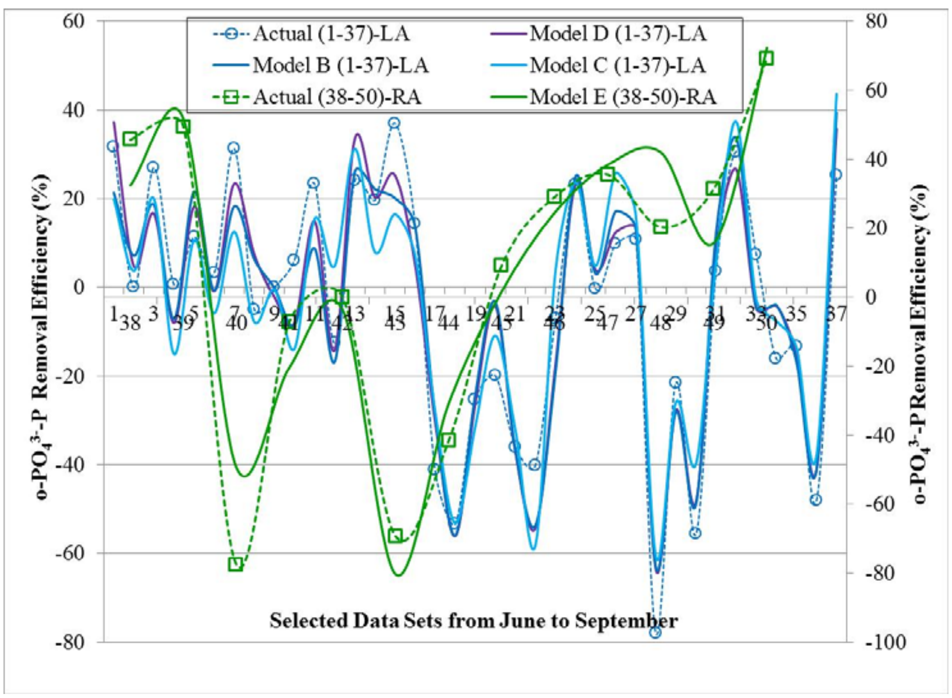

Figure 1 Comparison of actual and model predictions of o-PO_4^{3-}-P (OP) removal efficiency by the CW from June (datasets 1-14) through July (datasets 15-25) and August (datasets 26-31) to September (datasets 32-37) for Models B to D and from June (dataset 38) through July (datasets 39 & 40) and August (datasets 41-46) to September (47-51) for Model E.NB: LA = left axis and RA = right axis.

For the second subgroup (SG-2), which on the average was also moderate in the removal or release of OP (but on the whole leaning towards more efficient removal with average of 7.3 ± 45.5% and median 20.4% and with more consistent removal of 9-50% particularly in early summer (June) and early fall (September)), a different quadratic polynomial function (Model E(?) in Table 2) was derived to best describe the OP removal efficiency for the prevailing conditions in this subgroup (the goodness of the predictive model fit to the observed data can be seen in Figure 1). The regression analysis results showed the following order of reliability of the independent variables as predictors of OP removal efficiency: Rainfall (p = 0.0005) >pH and influent OP interaction (pH*OP) (p = 0.01) >$(OP)^2$ (p = 0.07) >Temperature (p = 0.12). Under the operating conditions of the SG-2 monthly subgroup, pH on its own did not significantly influence OP removal efficiency, but rainfall impact was very significant (statistically). The statistical significance of rainfall under the SG-2 conditions as against SG-1 reflects on the wider spread of the monthly data in the former (CV = 82.8%) versus the latter (CV = 53.6%). The more the spread of observations the lower the p value (Dahiru, 2008).

Once again, the magnitudes and direction of the predictor variables' impact did not necessarily follow the same order as their reliability or certainty as predictor variables. As with the case in spring and SG-1 conditions in summer/early fall, the interaction between pH and OP was the main factor responsible for OP removal for the SG-2 conditions in summer/early fall. This was earlier attributed to chemical and/or biological removal of OP associated to pH-speciation of o-PO_4^{3-} and on the average could result in ~100% OP removal efficiency. Yet, such removal effect is nullified by negative impacts from temperature (i.e. 3.16% increase - over inlet OP per degree rise (°C)) and rainfall (i.e. 0.80% increase - over inlet OP per mm of rain) as well as inlet OP (as a square in the regression equation). Based on the averages of 16.51°C, 41.86 mm, and 1.79 mg/L for this subgroup, temperature, rainfall and inlet OP could be responsible for mean releases of ~52%, 33% and 29%, respectively over the inlet OP. Thus, unlike under SG-1 monthly conditions where pH was the most adversely impactful variable on the removal of OP, temperature was the most adversely impacting factor under SG-2 conditions in summer/early fall.

The last subgroup (SG-3), which contained only reject monthly datasets from the best-fit models from the SG-1 and SG-2 subgroups during the months of June to September, was generally characterized by excessive OP release (-78.1 ± 95.6%). In fact, apart from July 2007 (8.5%) and June 2014 (73.2%) where the removal efficiencies were positive, they ranged from -21% to -233% for this subgroup. MLR analysis showed only the interaction term pH*OP to be of statistical significance (p = 0.001) in a 1-predictor model (R^2 = 0.72). A uniquely high removal in June 2014 occurred after the flood when revegetation was being re-established and plant uptake of OP was expectedly high. Furthermore, the two months demonstrating OP removal in this subgroup were characterized by high inlet BOD concentrations.

4.3 More general model(s) for the plant growing season (May to September)

Plant OP storage follows typically the pattern of a growing season (spring and summer) increase to a maximum, followed by a senescence-season decrease to a minimum, with the cycle repeating each year (Kadlec and Wallace, 2009). The senescence effect, however, may be delayed late into fall as death of CW macrophytes frequently result in standing dead vegetation rather than immediate leaf litter. Thus, the CW performance in September generally conformed more to the characteristics of plant growth (standing) rather than plant death (leaf litter); the former favoring plant OP uptake or retention and the latter promoting leaching of OP from leaf litter and decomposition.

4.3.1 Differences and commonalities in the spring versus summer/early fall OP removal models

Although the discussed models thus far for the spring to early fall conditions (i.e. Models A to E) are overall highly significant (p <0.001) and with the identified predictor variables accounting for at least 82% ($\bar{R}^2 \geq 0.82$) of the variability in the monthly OP removal efficiency (see Table 2), there are some significant differences as shown by the following: number of predictor variables (k); actual predictor variables present; magnitude and direction (signs) of the predictor coefficients; and variability in the level of confidence or degrees of significance in the variables as predictors (deducible from Table 2 by the p values, which range from <0.001 to 0.2). In the next few paragraphs, attempts are made to explain the basis for the differences in these models to inform their legitimacy (or not) and whether further refinements of the models are required. But before delving further into this discussion, the reader should note that estimated p values, which were very instrumental in the selection of the models, are themselves influenced by various factors: e.g. sample size (N), effect size (β) and spread of data (measurable by standard deviation or coefficient of variation) (Dahiru, 2008). These factors should hence also be given some consideration when making final decisions on a predictor model's suitability. Acknowledging these factors and variations in operating conditions (i.e. temperature, rainfall, and influent compositions of the wastewaters) associated with the models for OP removal, the following observations and remarks can be made:

