2 Decades Constructed Wetland Experience in Treating Municipal Effluent for Power Plant Cooling at the Shand Power Station, SaskPower Part III: Annual Treatment Performance on PO_4^{3-}-P, TP, Volatile and Total Suspended Solids, Inorganic Constituents, and Bacteria

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ABSTRACT

This paper is third in series of publications on 20-year period constructed wetland (CW) operational experience at SaskPower's Shand Power Station and highlights the yearly performance of the wetland on PO_4^{3-}, total phosphorous, volatile suspended solid (VSS), total suspended solids (TSS), bacteria, major inorganic constituents and trace elements. Moderately good phosphorous and VSS removals were realized in the initial two years when the inflow to the CW was a facultative effluent (56 - 60% and ~ 69 ± 27%, respectively). These however declined to only 1.2 - 7.4% and 35 ± 33% for the remaining years when the inflow to the CW was an upgrade to conventional secondary treated quality. TSS removal was more efficient in latter 18-year period of operation, but the efficiency was quite erratic (47 ± 43%). The CW generally was ineffective in removing major inorganic species and trace elements although K^+ (31 ± 5%) and Mn (50 ± 22%) removal were realized in the early 2-years of operation. Effective reduction of both total coliform (56% average) and faecal coliform (98% average) was demonstrated in the early two years of the CW. Yet, whereas total coliform removal was sustained or improved till a flood incidence in 2011 (77% average reduction), faecal coliform removal became erratic, showing some large net exports which is attributed to different warm-blooded animals that inhibit or frequent the CW including duck population in the storage pond (the CW outlet).

Keywords: Wetlands; municipal wastewater; phosphate; total and volatile suspended solids; coliform

1. INTRODUCTION

The abundance and reliability as a supply source have made municipal effluent a prima-wastewater source for reuse in industrial applications, especially insteam electric power plants for cooling purposes (Cooper, 2012; USEPA, 2004; Veil, 2007). Treatment to a minimum of secondary standard is typically required for municipal wastewater (MWW) used for power plant cooling at the MWW treatment plant-MWWTP (USEPA, 2004; Veil, 2007), but operational concerns such as scaling, corrosion, and bio-fouling potentials of the reclaimed water would usually demand further treatment of the secondary effluent

(Barcelo and Petrovic, 2011; Puckorious, 2015; Rebhun and Engel, 1988; Selby et al., 1996; Veil, 2007).

In the first of this series of publications, the literature on Constructed Wetlands (CWs) to polish MWW treated to different standards (raw, primary, secondary and tertiary) was reviewed (Quagraine, 2017). Most reports were on newly CWs (within the first few years of operation), which may not characterize long-term performance. For instance, new plants growing in a freshly planted CW will uptake more P than a matured CW, which will have P leaching from dying (senescent) plants as well as uptake by growing plants (USEPA, 1999). Likewise, newly placed soils or media will have a greater P sorption capacity than a matured system which will have most sorption sites already saturated (USEPA, 1999). Furthermore, for the few reports on matured CWs, the reported data were consistent only for the early years of operation (Quagraine, 2017); data for latter years of operation being mostly sporadic.

With results covering a 20-year period, the longevity of CWs to polish MWW effluents for power plant cooling application could be better assessed. This was the basis for the second paper in the publication series (Quagraine et al., 2017), which dwelt on actual annual performance of the CW as a treatment process for condenser cooling (since 1994) and hence assessed numerous parameters such as ammonia, nitrate, total organic carbon, pH and alkalinity, all of which have operational implications in power cooling plant cooling application. For brevity however, other parameters such as phosphate (PO_4^{3-}), total phosphorous (TP), total suspended solids (TSS), volatile suspended solids (VSS), major inorganic constituents, trace elements, and bacteria were omitted in the second paper and are discussed in this current manuscript as third in the publication series.

2. MATERIALS AND METHODS

2.1 CW design and operation

In the earlier papers (Quagraine, 2017; Quagraine et al., 2017) details of the wetland design and operation were outlined. The CW typically begins pumping operations in May and cease in October, although various logistic factors sometimes allow inclusion of April and November. Fig. 1 shows the aerial view of the SaskPower CW. As shown in Fig. 2, the vegetation for the SaskPower CW consists mostly of planted bulrush and cattails, although a variety of natural sedges and marsh have also developed in the wetlands.

Figure 1   Aerial View of the SaskPower Constructed Wetlands in a) September 2010 and b) September 2014 (i.e. post 2011 flood)

Figure 2 Photo of vegetation within the constructed wetlands (July 8, 2014)

2.2 Water sampling and testing

Typically, sampling of Cell J (feed pond to the CW) and the Storage Pond (outlet pond from the CW) occurred weekly. The samples were then sent to an accredited third party laboratory for analysis of various parameters including VSS and TSS as suspended solid fractions; total dissolved solids (TDS), specific conductivity, and major inorganic constituents as general measure of the mineral and salt content in the wastewater; trace elements to include heavy metals of operational and environmental discharge concerns; fecal and total coliform as measures of sanitary quality of the water and indicators for potential presence of pathogenic organisms; chlorophyll A as a measure of algal (and other phytoplankton) concentrations; and nutrients in various speciated forms as discussed earlier for nitrogen (Quagraine et al., 2017) or below for phosphorus (P).

P compounds, as ortho-phosphate (o-PO_4^{3-}) and total phosphorous (TP), are all reported as mg/L P. In the manuscript, the term PO_4^{3-}-P as reported, is a generic term referring to the sum of all soluble inorganic phosphorous compounds reactive in molybdate analytical test. Thus, o-PO_4^{3-} does not only include the pH dependent monomeric PO_4^{3-} speciated forms: PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$ and H_3PO_4 but as well, the condensed forms: poly-phosphates, meta-phosphates, and pyro-phosphates that are reactive in the molybdate analytical test. TP is the sum of particulate phosphorous-PP (containing both organic and inorganic fractions to include non-reactive and large polymeric phosphates), soluble reactive phosphorus (aka o-PO_4^{3-}), and dissolved organic phosphorus (DOP). In fact, some DOP may be readily hydrolyzed and hence reactive in the molybdate analytical test (Kadlec and Wallace, 2009), but this fraction is not expected to be significant and hence such distinction is not made in this manuscript. As only TP and o-PO_4^{3-} were measured, the difference in these measures are discussed as sum of DOP and PP, and referred to as DOPP (i.e. the non-phosphate portion of TP). The monitored major ions as discussed in the current paper include sulfate (SO_4^{2-}), chloride (Cl^-), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), as well as total hardness. Variations of carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), total alkalinity and pH across the CW were previously assessed (Quagraine et al., 2017), but are nevertheless discussed also in the present

manuscript due to their interrelation with other parameters such as PO_4^{3-} discussed here. The samples were also analyzed for metals such as boron (B), mercury (Hg), selenium (Se), silver (Ag), arsenic (As), cadmium (Cd), cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), lead (Pb), strontium (Sr), and zinc (Zn).

2.3 Regression analysis

As described earlier (Quagraine et al., 2017), to determine the correlation and functional relation between any two sets of separate measures, an XY chart on an Excel spreadsheet was first plotted and the regression type of best fit selected to display the equation and the R^2 value (representing the correlation strength).