a) Influence of BOD (z_4) was important (Models C & D$^@$) only under conditions of relatively high and variable influent BOD concentrations (i.e. 9.6 ± 5.2 mg/L for SG-1 operating conditions, ranging from 1.9 to 20.4 mg/L). Lower influent BOD conditions (e.g. 4.0 ± 2.7 mg/L for the SG-3 subgroup) did not display any statistical significant impact on OP removal (i.e. p >0.2). BOD influence on OP removal is well reported in the literature in various forms: i.e. directly, as labile dissolved organic carbon-DOC (an equivalent of biodegradable organic carbon) or as a ratio of BOD or DOC to OP (Mulkerrins et al., 2004). For example, the influence of labile DOC on bacterial OP uptake was reported by Stets and Cotner (2008). Vabolienė and Matuzevičius (2005) reported an increase of BOD to TP ratio (i.e. BOD/TP) to positively impact biological removal of TP. In fact, in the present study, a re-run of the MLR analysis on the SG-1 monthly datasets (after replacing BOD with BOD/OP ratio) did not affect the overall model outcome ($\bar{R}^2$ = 0.88; p = 0.0000), but did show a good level of confidence in BOD/OP ratio (p = 0.02) as a predictor variable against BOD (p = 0.09); having excluded one discordant dataset (i.e. N = 36). This is in addition to strong statistical significance (p <0.001) for all the other predictors identified in Model D$^@$. The expression for this alternate to Model D$^@$ is shown in Eq. 3:

$$\Delta(OP)\% = -3.71(OP)^2 + 4.17pH(OP) + 2.38\frac{(BOD)}{(OP)} - 3.55T - 20.98pH + 170.57 \qquad (3)$$

However, despite similarly high monthly average BOD in May (12.1 ± 5.7 mg/L), BOD did not show as are liable (p >0.2) predictor (either alone, as BOD/OP or as BOD*OP) in the generated model for that season (Model A). It is noteworthy however that with sample size of only 9 for Model A against 37 for Models C

& $D^{@}$, it is possible that the high *p* value in the former case may as well be associated with the smaller sample size in the regression analysis. The smaller a sample size, the more likely a difference may go undetected. As discussed earlier, even for the SG-1 condition, BOD appears as an unstable predictor variable - likely due to its correlation with pH and TAN (i.e. due to multicollinearity).

b) Influence of pH alone (z_5) was also important only under SG-1 operating conditions with an influent pH ranging from 8.0 to 9.7 (Models B, D, D*, $D^{@}$ & $D^{@2}$). The pH effect was not statistically significant for monthly observations of smaller pH range or towards more basic regions (e.g. pH 8.3-9.4 for subgroup SG-2) (Model $E^{(?)}$). It is worth noting however that despite the pH range in May being also within less alkaline region (8.1 to 9.0) as SG-1, its effect was still statistically insignificant ($p > 0.2$). So, it does not appear it is the region of pH which is dictating the significance of the pH effect on OP removal, but rather the spread in the pH data. The spread (SD) in May was small; smaller spreads in observations lead to higher *p* values. In fact, the CV in pH for the SG-1 conditions is 5.3% versus only 3.1% for May and 3.5% for the SG-2 conditions. Also and as argued for BOD, the limited number of observations in May (small sample size) might also explain why the pH was found to be statistically insignificant as predictor for Model A. The negative impact of pH on OP removal had previously been reported by Mohansingh et al. (2006) and within a pH range of 6.6 to 9.0. However, the reported magnitude of effect on OP removal (in terms of loading rates) was substantially lower than what is derived here for the SG-1 conditions (i.e. 0.11 versus 21.59 to 28.52% release per unit rise in pH).

c) Seeming paradoxical, adverse effect of rainfall (z_3) on OP removal was statistically significant (i.e. a reliable predictor variable) only for data observations of more moderate average monthly precipitation (i.e. 41.9 ± 34.7 mm) (i.e. Model $E^{(?)}$ for SG-2 subgroup). Higher monthly average rain periods as in SG-1 (65.2 ± 34.9 mm) and SG-3 (61.4 ± 27.8 mm) observations did not generate models with any reliable influence of rainfall on OP removal (i.e. Models B to D). Though tempting to associate differences in reliability of rainfall effect amongst the models to average intensity of rains, the actual reason seems to be with variability in the data as shown by CVs in the datasets for these subgroups of observations: SG-2 (CV = 82.8%) versus SG-1 (CV = 53.1%) and SG-3 (CV = 45.4%). Once again, smaller spreads in observations lead to higher *p* values. Thus, the rainfall effect may indeed be real; only nulled under SG-1 and SG-3 subgroup operating conditions due to the lacking spread in data. Association of OP release with rainfall is reported in the literature (e.g. Adhishwar and Choudhary, 2015; Schwemm et al., 2004), but such effects appear irregular (Adhishwar and Choudhary, 2015). It is expected that the adverse effect of rainfall on OP removal is linked to sediment perturbation under the following conditions, which make them susceptible to release OP into the overlying water: anaerobic conditions where o-PO_4^{3-} bonded Fe (III) is reduced to Fe (II) to release OP into the CW water column (Adhishwar and Choudhary, 2015); and conditions for oxidative respiration and fermentation of organic matter in a) the mineralization of organic P compounds to produce soluble o-PO_4^{3-} and/or b) to produce organic acids that either directly dissolve inorganic mineral o-PO_4^{3-} as a result of anion exchange of o-PO_4^{3-} by carboxylates or can chelate Fe, Al and Ca ions associated with P to release o-PO_4^{3-} (Ahemad et al., 2009; Sharma et al., 2013).

d) Influence of TAN was important only under SG-1 operating conditions with an influent TAN ranging from 0.1 to 16.2 mg/L (Models D and $D^{@2}$). It is noteworthy that biological co-uptake of TAN and OP from

MWW is reported in the literature (Delgadilo-Mirquez and Pareau, 2016). The TAN effect was however not statistically significant for monthly observations in spring or for the subgroups SG-2 & SG-3 in summer/early fall, but that cannot be assigned to smaller spread of the data, which ranged comparably from 0.4 to 22.5 mg/L-N in spring and 0.1 to 18.0 mg/L-N for the SG-2 subgroup. The non-significance of TAN in these cases is rather likely due to the smaller sample sizes for these datasets.

Thus far in this discussion, the following summaries can be made: The influence of BOD, TAN, pH - as stand-alone parameter and rainfall have been shown from this present study (at least under some operating conditions) and they have confirmations in the literature. For cases where such effects were shown not to be of statistical significance, there are arguments to suggest either the smallness of sample sizes or/and lack of good spread in the data as likely reasons and it is possible to show relevant impact in a more general model with right sample size and data spread. The next paragraphs therefore continue with the discussion, but this time focuses on the similarities in the models with respect to the identified predictor variables and the estimated magnitude of their effects on OP removal efficiency.

It is noteworthy that despite the obvious differences between the models describing the OP removal under various spring and summer/early fall conditions (Models A-E), there were two main common features notable with them all:

a) Consistent adverse impact of temperature ranging from 3.16 to 4.54% OP release (over inlet concentration) per degree rise in temperature (^oC); i.e. an average of 3.79 ± 0.37% and median of 3.78% release per degree rise in temperature (^oC).

b) A combined effect from the OP dependent quadratic term $(OP)^2$ and the interaction term pH*OP, which on average (assuming equal weighting for the models from May to September may be summed as: 4.86 (± 1.11) pH*OP – 4.52 (± 0.84) $(OP)^2$. This would mean an optimum OP removal stage; where OP = 0.54 pH. But the number of datasets in the subgroups are not the same and also (as discussed earlier) the statistical insignificance of factors such as pH and BOD (either alone, as BOD/OP or as BOD*OP) may only be due to lesser number of sample sizes in those models. Therefore, combination of the various monthly subgroups of data (i.e. May, SG-1 and SG-2) to embrace the common terms was warranted to refine the models (A to E). In fact, to produce more accurate estimations of the magnitudes of the predictor variables, it was necessary not only to include the common terms, but also to consider those of otherwise weaker statistical significance due to smallness of sample sizes and/or low data spread.