3. RESULTS AND DISCUSSION

Nutrients removal by CW commonly follows seasonal patterns, which may not necessarily reflect annual patterns. Seasonal patterns of vegetation growth and nutrient storage involve complex pattern of biomass allocation and stoichiometry among plant parts-both living and dead, whilst on annual average basis, the only concern is net removal to permanent storage. It is believed that after plants are fully matured, there is, on average no net year-to-year increase in plant storage; although on seasonal basis, plant uptake can be very large part of nutrient removal or release (Kadlec and Wallace, 2009). Shorter term and sporadic monitoring can therefore give deceptive prediction of the longevity of a CW as treatment technology. Therefore, in the second of the publications series on 20-years operation of the SaskPower CW, we purposefully decoupled the CW performance on annual basis from its seasonal performance, which is deferred for latter publications. For brevity however, the second paper focused on annual removal performance to some limited parameters leaving others such as PO_4^{3-}, TP,

TSS, VSS, major inorganic cations and anions, trace elements and bacteria, which are discussed as continuation of the second in this present manuscript.

CWs are well known for their strong interactions with and/or removal of nutrient elements particularly carbon (C), nitrogen (N), and phosphorus (P) present in several forms of compounds, variously measured (Kadlec and Wallace, 2009). For instance, P-compounds in CWs usually exist as the inorganic phosphate ion forms or organic P form and are usually measured and reported, as in this study, as PO_4^{3-}-P and TP. The interactions of C, N, P compounds with CW may however either be influenced or rather influence some physico-chemical properties of the wastewater such as pH, dissolved oxygen, redox states, etc. The interactions are usually in such complicated fashions to affect the CW's capability in removing or releasing these nutrients whilst simultaneously causing changes to the physicochemical parameters. In the second paper, the yearly removal efficiencies for variety of water quality parameters involved in the removal of compounds of C (as TOC and BOD) and N (as total ammonia nitrogen-TAN, NH_3-N, NH_4^+-N, and NO_3^--N) were discussed and included the relationships between the removal efficiencies of these parameters with each other and with various physicochemical properties including pH, dissolved oxygen (DO), and the dominant inorganic carbon species-HCO_3^- and CO_3^{2-}. We continue the discussion in the present paper, but this time focus on the removal of P compounds (as TP, PO_4^{3-} and DOPP) and suspended solids (as TSS and VSS). Likewise, we evaluate the relationships between their removals and various physicochemical properties including pH, HCO_3^- and CO_3^{2-}. The annual performance with respect to the treatment of major inorganic species, trace elements, and bacteria are also discussed.

3.1   Phosphorous and pH interactions

Biological purification of wastewater is generally accompanied by a change in pH (Lijklema, 1969); whilst the original wastewater pH in itself has direct influence on the processes-including biological, and physicochemical processes that effect the purification. Low pH (< 6.8) is undesired in biological wastewater treatment processes; it slows enzymatic activity and treatment of CBOD and TSS, inhibits nitrification, interrupts floc formation, and promotes quantitative production and release of molecular hydrogen sulfide (H_2S) from the conversion of ionized sulfides (S^{2-} and HS^-) (Gerardi, 2015), which can influence the deposition of some inorganic species. High pH, on the other hand, will cause conversion of NH_4^+ions to NH_3, which can be harmful to life including that of microorganisms. For plants, elevated pH can inhibit algal growth by making free CO_2 unavailable through conversion to carbonate and bicarbonate (Azov and Goldman, 1982; Craggs, 2005). Free NH_3 produced from elevated pH above 8 can inhibit photosynthesis by disrupting algal cell chloroplast function. On the other hand, H_2S released at low pH are even more toxic to algae than NH_3 and can significantly reduce algal growth (Craggs, 2005).

In the second paper, pH influence on, and/or influence on it by the removal of various parameters were evaluated and included BOD, TOC, DO reduction, TAN, NH_3-N, NH_4^+-N, HCO_3^-, and CO_3^-. We continue the discussion by looking at the influence of pH on the removal efficiencies of other parameters such as TP or DOPP, PO_4^{3-}, TSS and VSS, as well as how these changes also impact pH. In the next subsections, we discuss the influence of pH on PO_4^{3-} and TP (Section 3.1.1) and the impact ofPO_4^{3-} and DOPP removal on pH (Section 3.1.2). The interactions between TSS and VSS with pH are deferred to Sections 3.3.1 and 3.3.2, respectively.

3.1.1   Effectof pH on TP and PO_4^{3-} reduction

A good correlation is observed between influent pH (x) and percentage total phosphorous removal-TP (y). With exclusion of 2008 and 2010 (i.e. n =17), linear inverse relation y = -66.3x + 587, R^2 = 0.84 is attained; a weaker correlation (R^2 = 0.6) is however found with inclusion of all data (i.e., n = 19). Similarly, a linear inverse relation y = -72.5x + 637.5, R^2 = 0.82 is attained between influent pH (x) and percentage phosphate (PO_4^{3-}) removal (n = 17) and R^2 = 0.62 when n = 19. To be expected, logarithmic relations with same correlations exist also between NH_3/NH_4^+ ratio and percentage TP or o-PO_4^{3-} reductions. Whether or not the TP and o-PO_4^{3-}reductions is due actually to pH changes (acidity) or NH_3/NH_4^+ distributions is further discussed in Section 3.2.1.

3.1.2   Influence of PO_4^{3-} and DOPP removal on pH

With respect to phosphorous (P), a fair to good correlation was found between ΔpH (y) and PO_4^{3-} removal efficiency (x) and in a linear relation (y = 0.010x + 0.534, R^2 = 0.54, n = 19; and y = 0.013x + 0.594, R^2 = 0.75, n = 15). The years 1999, 2005, 2010 and 2013 seem to distort the linear relation; with the first demonstrating more enhanced pH depression than expected, whilst the last three showed less pH depression than expected. The 1999 result may be due to enhanced microbial activity leading to more pH decline. The outlier behavior in 2005, 2010 and 2013 had earlier been noted and attributed to enhanced plant photosynthetic growth resulting from NO_3^- assimilation (Quagraine et al., 2017). Thus, co-assimilation of NO_3^- and PO_4^{3-} in cases where ammonia uptake is inhibited (or where influent NO_3^- is high) would account for the unique behavior in these years.

Correlation between non-phosphate P (DOPP) removal efficiency (y) and ΔpH (x)

was generally poor in comparison to PO_4^{3-} removal (y = 27.7x + 25.3, R^2 = 0.26, n = 19). This would imply that the mechanism for the removal of DOPP is different from that of PO_4^{3-}.

3.2 Phosphorous Uptake: TP, PO_4^{3-}, and DOPP

P can enter CW as a constituent of suspended solids or as dissolved P. Wetland soils, bed aggregates, plants, litter and microbiota all interact significantly with Pin the various forms. There are there principal means of P removal in FWS CWs: sorption, utilization by plants and microbes in biomass storage, and storage as newly created, refractory residuals (burial) (Kadlec and Wallace, 2009). The first two mechanisms have finite P retention capacities involving storage and release, whereas the third- sediment accretion, is a sustainable process involving the use of P as part of the creation's structure and hence commonly seen as a burial process (Kadlec and Wallace, 2009). In addition to these, secondary processes such as particulate settling, and movement among storage compartments also exist. $PO_4^{3-}$and other forms of P can be precipitated via direct reaction with a variety of cations under certain conditions or co-precipitate with other minerals, and be part of the particulate P. In alkaline CWs, PO_4^{3-} precipitates with calcium (Ca) and to a lesser extent magnesium (Mg) as the corresponding metal phosphate. In acidic CWs, dissolved P may be removed from the water via adsorption by aluminum (Al) and iron (Fe) oxides/hydroxides or from precipitation with the ionic form of the former metal. Redox conditions also influence the removal of P by metal ions. For example, oxidizing conditions favor the removal of P compounds from the water column (via Fe^{3+} interactions), whilst reducing conditions lead to solubilization of iron minerals (as Fe^{2+}) and release of P co-precipitates (Kadlec and Wallace, 2009).