4.3.2 Derivation and description of the main model: Model F

Re-running the MLR analysis generated a refined multivariate quadratic function shown as Model F in Table 2. Several datasets within the SG-2 group, where rainfall was a significant factor, did not however conform to this new model (i.e. the absolute standardized residuals were greater than 2) and hence excluded. 49 out of the 73 (~67%) of the May to September monthly datasets that qualified for the MLR analyses conformed to this model and the goodness of the model fit to the experimental data is illustrated in Fig. 2. Based on this quadratic function, the optimum inlet composition for OP removal would occur when the inlet OP = 0.47 pH + 0.05 BOD. Therefore, for wastewater compositions with OP concentrations (mg/L) <0.47 pH + 0.05 BOD, an increase in the influent OP concentration would result in increased efficiency of removal. Contrary, for those with OP concentrations (mg/L) >0.47 pH + 0.05 BOD, increase in influent OP concentration would result in decreased efficiency of removal. Based therefore on the average monthly influent pH of 8.69 (± 0.43) and influent BOD of 10.00 (± 6.06) mg/L for the conditions conforming to this relation, optimum OP removal was to occur at ~4.6 mg/L OP. In fact, only 4 out of the 49 qualified monthly datasets showed OP exceeding this value suggesting that increasing OP generally resulted in OP removal.

4.3.3 Interpretation of the main model: Model F

There are three vital qualitative deductions that can be made from the above results and they are as follows:

a) High pH interactions with influent OP concentration favor OP removal.
b) High BOD concentrations favor OP removal with increase in influent OP concentrations to a threshold value; after which reduction in removal occurs.
c) The associated removal mechanism to account for the core OP dependent quadratic relation in Model F (i.e. $-2.78 (OP)^2 + 0.29$ BOD*OP + 2.63 pH*OP) is morelikely biological (not chemical) in nature considering the co-dependence on both pH and BOD (in the expression) for the OP removal. In fact, it is more likely microbial at core (because of the BOD term) although there is no evidence from the study to discount also association with plants uptake.

The implications or interpretations of these remarks with respect to the CW operation and the current perceptions in the literature will be made in this section, but before then, it is important for the reader to note that OP removal or release in CW systems are in constant dynamic changes due to variations in water chemistry and biological activities (Uusitalo et al., 2013). The water chemistry-driven changes involve reactions such as OP release from particulate pool (including bottom sediment) into the water column, retention of OP to particle surfaces (adsorption), and precipitation/dissolution reactions (Herskowitz, 1986; Liu et al., 2012; Uusitalo et al., 2013). The partitioning of OP in soluble or insoluble pools is driven by changes in OP concentration in water, pH, the redox state of sediment and water, and the concentrations of dissolved ions in water (i.e. ionic strength of water). Generally, OP removal by retention on particle surfaces is increased with an increase in concentration of OP in water, a decrease in pH, the presence of DO, and an increase in ionic strength. On the other hand, OP release by solubilization from particles to dissolved pool is increased at low OP concentration in water, a high pH, a low supply in DO (anaerobic conditions), and a low concentration of dissolved ions (Herskowitz, 1986; Uusitalo et al., 2013).

4.3.3.1 PO_4^{3-}/pH interaction effect

Based on the first and third deductions above and that the pH range spanned only from 8.0 to 9.7, it can be inferred that HPO_4^{2-} (and not the commonly purported $H_2PO_4^-$) is the preferred o-PO_4^{3-} species of biological uptake within the CW. In fact, estimation of HPO_4^{2-}-P and $H_2PO_4^-$-P concentrations based on the inlet pH and OP data and pk_{2a} (H_3PO_4) = 7.19 (Hagen and Hopkins, 1955) reveals a linear correlation between HPO_4^{2-}-P concentration and OP removal (r = 0.77) (Fig. 3) attributable to the quadratic functional relation. The corresponding relation with $H_2PO_4^-$-P within the same pH and OP concentration range shows a logarithmic relation with OP removal (r = 0.75) where barely any further change in removal is shown at higher concentrations (of $H_2PO_4^-$-P) after an initial increase (Fig. 3). However, these conclusions contrast several reports in the literature stating $H_2PO_4^-$ as the likely/preferred (e.g. Ahemad et al., 2009; Alam et al., 1999; Hendrix, 1967; Schachtman et al., 1998; Sentenac

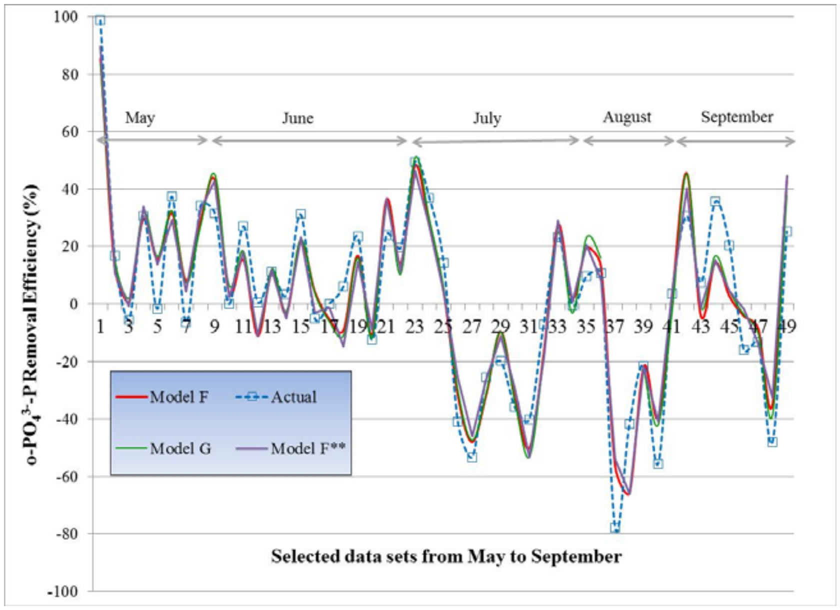

Figure 2 Comparison of actual and model predictions of o-PO_4^{3-}-P (OP) removal efficiency by the CW from May (datasets 1-8) through June (datasets 9.22), July (datasets 23-34) and August (datasets 35-41) to September (datasets 42-49) for models F & G

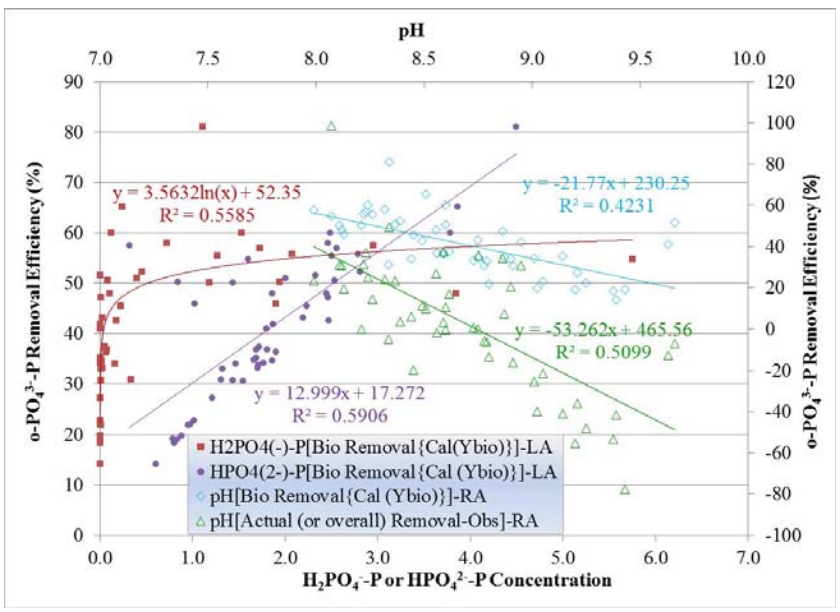

Figure 3 o-PO_4^{3-}-P (OP) removal efficiency (estimated from actual observation or by the core OP dependent quadratic relation (Y_{bio}) in Model F {i.e. $Y_{bio} = -2.78\ (OP)^2 + 0.29\ BOD*OP + 2.63\ pH*OP$} to indicate the biological portion of the removal) as a function of pH, $H_2PO_4^-$-P or HPO_4^{2-}-P concentrations; LA = left axis and RA = right axis. NB: The functional relations between the actual (or overall) OP removal efficiency and $H_2PO_4^-$-P or HPO_4^{2-}-P are omitted to avoid congestion, but they are similarly of logarithmic and linear relation as shown: i.e. y= 8.039 In x + 28.158 and y = 17.526 x – 29.368, respectively.

and Grignon, 1985) or kinetically favored (e.g. Datta et al., 2015; Gaxiola et al., 2011; Mitra, 2015) o-PO_4^{3-} species (over HPO_4^{2-}) in plant uptake of OP.

The argument for $H_2PO_4^-$ has been based on observations of decreasing o-PO_4^{3-} absorption rate with increasing pH (e.g. Hagen and Hopkins, 1955) or on optimum uptake rates typically at near neutral pH values or lower (e.g. Barrow, 2017; Ullrich-Eberius et al., 1984) and/or on simple correlations of o-PO_4^{3-} absorption with $H_2PO_4^-$ concentration (Hendrix, 1967). This is despite early caution against assigning such adsorptive tendencies (or lack thereof) to o-PO_4^{3-} ionic species solely because of their predominant concentrations in the system (e.g. Hagen and Hopkins, 1955). In fact, in most of these plant studies (e.g. Hendrix, 1967), the experiments were performed at fixed o-PO_4^{3-} concentration with pH adjustments typically between ~4 and ~9; pH correlation, negatively with the monovalent and positively with the divalent o-PO_4^{3-} species, are therefore to be expected. Assigning o-PO_4^{3-} uptake to either species simply based on correlation therefore is fraudulent as such experimental conditions do not allow distinction of the pH per se effect from its effect on o-PO_4^{3-} speciation in the uptake process.

In this present study as well, an inverse (linear) relation between OP removal and pH ($R^2 = 0.51$; $r = -0.71$) is observed within the pH range 8.0 to 9.7 (Fig. 3). In fact, in the literature, the phenomenon whereby increasing pH causes decline in o-PO_4^{3-} uptake/removal is not limited to plants but also to microbes (e.g. Yan et al., 2007) as well as abiotico-PO_4^{3-} removal (e.g. adsorption and/or precipitation) from solution (e.g. Liu et al., 2012). Hagen and Hopkins (1955) suggested a pH effect, per se, expressed in the sense of hydroxyl ion (OH^-) competition with both $H_2PO_4^-$ and HPO_4^{2-} absorption, as a plausible reason for the decreasing OP removal efficiency commonly observed from pH ~5.5 to ~9 (Hagen and Hopkins, 1955; Hendrix, 1967). Similar reason was given for a decreasing o-PO_4^{3-} removal in an abiotic chemical removing system (adsorption on calcite) with increasing initial pH from 5.0 to 10.0 (Liu et al., 2012).

Analogous to biological systems, pH effect in abiotic systems are shown both in changes at adsorptive sites and in speciation of o-PO_4^{3-} in solution (Gunawan et al., 2010; Liu et al., 2012). Additionally, pH effect on o-PO_4^{3-} removal in both biotic and abiotic systems would relate to the degree of super-saturation and the type of precipitates formed in solution; though this effect was previously described by Gunawan et al. (2010) only for an abiotic system, and is in fact strictly chemical (not biological) in nature irrespective whether occurring in biotic or abiotic treatment system. Therefore, based on the model (F) equation and the information presented thus far, two main distinct effects of pH on OP removal by the CW are being proposed here: (a) one which is mainly biological in nature (more likely microbial at the core) and favors net OP removal by speciation of o-PO_4^{3-} into the active ionic form (HPO_4^{2-}) for BOD related uptake directly by bacterial and/or indirectly by plant cells; and (b) a second effect, which presumably may be both biological and chemical in nature and may impact o-PO_4^{3-} removal adversely by, for example, the provision of OH^- as an interfering anion to the uptake, adsorption, or precipitation of o-PO_4^{3-} species from solution or by promoting their release from sediment or suspended solid sources with increasing pH (under anaerobic conditions). Other pH effects are also possible as discussed below (Section 4.3.3.2). Note! The influence of other factors such as the ionic constituents in the MWW (as discussed below), which did not appear significant in this present study, may cause this second pH effect to reverse in nature; becoming more favorable for o-PO_4^{3-} removal.

With respect to the effect of pH on biological cell uptake of o-PO_4^{3-} species, it is to be noted that the commonly observed declining uptake with increasing pH in the literature, as well as in the present study, is not actually universal. Optimum uptake of o-PO_4^{3-} by bacteria and protozoa were observed actually at the highest pH from two separate studies within pH range of ~5 to ~9 (Akpor et al., 2008; Sicko-Goad et al., 1978). Similarly, o-PO_4^{3-} removal by intact higher plants had long been reported at pH of 9 and the absorption ascribed to HPO_4^{2-} species (Arnon et al., 1942). Also in certain algae, o-PO_4^{3-} uptake was optimal in alkaline pH range (Ullrich-Eberius and Yingchol, 1974). It is therefore reasonable to suggest based on the discussions thus far that o-PO_4^{3-} speciation to HPO_4^{2-} indeed promotes effective o-PO_4^{3-} uptake in alkaline media and it is some other pH effects (e.g. influence from pH per se) which is responsible for the commonly observed declining impact at increased pH. Why then the conflicting observations in the literature with respect to o-PO_4^{3-} uptake efficiencies in alkaline pH conditions? Attempts are made in the next section to answer this question.