Biota within CWs, including algae, bacteria, macrophytes, and duckweed form the initial Premoval mechanism. They however undergo a cycle of growth, death and partial decomposition. Thus, as much as they utilize P, the decomposition and dead processes release P back to the water column. The microbial component is of lesser quantity; however, they cycle much more readily than macrophytes and hence serve as the first line of interaction with added P in a wetland and not the macrophyte (Kadlec and Wallace, 2009).

Although most soils/sediments do have sorptive capacity for P, this storage is soon saturated under any long-term increase in P-loading. This seems to be the case with the SaskPower CW, as initial PO_4^{3-} removal was excellent (~ 78% in 1994) but declined quite rapidly to only ~21% by the third year of operation (Fig. 3).

Over the 1994 to 2014 period, the average concentration of PO_4^{3-} in the influent fluctuated from 4.80 mg/L in 1995 to 1.04 mg/L in 2001: 4.09 ± 1.00 mg/L in 1994-95 when it was lagoon treated; and 1.77 ± 0.62 mg/L in 1996-2014 when it was by conventional secondary treatment (Table 1). As also shown in Table 1, the average PO_4^{3-} removal efficiency on treating the facultative lagoon effluent in the early years of the CW operation (1994 - 1995) was $58.7 \pm 27.0\%$, which declined to only $1.2 \pm 14.0\%$ on treating conventional secondary treated effluent in the latter years.

With PO_4^{3-} constituting an annual average of 90% TP with a standard deviation of only 6.6%, the annual removal efficiency of TP (not shown) was generally similar to that shown for PO_4^{3-} in Fig. 3. The initial (1994) TP removal was ~ 74%, but likewise declined rapidly to ~ 46% in 1995 and to only 19% in 1996 (just three years of operation). It is also noteworthy, that the influent quality to the CW in the first two years was of facultative lagoon treated standard of average TP = 4.92 mg/L-P and

PO_4^{3-} = 4.09 mg/L-P (Table 1). Despite these higher influent P concentrations, the annual mean effluent TP quality in the first year (1.07 mg/L) was the lowest achieved during the 2-decades of investigation (as also the case for PO_4^{3-}-P; See Fig. 3). As shown in Table 1, the average TP removal efficiency on treating facultative lagoon effluent in the early years of the CW operation (1994 - 1995) was 59.8 ± 19.9%, which declined to only 5.5 ± 11.6% on treating conventional secondary treated effluent in the latter years. Therefore, the excellent P (TP and PO_4^{3-}) removal experienced in the initial stages of the CW was not sustained.
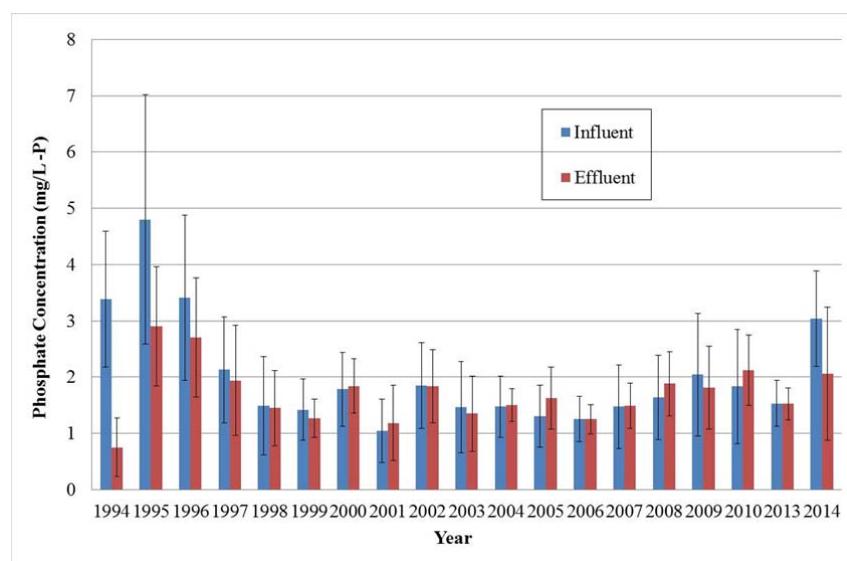
Figure 3 Annual mean PO_4^{3-}-P concentrations

Table 1 Mean inflow and outflow concentrations, as well as mean removal efficiency of various nutrients and physicochemical parameters in municipal treated wastewater across the CW in 1994-1995, when the inflow quality was of facultative lagoon standard and in 1996-2014 when the quality was of a conventional secondary effluent standard. Values in parenthesis are the standard deviation values for the corresponding mean data. All inflow/outflow concentration units are in mg/L, except pH which is in its standard pH units

Parameters	1994 - 1995			1996 - 2014		
	Inflow	Outflow	% Removal	Inflow	Outflow	% Removal
TP-P	4.92 (1.15)	2.09 (1.44)	59.8 (19.9)	1.94 (0.64)	1.79 (0.43)	5.5 (11.6)
PO_4^{3-}-P	4.09 (1.00)	1.83 (1.52)	58.7 (27.0)	1.77 (0.62)	1.69 (0.39)	1.2 (14.0)
DOPP-P	0.83 (0.15)	0.27 (0.08)	56.0 (22.6)	0.17 (0.12)	0.10 (0.10)	7.4 (7.2)
DO	-	-	-	6.60 (1.79)	7.56 (1.31)	-22.9 (38.9)
pH[a]	8.13 (0.23)	8.27 (0.07)	0.14 (0.16)	8.76 (0.29)	8.23(0.18)	- 0.53 (0.26)
VSS	50.3 (50.7)	5.5 (1.8)	69.4 (27.4)	7.9 (4.0)	4.8 (3.5)	34.6 (33.2)
TSS	23.9 (13.6)	20.1 (10.0)	15.8 (-)	23.8 (11.5)	12.0 (10.3)	46.9 (42.7)
TDS	1936 (195)	2011 (195)	-3.9 (0.4)	1779 (291)	1897 (285)	-7.4 (13.8)

[a] removal efficiency is expressed as ΔpH= (effluent pH-influent pH); (+) means reduction in acidity or increase in pH, whilst (-) means increase in acidity or decrease in pH