4.3.3.2 Other pH effects

As shown in Fig. 3, a clear distinction can be made between the impact imposed indirectly by pH with the formation of different concentrations of o-PO_4^{3-} of species (susceptible to different kinetic and thermodynamic uptakes) and the "direct" impact of pH on OP removal. The pH speciation effect on o-PO_4^{3-} results in a net OP removal; whilst the "direct" pH effect results in net OP release. From the discussions thus far, the negative coefficient term for the pH per se (Model F) is consistent with solubilization or desorption of particulate pool of P from the bottom of the CW sediment or from suspended solids within the water column. This may be driven chemically under reducing (low oxygen) soil redox conditions (Herskowitz, 1986; Patrick and Khalid, 1974; Uusitalo, 2013) or biochemically by the so-called phosphate solubilizing microbes (PSM) (Ahemad et al., 2009; Sharma et al., 2013). The latter is achieved with the production of organic acids to solubilize inorganic sources of o-PO_4^{3-} by either of the following (Sharma et al., 2013): (i) lowering the pH, (ii) competing with o-PO_4^{3-} species for adsorption sites on the soil or (iii) forming soluble complexes with metal ions (e.g. Ca, Al and Fe) associated with insoluble o-PO_4^{3-} and thus releasing o-PO_4^{3-}. Organic P is also mineralized by microorganism under anaerobic conditions.

Model F (bearing in mind a background removal of + 169%; i.e. the intercept) suggests ~16% OP release (over the inlet concentration) per unit rise in influent pH. Bearing in mind also the slope differences in the two OP removal efficiency versus pH linear lines in Fig. 3 (one attributable to BOD related removal and the other as the overall net removal), one can conclude (at least qualitatively) that there are other causal factors to the BOD related influence to account for the overall pH effect in releasing OP.

As noted earlier, although increasing pH (as stand-alone variable) within alkaline regions usually results in increasing OP release or decreasing OP removal, others have observed the contrary. In fact, part of the controversy around pH effect on o-PO_4^{3-} removal is related to differences in ionic constituents of the solutions used in the various studies (Hendrix, 1967). For instance, o-PO_4^{3-} uptake from dilute salt solutions is greatest in the presence of the divalent cations Ca^{2+} and Mg^{2+}, especially under high pH conditions (Sicko-Goad et al., 1978; Wu et al., 2006). Mg^{2+}, in particular, was proposed to stimulate o-PO_4^{3-} uptake through an $MgHPO_4/H^+$ carrier in aerobic zones and inhibits its release in anaerobic zones. Also in chemical o-PO_4^{3-} removal systems, these two cations (Ca^{2+} and Mg^{2+}) can increase the adsorption of o-PO_4^{3-} by calcite (Millero et al., 2001). Hence, on its own, pH effect in both biological and chemical o-PO_4^{3-} removal or release in alkaline medium is dictated also by the concentrations of the divalent metal ions.

In wastewaters or solutions of relatively low Ca^{2+} and Mg^{2+} concentration, increasing pH for low o-PO_4^{3-} conditions implies the OH^- present would outcompete both $H_2PO_4^{3-}$ and HPO_4^{2-} for biological uptake (Hagen and Hopkins, 1955); and particularly for wastewaters with high alkalinity, the increasing pH would create competition also from other anions like CO_3^{2-} for the divalent cations in adsorption and/or precipitation thereby reducing o-PO_4^{3-} removal by precipitation (Johansson and Gustasson, 2000; Liu et al., 2012). In fact, reducing the availability of soluble Ca and Mg ions would also impact adversely the uptake of available HPO_4^{2-} as they seem required for the biological sorption process (Sicko-Goad et al., 1978; Wu et al., 2006). Thus, as in this study, increasing pH under the described conditions results in increasing release of OP. It is only at pH >10 would increase in OP removal be observed with increasing pH and that is because of the competitive advantage of PO_4^{3-} over OH^- and CO_3^{2-} for the divalent ions (Liu et al., 2012). On the other hand, in wastewaters and solutions high in Ca^{2+} and Mg^{2+} concentrations, although adsorption and precipitation of the competing OH^- and CO_3^{2-} anions with the divalent cations are still expected, because of the availability of excess of these cations, increasing pH would promote biological uptake of the increasingly formed HPO_4^{2-} (Sicko-Goad et al., 1978; Wu et al., 2006) or be removed chemically from solution by adsorption and/or precipitation.

The ionic constituent influence associated with pH impact on biological o-PO_4^{3-} uptake is not only related to differences in charge valences, but also the actual types of ions even of similar charge valences. As with Mg^{2+}, K^+ also acts as an important counter ion for the simultaneous uptake and release of o-PO_4^{3-}; it defines cell membrane permeability and plays a major role in o-PO_4^{3-} transport between surrounding environment and cell (Machnicka et al., 2004, 2008; Medveczky and Rosemberg, 1971; Schönborn et al., 2001; Van Groenestijn et al., 1988). Under alkaline media, K^+ seems to exert greater influence than Na^+ in o-PO_4^{3-} uptake (Sicko-Goad et al., 1978). Although the average inlet concentration of Mg, Ca and K during the study period was 71 ± 11, 95 ± 11 and 29 ± 5 mg/L, respectively and in excess over OP (average of 2.0 ± 1.0 mg/L), one cannot assume that limitation of these ions in affecting o-PO_4^{3-} removal is unlikely as has been suggested by some (Randall et al., 1992). In fact, for high alkalinity wastewater such as in this present study (i.e. 362.8 ± 61.5 mg/L $CaCO_3$), these ions may be rendered unavailable and be prevented as co-transporter with HPO_4^{2-} for biological uptake.

The discussion so far in this section has dwelt on pH as a factor responsible in generating anions such as OH^- and CO_3^{2-} to be in competition with speciated forms of o-PO_4^{3-} for various cations as co-transporters in biological uptake or in adsorption/precipitation processes of removal from wastewaters. As much as pH per se may play a unique role in, for example, OH^- influence on biological activities; in the case of CO_3^-, its main role seems to be speciation and it may play similar roles with other chemical constituents such as ammonia. From the analysis of the annual average data for the SaskPower CW, increasing influent $[NH_3]/[NH_4^+]$ ratio was shown to correlate with decreasing OP removal (Quagraine et al., 2017b). Furthermore, in an earlier paper (Quagraine et al., 2017a), increasing $[NH_3]/[NH_4^+]$ ratio was noted to inhibit total ammonia removal and to result in pH decline across the CW; it was attributed mainly to inhibitory assimilation of TAN for algae (plant) growth at high pH values. The monthly increasing pH effect in reducing OP removal, as discussed here, may as well be linked with pH speciation of ammonia. Even though the major source of plant nutrients for emergent vegetation (such as cattail plants) is the CW sediment rather than the overlying water, OP is assimilated by algae and duckweed within the overlying water, as well as by cattail and other emergent plant roots exposed to the water (Herskowitz, 1986). Growth of water hyacinth (another floating plant), as determined by dry weight, was observed to inversely correlate with pH in an excellent manner (r = 0.92) from pH 4.0 to 10.0; i.e. increasing pH adversely affected the growth of the plants (Haller and Sutton, 1973). So, it is possible that the inhibitory effect from increasing pH on OP removal observed in this present study may at least partially be associated with NH_3 toxicity to growth of susceptible (floating) plants such as the algae, duckweed, water hyacinth, etc. This would subsequently result in reduced uptake of OP in the plant growth and/or its increased release from the plant death/decay processes. The effect of TAN and its interactive term pH*TAN on OP removal is discussed separately in Section 4.3.3.5.

4.3.3.3 Temperature effect

From Table 2, the temperature dependence in Model F is highly significant ($p < 0.0000$) and of large effect size on OP removal efficiency, though negative (i.e. 4.38% release per ^{o}C). The release of stored P from CW sediments during warm season (consistent in most cases in July and August as in Fig. 2) has been attributed to potential anaerobic conditions that may develop during such periods (Andersson et al., 2005). However, under some other (e.g. dry and aerobic) conditions, temperature may also influence microbial oxidation or breakdown of P rich organic matter in forms such as detrital plant tissue from sediment sources or particulate (including dead algae) in the water column to result in net release of OP (Ardón et al., 2010; Kadlec and Reddy, 2001; Kadlec and Wallace, 2009; Silveira and O'Connor, 2013; Van Dijk et al., 2004).

Consistent with the results in this study, Kadlec and Reddy (2001) observed that OP release from an organic wetland soil was strongly dependent on temperature. The release under anaerobic conditions was slightly higher than that under aerobic conditions. The results here however contradict reports on a vertical-flow CW (Scholz, 2016), some large subtropical FWS CWs with low total P loading rate (Jerauld, 2010), and some temperate FWS CWs operated for over a 4-year period with plant harvesting (Herskowitz, 1986; Kadlec and Reddy, 2001), where OP removal seemed independent of temperature or its effect as minor. Such lack of temperature dependence on P removal has been explained either by dominance of physical (as opposed to biological) removal processes or by near zero net biological uptake (i.e. small difference between uptake and release) across the seasons (Kadlec and Reddy, 2001; Scholz, 2016; Yeh et al., 2006). In the latter case, it is further explained by a balance between slow rate of detrital tissue decomposition in OP release and reduced OP removal due to translocation to belowground biomass in winter; in summer, the balance is mainly between significant plant uptake and rapid OP release by microbial decomposition of detrital tissues. The results here also contradict findings by Merlin et al. (2002), who reported higher OP removal efficiency to a maximum of 90% in summer than in winter with minima as low as 20-30% by a horizontal subsurface flow CW which had been in operation for 6 years with annual biomass harvesting. The features of all these exemplified CWs (i.e. either by the type of hydrology or flow direction, areal P loading rate, the period in operation or the harvesting practice) are notable in terms of their nominal tendency to have accumulated huge P-rich sediment biomass by the study period, and that may explain the lacking OP release or temperature dependence observed with respect OP removal efficiency by these CWs.

The answer to the query as to whether the net OP uptake by CWs is positive (higher) or negative (lower) was left open in the report by Kadlec and Reddy (2001). Contrasting the CW conditions that yielded the results here to those in the examples above, it is logical to suggest that seasonal or temperature dependent OP release (i.e. net negative uptake) is more likely to be displayed by CWs only when excess accumulated P-rich biomass sources persist than required or utilizable by plants, microbes or other means. In other words, the CW becomes a source of TP or OP rather than sinks due to increased P recycling from the sediment than can be utilized (Wang et al., 2006).

4.3.3.4 Influent BOD effect

In biological phosphate removal (BPR) systems, the ratio of BOD to P influences the BPR removal capability, with the general consensuses being that efficient BPR requires that the influent to the anaerobic zone should have a BOD: TP ratio of >20:1 (Mulkerrins et al., 2004; Randell et al., 1992). As discussed earlier, although BOD to OP ratio could be shown in this study as a statistical significant variable to positively influence OP removal efficiency, it was only on a limited set of monthly average data with BOD/OP ratio of only 4.3 ± 2.1 (i.e. the SG-1 subgroup). For a wider range of monthly average data, it was rather the product term (BOD*OP) which showed more statistical significance (Model F) in predicting OP removal efficiency at $p < 0.05$; i.e. the higher the product of these two parameters the more efficient was the removal of OP.

For a vertical flow CW, high COD (BOD plus oxygen required to oxidize the non-biodegradable portion of organic matter) inflow concentrations showed significant positive impact on the treatment efficiency of OP (Scholz, 2016). Increased organic load in wastewaters has also been reported to improve OP removal efficiency (Charlotte et al., 2013).

4.3.3.5 Influent TAN and NO_3^--N effects

From Table 2, the influent TAN dependence in Model F is significant ($p < 0.05$) but of moderate effect size on OP removal at 1.87% removal per mg/L-TAN; i.e. contributing to TAN removal of a minimum 0.1% (in August 2003) and a maximum 42% (in May 1995). Replacing TAN with its interaction term of pH*TAN with the aim to assess speciation effect of pH on TAN in influencing OP removal did not affect the Model F in any significant way (See Model F* in Table 2). Inclusion of both terms as variables in the MLR analysis however produced a poorer regression outcome (not shown) with a larger overall p value and misleadingly showing each as statistically non-significant predictor ($p \geq 0.48$) together with pH ($p = 0.23$), although $\bar{R}^2$ stayed almost invariant. This is due to multicollinearity as TAN correlates excellently with pH*TAN ($R^2 = 0.999$). The lacking distinction between Models F and F* is not an indictment against a pH-dependent TAN speciation effect on OP removal as noted in an earlier report (Quagraine et al., 2017b), as this effect is indeed inherent with the presence of pH as a predictor variable in the model. In fact, this is precisely the case as shown in Model F** in Table 2, where pH is excluded from the model.

It is interesting that by nullifying the categorical effect of pH from the analysis (Model F**), its speciation effect both in terms of o-PO_4^{3-}-P (OP) ($p < 0.0000$) and TAN ($p < 0.01$) becomes more obvious, being statistically relevant. Furthermore, distinction could be made between the influence of TAN as a categorical term and the pH influence on TAN's impart, which was previously attributed to ammonia toxicity on algae (plant) and microbial growth (Quagraine et al., 2017a, b). Although overall (i.e. by $\bar{R}^2$ and F statistics), Model F** seems marginally inferior to Model F (and F*) in fitting to the observed data, it is a more meaningful model and shows stronger statistical relevance for the predictive variables (i.e. lower *p* values for the t-statistics of the independent variables). Model F** fits similarly well to the observed data as Model F (Fig. 2).

However, the relatively weaker overall predictive power for Model F** as compared to Model F and Model F* seems to suggest other ignored but relevant pH effects, which apparently show up as significantly higher variability in the estimated intercept (C*) values ($p = 0.39$ for Model F** vs $p = 0.002$ for Model F). It is noteworthy that apart from temperature, the differences in magnitude of the estimated coefficients between Model F and Model F** (i.e. $(OP)^2$, OP*BOD, OP*pH and TAN) are significant and further investigations seem warranted in the future to identify the categorical pH and/or other pH related speciation (e.g. $H_2CO_3^-/HCO_3^{2-}$) effects and refine the estimated coefficients, but for now the estimated coefficients for Model F** seem more reliable for reference because of the lower *p* values for these estimates. The implications of the C* values are further discussed in Section 4.3.5.

As observed for Model D, inclusion of NO_3^--N as a predictor variable in Model F barely affects the predictive power of the model with $\bar{R}^2$ essentially the same (0.86), although this time it is more clearly noted as a non-significant predictor variable ($p = 0.36$) alongside a worsened *p* value for significance of F (ANOVA). Further, apart from pH, there was a general worsening of the statistical significance of the other predictor variables including TAN when NO_3^--N is included in the model. Therefore, overall, NO_3^--N did not appear to be a relevant predictor variable during the plant growing period, especially in presence of TAN.