3.2.1 The typical PO_4^{3-} uptake behavior

The PO_4^{3-} removal efficiency correlates strongly with that of TP ($R^2 = 0.96$); and in a linear fashion with $y = 0.88x + 4.8$, where y is the percentage TP removal and x as the percentage PO_4^{3-} removal. This is consistent with the fact that TP was dominantly in the PO_4^{3-} form. At some point after initial P sorption in a CW, equilibrium is somewhat established between pre-sorbed P and that in the overlying water column: water at lower concentrations causes desorption, while water at higher concentration causes adsorption (Kadlec and Wallace, 2009). Thus, the seemingly inconsistent removal or release of PO_4^{3-} from 1997 - 2014 as shown in Fig. 3 (i.e., after the initial good and consistent removal) may, in part, be attributed to adsorption or desorption of PO_4^{3-} into or from the CW sediment. It is worth noting that with conversion of the city's WWTP from facultative lagoon to conventional secondary treatment standard, the quality improved significantly; TP of 4.9 mg/L-P for 1994 - 1995 vs. 1.8 ± 0.3 mg/L-P for 1997 - 2013 (an increase to 3.2 mg/L-P of TP was however realized in 2014). It is necessary to further mention that despite the declining removal efficiency and the improved influent quality to the CW, annual net P export (PO_4^{3-} or TP) from the CW did not actually occur until 2000. Of particular note is the net PO_4^{3-} export in 2005, 2008 and 2010. The reader is referred to the exceptional behavior in these years also in terms of NO_3^-, NH_3, and proton uptake or release across the CW (Quagraine et al., 2017). In 2014, the removal efficiency increased substantially when compared to the previous years. This is more likely due to the regrowth of the CW system after the flood removed top soil and vegetation in 2011. The rejuvenated soil and plants would be able to uptake more phosphates from the influent.

A fair correlation existed between the inflow PO_4^{3-}-P concentration and its removal efficiency ($R^2 = 0.58$ (n = 19) or $R^2 = 0.65$ (n = 18; i.e., excluding the first year); with the correlation further strengthening when the anomalous years of 2005, 2008, and 2010 are also excluded ($R^2 = 0.80$; n = 15). As to be expected, similar correlations were found between inflow TP concentration and its removal efficiency; $R^2 = 0.85$ for n = 15. These suggest the influence of the inflow PO_4^{3-} or TP on their removal efficiencies and thus potentially a limiting nutrient for (plant and bacteria) growth within the CW. Some other factors however seem to also play significant roles in their uptake considering the limitation in the correlations.

Earlier in the discussion (Section 3.1.1), a good inverse relation between influent pH and % TP or PO_4^{3-} removal was noted. Inverse exponential relations with same correlations also existed between NH_3/NH_4^+ ratio and % TP or o-PO_4^{3-} reductions. The question as to whether or not the TP and o-PO_4^{3-} reductions are attributable to actual pH changes (acidity) or NH_3 and NH_4^+ distributions was however deferred till now. For simplicity of the discussion, better fitted relations from some limited data (n = 14; i.e., excluding 1998, 1999, 2003, 2008, and 2010) is shown in Fig. 4. Other factors/ processes predominant in these exceptional years and influencing P uptake or release may be responsible for their non-conformity to the pH or NH_3/NH_4^+ dependent removal or export of P across the CW. These exceptionalisms are discussed in Section 3.2.2.

As shown in Fig. 4, PO_4^{3-} removal is favored by decreasing influent pH. Stated otherwise, increasing pH resulted in reduced PO_4^{3-} uptake or increased export across the CW. In alkaline media, P may be precipitated and thus removed from the water column by direct chemical reaction or co-precipitated with Ca and Mg ions or compounds (Kadlec and Wallace,

2009). Although Ca and Mg are both present in fairly high concentrations in the CW (i.e., 36-40 mg/L and 63-86 mg/L (Quagraine, 2017), respectively), the data here do not support their co-precipitation with PO_4^{3-} for removal.

Al and Fe, as chemical coagulants, may fix P under acidic conditions (Kadlec and Wallace, 2009; Qualls et al., 2009), but their concentrations in the SaskPower CW water are stoichiometrically lower (e.g. annual mean influent total Al and Fe in the CW water column from 1996 - 2014 were 0.11 and 0.62 mg/L or 4.1 and 11.1 µmol/L, respectively) in comparison to the annual mean PO_4^{3-}-P level (1.77 mg/L or 57.1 µmol/L) to contribute significantly to the PO_4^{3-} removal. Jointly, a quantitative utilization of these metals (in water) to fix P would account for only 26.6% of the PO_4^{3-} removal and 24.2% of the TP removal. Furthermore, organic carbon in water is observed to interfere with P removal by these metals (Qualls et al., 2009); hence the annual
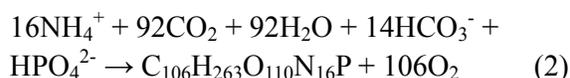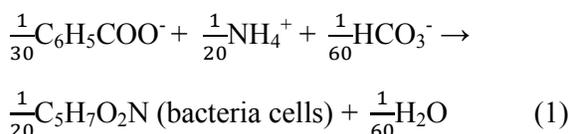
mean TOC of 20.5 ± 5.7 mg/L in the CW would proof also to be inhibitory to this process of P removal within the CW. (The reader should note however, that the discussion above does not preclude possible sedimentary PO_4^{3-} removal by these metals).

Bacterial action and plant uptake are two other CW processes for P removal (Mann, 1990), whose function may also be influenced by pH. PO_4^{3-} (and not DOP) is the preferred P-source of uptake by both algae and bacteria (Cotner and Wetzel, 1992). Evidence exist that the initial PO_4^{3-} uptake in aquaculture systems is by bacteria especially at low concentrations, but their uptake becomes more readily saturated (Cotner and Wetzel, 1992; Paerl and Lean, 1976).Therefore at high concentrations, PO_4^{3-} is more taken by phytoplankton than bacterioplankton. Many taxa of phytoplankton can store significant quantities of P as polyphosphate when P supplies are abundant (Cotner and Wetzel, 1992).
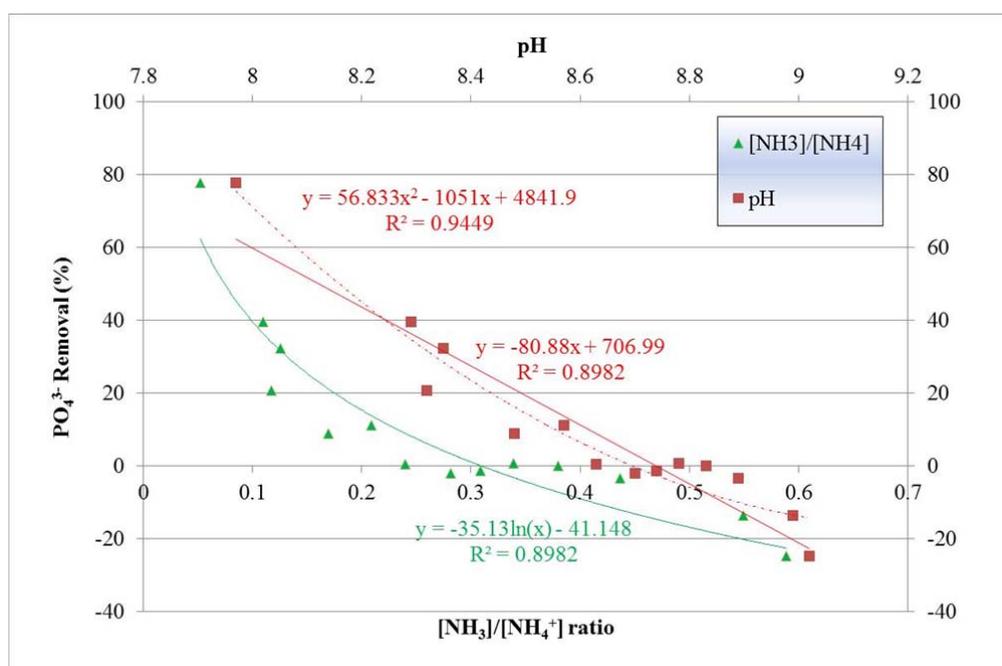