4.3.4 Accounting for CW aging effect: Model G

As shown in Table 2, inclusion of CW age in the general model F or its analogue F** did not change the coefficient of determination ($\bar{R}^2$) to any significant level. However, despite the CW aging effect being only weakly significant ($p = 0.2$), its presence in the model consistently improved the reliability of the other variables to predict OP removal efficiency (i.e. lower *p* values). The OP removal efficiency decreased with age of the CW by only ~0.45% per annum. Decline in OP removal from 45 to 22% with increased years of CW operation on swine wastewater is reported in the literature (Reddy et al., 2011). CW age was also found a prominent factor in regression models describing P removal in some large CWs (Jerauld, 2010). In all cases of that investigation, the sign on the aging coefficient showed decreasing performance with increasing age; an average increase of 0.0051 mg/L per annum in the effluent TP (i.e. 5.1% increase per year based on a hypothetical wetland with outflow TP concentration of 0.10 mg/L (Jerauld, 2010).

CW age is noted as a "lumped" parameter, integrating the effects of multiple wetland characteristics that change over time: e.g. soil P, internal hydraulics, plant biomass and tissue P (Jerauld, 2010). As data for such parameters were not available at the monthly scale for the regression analysis, it was not possible to specifically isolate the influence of such factors from the integrated effects of age. Nevertheless, due to interaction and/or interrelation of such "lumped" factors with (or influence by) some compositional and climatic factors such as pH, temperature, rainfall, etc., their influence on OP removal or release may indirectly (at least partially) be captured in terms of the effect by these latter set of parameters (which were included in the regression analysis). This may explain the relatively small size of the aging effect as identified here, which (on its own) is not large enough to be a principal factor for the poor performance of the CW in removing OP during the study period. Yet, there is evidence from the present investigation to suggest that integrated age-related factors such as plant biomass, sediment P concentration and other soil characteristics had more sizeable detrimental influence on OP removal efficiency than as shown by the regression analysis for aging effect “per se”.

For the post-flood conditions, where wash-off of accumulated top organic sediment expectedly occurred, significant improvement in OP removal (to levels similar to the initial periods on treating CS effluent) was observed with vegetation re-establishment (Quagraine et al., 2017b). This occurrence seems analogous to a case ata490 ha Orlando Easterly Wetland (Florida, USA) where removal of plants and organic top sediment followed by re-vegetation improved OP removal efficiency significantly with the treatment of tertiary MWW (Black and Wise, 2003; Wang et al., 2006). After over 10 years of operation and prior to the rejuvenation project, some seasonal decline similar to the observed in this study (Fig. 2) developed; albeit the declines in these two cases occurred at different seasons: summer in the present study but winter in the Orlando case-both seasons for which anaerobic conditions prevail. Spikes, in the case of the latter, was attributed to decomposition of floating aquatic vegetation (FAV) and subsequent release of OP stored in their tissue after the FAV senesce in winter (Wang et al., 2006); whilst OP release in summer has been attributed to anaerobic activities (Andersson et al., 2005). During anoxic conditions, iron (III) bound o-PO_4^{3-} may be reduced to iron (II), resulting in the release of iron-bound o-PO_4^{3-} (Ardón et al., 2010; Reddy et al., 1999). Yet, o-PO_4^{3-} release from CW sediment may also occur via mineralization of organic Punder aerobic conditions during dry periods (Ardón et al., 2010; Van Dijk et al., 2004).

Maximum OPretention capacity of soil/sediment is generally reached after saturation of all sorption sites (Reddy et al., 1999), which for natural wetlands occur only after a few years of operation (Kadlec and Wallace, 2009); though that for CWs is variable, being observed at as early as less than 4 years (Herskowitz, 1986; Quagraine et al., 2017b), after 10-13 years (Black and Wise, 2003; Wang et al., 2006) or even longer (Kadlec, 2016). The period of CW operation before saturation of the sorption sites depends on the cumulative o-PO_4^{3-} loading (Herskowitz, 1986). How much of added o-PO_4^{3-} can be stored via sediment accretion, once the saturation point is reached, dictates what remains together with released o-PO_4^{3-} from the internal P cycling sources into the overlying water to elevate the outflow concentration. Therefore, to avoid premature saturation and/or long-term sediment accumulation of organo phosphorus matter, harvesting of plants (e.g. biannually) is thought to be an important management strategy to maintain OP removal capacity of the CW (Álvarez and Bécares, 2006; Andersson et al., 2005) and may reduce the possible long-term problems in CW operation associated with the accumulation of organic matter (Herskowitz, 1986), but this practice is not universally embraced. It is deemed not cost-effective as only a small part (<10%) of the total annual N and P input to a CW was removed by plant harvesting. A considerable amount of nutrients in emergent plants (e.g. cattail) are stored in the underground parts, roots and rhizomes, particularly in the latter part of the growing season when there is a net movement of nutrients from the shoots into the winter storage organs (Herskowitz, 1986). Frequent plant harvesting also has downside in denitrification as the denitrifying bacteria may be deprived of organic matter as energy source (Andersson et al., 2005).

4.3.5 Relevance of the intercept or constant term (C*)

Mathematically, it is correct that the Y intercept (see Eq. 2) is the mean predictable response value when all the predictors in the model are simultaneously each of 0 values. However, this condition is usually improbable, as in the case of Model F, which involves a pH term where a 0 value is of no practical sense. And even if that were possible in nature, in the current study none of the datasets contained a pH value remotely close to 0 (pH >8.0); in other words, all-zero predictor datasets, even if possible, would be outside the data range used in the model prediction. Conditions such as these have normally been considered as prerequisite to declare intercept values derived from MLR analysis meaningless; but should it always? Subsequently, whether the intercept or constant value is insignificant or significant has commonly been considered irrelevant. Nevertheless, in practical terms, as depicted in Eq. 4, the intercept (or constant C*) is actually a lump term or the net average value of all other additional response variables outside those from the predictor variables identified in the model. In other words, it is a composite term to include all other influencing factors not acknowledged (or inherently represented due to correlation-collinearity) in the model. Thus, the intercept/constant value includes all potential predictor variables (continuous and/or categorical) as well as an actual constant or background contributing response. Inclusion of a large proportion of predictor variable terms (especially if they are of large size of influence) is therefore likely to render the intercept/constant term of less statistical significance (because of its potential variability between different observations and hence large standard error in the estimated value).

$$\mathrm{Y} = \left(\sum_{i=1}^{i=k} \beta_i z_i = 0\right) + \mathrm{C}^* \tag{4}$$

From the above discussion (also see Eq. 4), it is conceivable to have a case in a MLR analysis where one or multiple predictor variables (e.g. pH) in a model may indeed be of no practical significance at value 0 and yet provide a meaningful intercept value; at least of semi-quantitative or at worst of qualitative significance. The regression outputs in the present study provide some basis to offer some meaning to the intercept values in the models; particularly the general model (Model F) and its analogue Model F**. As shown in Table 2, C* when displayed as negative or small positive number in any of the proposed preliminary models for the May to September months of operation (i.e. Models A, C & E) was not a statistically significant term (p > 0.39-0.97) suggesting uncertainty in the values; even though the overall model predictive power (R^2) of each of the model is high. Furthermore, the high p values with associated high standard errors in these estimates suggest that the "real" constant in each of those models is likely lumped with other variable(s) making the intercept terms highly variable rather than being true constants. In contrast, inclusion of pH (particularly) in the models improved significantly the reliability of the intercept term (p > 0.05) and with modest standard errors; suggesting that, at least, pH effect was lumped with the "real" constant (C*) in models A, C and E. Refining the models to include the interaction terms involving BOD, TAN, pH and OP as well as the aging effect (*vide infra*) of the CW yields a constant background OP removal of ~169% with high degree of certainty (p = 0.002) in Models F and G. Replacing pH with the interaction term pH*TAN as predictor variables however yields models with background OP removal of ~9% and 14% with high degree of uncertainty: i.e. p = 0.39 for Model F** and p = 0.20 for Model G**, respectively. But are these numbers of any practical meaning?

On its face value, the former case above suggests at least qualitatively, that there is a constant inherent month-to-month net background removal of OP by this CW (independent on effects by the identified predictor variables) which actually exceeds the input concentration; being supplemented by sedimentary sources. However, the extra effect size of TAN as predictive variable in the latter cases (Models F** and G**) compared to the former (Models F and G) and the fact that TAN is statistically significant in all these models suggest there is a portion of TAN's influence (fairly invariant and independent on pH) which is lumped with the "real" background contributing response in Model F or G. Furthermore, comparison of these two sets of analogue models suggests an additional effect of pH (other than via TAN and o-PO_4^{3-}-P speciation) that is not directly accounted for in Models F** and G** and hence inherently lumped with the "real" background response in the model creating the uncertainties in the estimated C* values. Therefore, whether considering Models F/G or Model F**/G**, it is not unreasonable to suggest that there is a large background OP removal process related to TAN uptake, which is somehow negated by increase in pH (see Section 4.3.3.2): via TAN speciation to form toxic ammonia (NH_3) and by other yet to be characterized pH effect (which may potentially include $H_2CO_3^-$/HCO_3^{2-} speciation and direct pH inhibition). This relatively large background removal (C*) in Models F and G or sum of the extra effect size of TAN (between the Models F**/G** and F/G: i.e. ~57% OP removal per mg/L TAN) and the C* in Models F** and G** is attributed to the photosynthetic co-uptake of OP and TAN by plants. Consequently, with proper management of all the identified predictor variables (including their interaction effects), the CW can efficiently remove OP regularly during the plant growing season. In particular, the results here suggest pH as an important variable, whose proper control and optimization could lead to more efficient CW performance.

In fact, the seeming distinction of categorical TAN effect (with minimal or no pH influence): i.e. a large one of effect size ~57% (*vide supra*) and a smaller one of effect size ~2% (see Models F/G in Table 2) may suggest two different TAN/OP co-uptake processes. Since the pH speciation effect on TAN is somehow accounted for in both sets of models (directly in Models F**/G** and indirectly in Models F/G), the two distinct TAN uptakes are likely due to "macro" NH_4^+ uptake by emergent plants (e.g. cattails, bulrushes and sedges) and "micro" uptake by algae and microorganisms. Indeed, as most of the input P to this CW is in the form of o-PO_4^{3-} and its soil sorption capability seems to have exhausted in the early years of the CW operation (Quagraine et al., 2017b), most of the background OP uptake is expected to be biological in nature (i.e. uptakes by vegetation, periphyton and microorganisms). Yet, apart from OP assimilation, plants do also provide favorable environments for treatment mechanisms which may depend upon bacterial metabolism, adsorption and precipitation reactions (Herskowitz, 1986). Vegetative uptake of OP is at its maximum during peak growing seasons. Water column OP can be readily removed by periphyton uptake (Kadlec and Reddy, 2001). In FWS CWs, uptake in filamentous algae and submerged plants are reported to account for an important part of OP removal during the growing season (Andersson et al., 2005).

4.4 Model describing OP removal efficiency during late fall (plant senescence) season

OP Removal in FWS systems follows a seasonal pattern in most temperate climate conditions (USEPA, 1999). Among other factors, the form of OP, the density of the aquatic plants, the OP loading rate and the climate, all of which may vary significantly between plant growing and plant senescence seasons, determine the pattern and amount of

OP removed over any given time period. Aquatic plants serve as the seasonal reservoir for OP as they take it up during the growing season. In fall however, where senescing of plants occurs, the majority of the OP taken up are released back into the water column (USEPA, 1999). These differing phenomena between the growing and senescing seasons are precisely what are displayed here by the MLR output data (Models F/G versus Models H/I) in Table 2. As shown in the table, though these models all are multivariate, the former includes polynomial and interaction terms, which are absent in the latter. Furthermore, with the exception of temperature, the derived regression coefficients (β_is) and constant (intercepts) are vastly different in magnitude and in some cases by the direction of influence.

Notable characteristics of Model H or I, the best model fits for the observed late fall monthly data, which contrast that for the growing season (Model F or G) are as follows:

a) There is a net background (C*) release of OP in Model H or I; as against background removal in Model F or G. The former is attributed to senescing and plant dieback effects and the latter as to plant uptake.

b) The influent OP dependent removal of OP seems simpler in late fall, as that comprises only the stand-alone influent OP term; whereas its dependence during the plant growing period was more complicated involving interactions with BOD and pH and in a non-linear (quadratic) function.

c) No significant effect of pH on OP removal was observed in late fall, neither in o-PO_4^{3-} and TAN speciation or by more direct means, which contrasts its effect during the plant growing period.

d) Although the CW's age for both senescing and the growing periods leads to releases of OP, the effects (both statistically and by size) were more significant for the former.

CONCLUSIONS

Based on multilinear regression analysis on selected monthly average data spanning the SaskPower CW operating periods from May to November for about 2-decades, multivariate quadratic polynomial functions were derived to describe o-PO_4^{3-}-P (OP) removal efficiency of the CW during two main plant growth cycle periods: the plant growing season of May to September and during the senescing period of October to November. For the growing season, the OP removal efficiency by the CW was most sensitive to ambient temperature (T), sensitive to inlet OP, pH, TAN and BOD, but insensitive to rainfall. Two analogous quadratic models were identified to best describe the OP removal efficiency as follows: $-2.78\ (OP)^2 - 4.38\ T + 0.29\ OP*BOD - 16.39\ pH + 2.63\ OP*pH + 1.87\ TAN + 168.51$ and $-4.81\ (OP)^2 - 4.53\ T + 0.39\ OP*BOD + 4.25\ OP*pH + 58.88\ TAN - 6.91\ pH*TAN + 9.36$; where p for each coefficient is <0.05. The predictor variable terms responsible for OP removal were the interaction terms of OP with BOD and pH; alongside TAN and background constant removal (intercept term). Temperature and pH as stand-alone terms effected OP release. Between the two models, the latter was presumed to be more meaningful and with its estimated coefficients as more deserving for reference. CW aging also displayed some adverse impact on OP removal efficiency during the plant growing period, but the effect was statistically weak (p = 0.15-0.18) and caused only ~0.45% OP release per year. In general, the MLR analyses suggest there is a large background OP removal process related to TAN uptake, which is somehow negated by increase in pH: via TAN speciation to form toxic ammonia (NH_3) and by other yet to be characterized pH effect (which may potentially include $H_2CO_3^-$/HCO_3^{2-} speciation and direct pH inhibition). This relatively large background removal is attributed to the photosynthetic co-uptake of OP and TAN by algae/plants. Consequently, with proper management of all the identified predictor variables - especially pH (and their interaction effects), the CW can efficiently remove OP regularly during plant growing season. The models derived to describe the late fall CW operation were also multivariate functions, but were not polynomial and did not include interaction terms as during the plant growing period, and the derived regression coefficients (β_is) and constant (intercept) were also vastly different in magnitude (with temperature as the only exception) and in some cases by the direction of influence. In contrast to the model(s) for the growing period, the fall model was marked by: a net background release of OP; simpler influent OP dependent removal of OP; no significant effect of pH on OP removal (neither in o-PO_4^{3-} and TAN speciation nor by more direct means); and a more significant (both statistically and by size) CW aging effect.

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