Figure 4 PO_4^{3-} removal as a function of CW influent pH and $[NH_3]/[NH_4^+]$ ratio

In the second paper (Quagraine et al., 2017), increasing $[NH_3]/[NH_4^+]$ ratio was noted to inhibit total ammonia removal and to result in pH decline across the CW; this was attributed largely to inhibitory assimilation of NH_4^+ for algae (plant) growth. The same phenomenon is expected here; i.e., increasing NH_3 to NH_4^+ ratio inhibits plant (more likely algae) assimilation of PO_4^{3-}, as nutrient, for growth. Interestingly, a fair (y = 0.60x + 76.0, R^2 = 0.51, n = 17) to good (y = 0.59x + 75.0, R^2 = 0.87, n = 9) linear relation is found between PO_4^{3-} (x) and NH_4^+ (y) uptakes as percentage. Similar strength in correlation did not exist between PO_4^{3-} and NH_3 removal efficiencies, which showed corresponding R^2 of only 0.08 (n = 17) or 0.28 (n = 9). This confirms the earlier assertion (Quagraine et al., 2017) for plant and/or bacteria assimilation of fractions of TOC/BOD as C-source, NH_4^+ (not NH_3) as N-source, and now PO_4^{3-} as P-source for growth as in Eqs.1 and 2 and as the basis for the increasing pH trend with nutrient assimilation or decreasing trend with increasing ammonia toxicity from high $[NH_3]/[NH_4^+]$ ratios.

$$\tfrac{1}{30}C_6H_5COO^- + \tfrac{1}{20}NH_4^+ + \tfrac{1}{60}HCO_3^- \rightarrow$$

$$\tfrac{1}{20}C_5H_7O_2N \text{ (bacteria cells)} + \tfrac{1}{60}H_2O \qquad (1)$$

$$16NH_4^+ + 92CO_2 + 92H_2O + 14HCO_3^- +$$
$$HPO_4^{2-} \rightarrow C_{106}H_{263}O_{110}N_{16}P + 106O_2 \qquad (2)$$

On an extremely restrictive data (n = 6), which includes 2008 and 2010-two of the outliers noted earlier, a good linear relation (y = 1.19x + 28.2, R^2 = 0.91) is identified between PO_4^{3-} (x) and NO_3^- (y); reducing to only a fair correlation (R^2 = 0.41 for n = 9; i.e. ~ half the data). There was barely any correlation between these parameters for n ≥ 14; reaching an R^2 = 0.19 for n = 11. This confirms the earlier assertion (Quagraine et al., 2017) that

under some unique conditions (i.e., where NO_3^- abounds and $[NH_3]/[NH_4^+]$ ratio is high as in 2008), NO_3^- may also be co-utilized as an alternate N-source with PO_4^{3-} in plant photosynthetic growth-Eq.3.

$$16NO_3^- + 124CO_2 + 140H_2O + HPO_4^{2-} \rightarrow$$
$$C_{106}H_{263}O_{110}N_{16}P + 138O_2 + 18HCO_3^- \qquad (3)$$
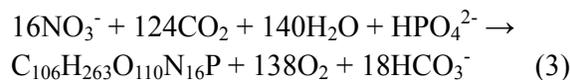
3.2.2 The exceptional PO_4^{3-} uptake behavior

Having discussed the correlations between PO_4^{3-} and NH_4^+ as well as NO_3^-, we are in a better situation to understand the conditions that prevailed particularly in 2008 and 2010 to distort the typical relation between PO_4^{3-} removal efficiency and $[NH_3]/[NH_4^+]$ ratio or pH. Earlier, we had related such deviations to NO_3^- uptake. Furthermore, these two years are amongst the few cases where PO_4^{3-} removal bore direct relation to NO_3^- removal. Following the trend in Fig. 4, significantly more net PO_4^{3-} export was expected in 2008 than observed, implying there was some PO_4^{3-} uptake attributable to some other means than co-assimilation with ammonia (actually NH_4^+). This is consistent with the high influent $[NH_3]/[NH_4^+]$ ratio (2.0) and low NH_4^+ uptake (only 46.8%) in 2008, forcing the co-utilization of the available high NO_3^- as alternative N-source with PO_4^{3-} for algal/plant photosynthetic growth, to counteract the toxicological effect of NH_3. However, considering the similar stoichiometry between PO_4^{3-} and these two N-sources (NH_4^+ and NO_3^-), as shown in Eqs. 2 and 3 (with respect to algae photosynthesis), the observed shortfall of PO_4^{3-} than expected in the effluent (i.e. the extra PO_4^{3-} uptake) would be due to uptake by higher P consuming species. It has to be noted that algae growth, for instance, is controlled by the relative availability of N- and P-sources of nutrients (Cheremisinoff and Davletshin, 2015). The P content of periphyton (complex mixture of algae, cyanobacteria, and heterotrophic microbes attached to surfaces of

underwater vegetation and other substrates) and phytoplankton (consisting of free-living algae) is higher than that for macrophytes, especially in P rich waters (Kadlec and Wallace, 2009). It is therefore likely that the more than typical uptake of PO_4^{3-} in 2008 was due to increased algal activity.

Unlike 2008, there was less uptake of PO_4^{3-} than expected in 2010. For some reason, the inhibitory impacts from influent $[NH_3]/[NH_4^+]$ ratio on NH_4^+ removal were magnified in 2010; thus less than expected NH_4^+ uptake occurred and consequentially less PO_4^{3-} uptake. The reduced uptake of NH_4^+ in 2010 did not necessarily induce significant uptake of NO_3^- as only ~15% of the 0.6 mg/L NO_3^--N influent concentration was removed in the year; neither did it promote PO_4^{3-} utilization. We suggest that the relatively small NO_3^- utilization in 2010 was mainly via denitrification process as earlier asserted (Quagraine et al., 2017), which did not require PO_4^{3-}. This would also be consistent with the observed reduced pH depression than anticipated for the $[NH_3]/[NH_4^+]$ ratio.

To a lesser extent, the 1998, 1999 and 2003 data did not also strictly fit the observed relation between PO_4^{3-} removal and $[NH_3]/[NH_4^+]$ ratio. There was more PO_4^{3-} uptake than expected for the observed influent pH (which was ≥ 8.8) and the $[NH_3]/[NH_4^+]$ ratio (which was ≥ 0.33). The more than expected PO_4^{3-} removal from the water column corresponds with relatively lower NO_3^- assimilation rate (i.e., 5-15% NO_3^- reduction) and more than expected NH_4^+ assimilation in 1998 and 1999. Thus, the increased PO_4^{3-} uptake here is less to do with NO_3^- uptake than it has to do with a more efficient NH_4^+ uptake for the level of $[NH_3]/[NH_4^+]$ ratio. These may simply be as a result of some plant or microbial species variation. The case in 2003 was different from 1998/1999; the more than expected PO_4^{3-} uptake matched relatively higher NO_3^- assimilation (i.e., 89.3%), but less than expected

NH_4^+ uptake (68.7%). Thus, the CW nutrient uptake behavior in 2003 was to some extent similar to that in 2008 discussed above (i.e. the potential toxicological inhibition of NH_4^+ uptake led to uptake of NO_3^- as alternate N-source). However, unlike 2008, the NO_3^- uptake in 2003 or the extra NH_4^+ uptake in 1998/1999 enhanced pH depression than typical for the study period (Quagraine et al., 2017). Enhanced microbial activity for these years, as a result of the boosted co-assimilation of PO_4^{3-} and the various N-sources, is implicated as being responsible for the improved pH depression. Microbes have been implicated for some high rate of uptake of PO_4^{3-} in submerged aquatic vegetation and such P immobilization is noted to be important factor in P removal in the wetland even though the biomass of these organisms is small (Kadlec and Wallace, 2009).

3.2.3 Uptake of the non-phosphate fraction

In most of the years, the non-phosphate portion of TP in the influent was less than 13% except in the early first two years of operation (1994 and 1995), 2004, and from 2006 to 2008 when this portion ranged between 15.5% (2004) to 20.5% (2007). In terms of actual concentrations, the highest non-phosphate P influent concentrations (like PO_4^{3-}) were recorded during the initial years of operation when the city operated a facultative lagoon treatment of their wastewater; the concentrations for the first and second years were 0.72 and 0.93 mg/L P, respectively (i.e., 0.83 ± 0.15 mg/L as average ± SD). The concentrations in 2004 and 2006 - 2008 ranged from 0.23 - 0.38 mg/L P. As shown in Table 1, the DOPP concentration when the inflow MWW effluent to the CW was of conventional secondary standard was generally low at 0.17 ± 0.12 mg/L. These non-phosphate portions would be in the form(s) of dissolved organic-DOP and/or particulate phosphorous-PP (and hence compositely abbreviated hereafter as DOPP for

dissolved organic and particulate phosphorous in the discussion).

Being part of TP, a somewhat fair correlation ($R^2 = 0.41$; n = 19) is found between the DOPP fraction and TP. The uptake behavior of DOPP however seemed different from PO_4^{3-}. First, a poor correlation ($R^2 = 0.27$; n = 19) is found between PO_4^{3-} removal efficiency and that of the DOPP fraction suggesting that the mechanism of removal of these dissimilar fractions of P were somewhat generally different. For example, in the first year of operation ~78% removal of PO_4^{3-} occurred, whilst only 40% removal of DOPP occurred; whereas in the second year only ~ 40% PO_4^{3-} removal occurred, whilst 72% reduction of DOPP occurred. Nonetheless, over half the data (n = 10) showed a good relation between PO_4^{3-} removal efficiency and that of the DOPP fraction ($R^2 = 0.87$) suggesting that there is potentially a sub-fraction of DOPP whose uptake process is fairly similar to PO_4^{3-}. A second notable difference between the PO_4^{3-} and DOPP removal trends is an observation that a stronger linear correlation existed between the influent DOPP concentration and its removal efficiency ($R^2 = 0.81$) as compared to that of PO_4^{3-} ($R^2 = 0.58$). Thus, DOPP removal was more dependent on its inlet concentration. Thirdly, apart from three cases which were all close to zero feed concentrations, net export of DOPP did not occur; unlike PO_4^{3-} where net export was common after the initial years of operation. Lastly, the inverse correlation between influent pH or NH_3/NH_4^+ ratio and DOPP was only fair, reaching a maximum R^2 of only 0.6 on a more restricted data (n = 10). This is unlike PO_4^{3-} (and TP) where the inverse correlation was stronger ($R^2 \geq 0.90$; Fig. 3) suggesting the involvement of plant uptake. Thus PO_4^{3-} seems to be a more ubiquitous and effective source of plant P uptake than DOPP.

The effect of influent pH or NH_3/NH_4^+ ratio on DOPP uptake can however not be completely discounted considering there was some fair to good correlation when apparent discordant data were excluded. In fact, over an eight year period, an inverse linear correlation ($R^2 = 0.78$) is found to exist between DOPP and influent pH. Both phytoplankton and bacterioplankton can utilize dissolved organic P (DOP), but PO_4^{3-} is the preferred P-form of uptake (Cotner and Wetzel, 1992). Considering competitive advantage of bacteria over phytoplankton for initial PO_4^{3-} uptake, and yet losing the advantage with increasing PO_4^{3-} concentration (due to limited internal P pool storage) (Cotner and Wetzel, 1992; Paerl and Lean, 1976), phytoplankton would expectedly have an advantage over bacteria for DOP uptake at moderate to high PO_4^{3-} concentrations. Bearing in mind however that the DOPP fraction measured here could constitute both DOP and particulate (organic and inorganic) P (PP) and that the relative proportions of these sub-fractions in the influent are variable, as well that uptake of either form could be through conversion to PO_4^{3-}, it becomes difficult to account generally for which of the sub-fraction(s) as responsible for any DOPP uptake or release. Nonetheless, DOPP uptake in this study seemed to result in two distinct impacts on pH and hence we attempt here to distinguish the dominant DOPP sub-fractions at various periods based on their pH variation.

The weaker correlation between PO_4^{3-} and DOPP uptake efficiency for the general data (n = 19) could be related to differences in uptake of these fractions by different biological species: uptake of the former by both bacteria and phytoplankton, and more exclusive uptake of the latter by phytoplankton if DOP is dominant. Consistent with phytoplankton as more exclusively responsible for DOP (and for that matter DOPP) uptake for some period, a good linear correlation is found between % DOPP removal (y) and ΔpH (x): y = 152.5x + 82.3, $R^2 = 0.86$, n = 8). This activity occurred in 1995, 2003, 2006-2009, and 2013-2014.

With the uptake of DOP for photosynthetic growth, the CO_2 utilization would result in pH rise or impede any pH depression as a result of other acid generating processes within the CW. A weaker correlation is found between % PO_4^{3-} removal (y) and ΔpH (x) for data where DOPP uptake versus ΔpH relation is significant (i.e., (y = 51.0x + 27.4, R^2 = 0.35, n = 8). In other words, the pH increasing impact from DOPP (DOP) uptake is more evident than that from PO_4^{3-} uptake as the former is likely due to a more exclusive uptake by phytoplankton and the latter as due to both bacteria and phytoplankton uptake.

For a different set of data, the DOPP uptake resulted in enhanced pH depression, suggesting microbial oxidative activity. An inverse linear relation is found between % DOPP removal (y) and ΔpH (x): y = -149.6x – 3.02, R^2 = 0.80, n = 13). This activity involved the following years: 1995-1996, 1999-2002, 2004-2005, and 2007-2008. A weaker, but direct correlation is found between % PO_4^{3-} removal (y) and ΔpH (x) for the same data where DOPP uptake is inversely related to ΔpH: i.e. (y = 34.9x + 15.3, R^2 = 0.32, n = 13). The pH response in DOPP removal for this second set of DOPP data is more consistent with microbial action on particulate phosphorous (PP) as a significant portion of DOPP and is further discussed as component of VSS in Section 3.3.2.

On some limited data (n = 9), DOPP removal (x) also related fairly to NH_4^+ removal (y = 0.15x + 86.34, R^2 = 0.65) consistent with the suggestion that there is a significant portion of DOP in DOPP which may be co-assimilated with NH_4^+– (but less universally).

3.3 Suspended solids

3.3.1 Total suspended solids

With some exceptions, TSS removal efficiency (y) correlated directly with the influent TSS load (x): y = 1.48x + 17.8, R^2 = 0.76 (n = 10). A fair correlation is also found between TSS removal efficiency and influent pH (R^2 = 0.46, n = 15). The TSS removal also fairly correlates well with CO_3^{2-} removal (R^2 = 0.49, n = 14) suggesting the potential for co-precipitation with carbonates as pH is increased. There is however a more restricted period of data where TSS removal was strongly inversely related to influent pH (R^2 = 0.82, n = 9). The period included 2000-2001, 2003, 2005-2009, 2013-2014.

Generally, TSS removal efficiency (y) correlated positively with ammonia removal efficiency (x): y = 0.064x + 91.6, R^2 = 0.75 (n = 16) for NH_3; and y = 0.276x + 71.8, R^2 = 0.63 (n = 15) for NH_4^+. The TSS removal also resulted in pH decline, although the correlation was weak (R^2 = 0.33, n = 17). With respect to P, TSS removal efficiency (y) was inversely related to influent TP (x): y = -39.2x + 127.9, R^2 = 0.65 (n = 15). It was also inversely and more weakly related to PO_4^{3-} removal (R^2 = 0.42, n = 14), but not with DOPP. These results suggest ammonia uptake in microbial metabolism as significant activity in TSS removal and with release of PO_4^{3-}. The main process for TSS removal from the CW is therefore microbial; herein referred to as "microbial TSS removal".

Consistent with the above proposition, the microbial TSS removal resulted in release of HCO_3^- (CO_2) into the effluent (Fig. 5). However, there seemed to be two distinct TSS removal processes associated with the HCO_3^- release, although they each showed an inverse relation between TSS removal efficiency (x) and HCO_3^- reduction efficiency (y): the first (Set 1) as y_1 = -0.55x + 14.8, R^2 = 0.85 (n = 9) and the second (Set 2) as y_1 = -0.57x – 19.3, R^2 = 0.9 (n = 8). These two linear relations are however quite similar showing the rate of % HCO_3^{2-} release per % TSS removed (the slope) to be approximately the same and indicating similar strength in correlation ($R^2 \approx$ 0.85-0.80); the only difference being with respect to the

intercept (i.e., HCO_3^- removal (+) or release (-) where there is zero TSS removal by the microbial process. The process or processes associated with this HCO_3^- removal or release when there is zero TSS removal by the microbial process is hereafter commonly referred to as "microbial TSS removal-independent" process.

The first linear relation which involved the years 1995, 1997, 1999, 2003 - 2004, and 2007 - 2010 showed ~14.8% "microbial TSS removal-independent" uptake of HCO_3^- (i.e., removal by a different process than microbial metabolism, which is implicated for the TSS removal). The second case involving 1996, 1998, 2000-2002, 2006, and 2013-2014 showed ~19.3% of "microbial TSS removal-independent" release of HCO_3^-; i.e., not attributable to microbial metabolism. In fact, both set of data showed fairly good inverse correlation between TSS removal efficiency and ΔpH (Fig. 5), which is consistent with the notion of microbial metabolism of organic matter to result in the reducing pH. The "microbial TSS removal-independent" contrasting uptake or release of HCO_3^- in these two different periods of data sets is indeed interesting and requires further investigation.

The TSS removal efficiency (x) of the first data set correlated directly and strongly with % CO_3^{2-} removal (y): $y = 1.58x - 33.6$, $R^2 = 0.83$, $n = 9$. The TSS removal efficiency (x) for the second data set also correlated directly but weaker with % CO_3^{2-} removal (y): $y = 1.03x + 21.2$, $R^2 = 0.33$ (n = 8). The reader's attention is being drawn to the reverse polarity of the intercept for HCO_3^- and CO_3^{2-} plots in the two cases. It is therefore possible that the seeming difference in these two data periods is due to interconversions between HCO_3^- and CO_3^-, which could be affected by pH and other factors such as temperature and salinity or TDS which influence the equilibrium between these species (Eq.4).

$$\frac{4.2x10^{-11}[HCO_3^-]}{[H^+]} = [CO_3^{2-}] \qquad (4)$$

The lower influent pH found for the first data set (8.55 ± 0.28) in comparison to the second (8.70 ± 0.24) should favor conversion of CO_3^{2-} to HCO_3^- (i.e. the removal of the former and release of the later), but this seems in contrast to what was observed. The same argument can be made with the Set 2 data period. The apparent contradiction is discussed further below.
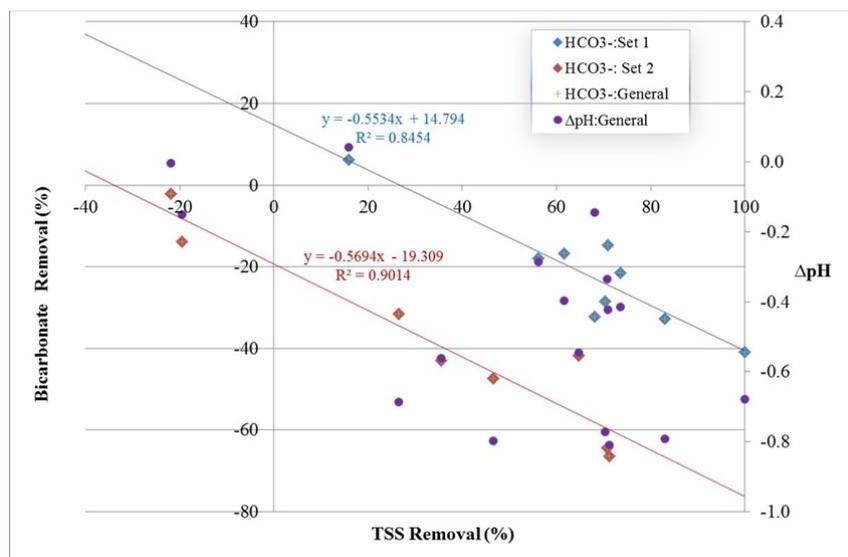
Figure 5 HCO_3^- removal/release (%) and ΔpH as a function of TSS removal (%)

The second dissociation constant (K_2) HCO_3^-/CO_3^{2-} is larger when temperature and/or salinity is higher, and hence conversion of HCO_3^- to CO_3^{2-} should be favored for the data Set 1 period when the temperature was relatively higher. However, the mean temperature for Set 1 operating period (13.75 ± 0.86^oC) is actually only marginally higher than Set 2 (13.70 ± 0.77^oC) and hence difficult to attribute such significant difference in behavior solely to temperature-induced HCO_3^-/CO_3^{2-} interconversion. The mean TDS (a different form of expressing salinity) for data Set 1 (1897.1 ± 324.9 mg/L) is also moderately higher than Set 2 (1671.0 ± 192.5 mg/L), but could this relatively small difference in salt levels fully account for the noted difference above? Interestingly, on a very restrictive data ($n = 5$) within Set 1, a very strong positive correlation ($R^2 = 0.99$) is established between % HCO_3^- removal (y) and influent TDS(x): $y = 0.077x - 159.1$. Similarly for the Set 2 data, a strong positive correlation ($R^2 = 0.93$, $n = 5$) is established between % HCO_3^- removal (y) and influent TDS(x): $y = 0.154x - 278.4$. The mean TDS difference between the two data sets can result in an estimated average of 26.1% HCO_3^- removal for the two data periods (i.e., 17.4 % and 34.9% removal for the first and second plots, respectively). Although, such semi-quantitative estimation is not rigorous enough for definite conclusions, the estimates and the observed results are in the order of magnitude close enough that it is possible for the TDS differences between the two sets of data to be responsible for the observed different "TSS removal-independent" HCO_3^- removal/release behavior. Nonetheless, there is still another plausible explanation for this difference, which is discussed next.

It is noteworthy that the mean pH depression for Set 1 data period ($\Delta pH = -0.36 \pm 0.34$) is less than for Set 2 ($\Delta pH = -0.49 \pm 0.30$), which is consistent with the observed "TSS (micro-

bial metabolism) removal-independent" removal of HCO_3^- in the former, if utilized in photosynthetic activity. Photosynthesis will result in the reduction of the pH depression derived from microbial metabolism of the TSS fraction in the water. On the other hand, extra utilization of other sources of organic matter than from the TSS source (i.e., microbial oxidation of DOC) can account for the extra HCO_3^- release and enhanced pH depression observed for the Set 2 data period. These ideas are consistent with DOC removal vs. HCO_3^- removal correlation results. An inverse correlation is found between % DOC removal (x) and % HCO_3^- removal (y) for data Set 2: $y = -3.51x - 47.9$, $R^2 = 0.82$ ($n = 7$) (the post flood data in 2013 distorts the correlation and hence excluded) confirming microbial metabolism of DOC as another source of HCO_3^-. Contrary, a direct and weak correlation is found between % DOC removal (x) and % HCO_3^- removal (y) for data Set 1: $y = 0.90x - 15.7$, $R^2 = 0.18$ ($n = 10$) and upon excluding some apparent discordant data reveals a stronger direct relation: $y = 1.42x - 12.9$, $R^2 = 0.78$ ($n = 7$). The results for data Set 1 are consistent with plant uptake of DOC (or TOC) and HCO_3^- for photosynthetic growth as discussed in the second paper (Quagraine et al., 2017).

Therefore, in theory, multiple reasons including lower TDS concentration, slightly cooler temperatures, and the inverse relation between DOC and HCO_3^- removal efficiency, as discussed above, could jointly be responsible for the unique "microbial TSS removal-independent" release of HCO_3^- in Set 2TSS data as compared to Set 1 where "TSS (microbial metabolism) removal-independent" HCO_3^- removal occurred. Unquestionably, microbial activities seem most likely the prevailing biochemical processes during the Set 2 period. In contrast, co-utilization of HCO_3^- and DOC in plant (and algae)

photosynthetic growth is likely the overriding biochemical processes during the Set 1 period. In fact, these two processes on their own (i.e. excluding impacts from TDS, temperature and other environmental factors such as pH) do convincingly explain the observed contrasting pH and HCO_3^- behavior across the CW during the two data periods.

It is noteworthy that there are two sub-divisions of the influent TSS data in terms of their relation with chlorophyll-A and VSS. The first involved a strong inverse correlation between chlorophyll-A (y) and TSS (x): $y = -2.05x + 106.6$, $R^2 = 0.79$ (n = 10) and the second in a direct relation: $y = 3.09x – 12.8$, $R^2 = 0.73$ (n = 9). Similarly, but to a limited extent, an inverse correlation existed between VSS (y) and TSS (x) in the first data set: $y = -0.32x + 20.0$, $R^2 = 0.80$ (n = 7) and in a direct relation for the second data set: $y = 0.49x – 1.24$, $R^2 = 0.49$ (n = 9). Thus, the first group which involved 1995-1998, 2001, 2003, 2005 and 2007-2009 had its TSS dominated by mineral matter (presumably clay, silt, sand or precipitated salts induced from biological activities), whilst the second (1995, 2000-2002, 2006-2008, and 2013-2014) was dominated by organic matter. See Section 3.3.2 for further discussions associated with VSS.

On purpose, we want to draw the reader's attention to the two separate classifications of TSS fractions noted thus far: i.e. one based on its removal relative to HCO_3^- removal/release (see Fig. 5) and the second based on the correlations between the influent (TSS) concentration and chlorophyll-A or VSS (*vide supra*). Significant overlapping years exists between the corresponding sets for these two TSS classifications (1995, 2003, 2007-2009 overlap for the first sets of the two classifications and 2000-2002, 2006, and 2013-2014 overlap for the second sets) to not discount the possibility of mineral matter dominance as a contributing factor to the "microbial TSS removal-independent" HCO_3^- uptakenoted

earlier for the Set 1 data and organic matter dominance as a factor to the "microbial TSS removal-independent" HCO_3^- release for the Set 2 data. We recall the strong correlation between CO_3^- (mineral source of C) removal and TSS removal for the Set 1 data. Thus, the net "microbial TSS removal-independent" HCO_3^- uptake (and not release) despite the relatively lower influent pH for Set 1 may not be due to lack of conversion of CO_3^{2-} to HCO_3^-, but rather due to effective utilization of HCO_3^- in plant photosynthetic growth as discussed earlier. Exceptions however do exist; hence, the lacking exact parity between these sets of classifications. Interestingly, exclusion of 1995 and 2003 from the Set 1 data shows a moderate inverse correlation ($R^2 = 0.55$) between influent TSS and DOC removal efficiency; whilst by excluding 1995 and 2013 from Set 2 data shows a direct moderate correlation ($R^2 = 0.64$) between influent TSS and DOC removal efficiency. The latter (Set 2) is consistent with microbial degradation of organic matter to yield CO_2 and subsequently the formation of HCO_3^- from CO_2 dissolution to H_2CO_3 and further equilibration at various water pH with other carbonaceous compounds. Release of DOC with increasing influent TSS in the former case is also consistent with plant uptake of HCO_3^- to release plant-synthesized organic compounds into the water column.

3.3.2 Volatile suspended solids

Volatile suspended solid (VSS) is a water quality measure of the organic solids in water obtained from the measure of loss in ignition of total suspended solids. It consists of two main fractions: active sludge composed of living microorganisms that act on the metabolism of the influent organic material and an inactive component composed of organic material including dead components of plants that does not exhibit metabolic activity. On annual basis, VSS of the SaskPower CW constituted $37.8 \pm 23.6\%$ of the influent TSS. Influent VSS versus

TSS correlation was generally very weak. A good positive correlation however existed between influent VSS and chlorophyll-A ($R^2 =$ 0.85, n = 18) suggesting significant general presence of viable algae in the VSS component. VSS was not measured in 2014. Such correlation involving chlorophyll-A was absent with TSS, although the data trend suggests two different set of data where influent TSS correlated in contrasting ways with chlorophyll-A or VSS as discussed above. VSS removal also correlated well with chlorophyll-A removal ($R^2 = 0.71$, n = 15).

As a measure of organic solids in water, a strong correlation ($R^2 = 0.81$) is indeed found between influent VSS and the difference between influent TOC and DOC (referred to here as Suspended Organic Carbon-SOC) for the entire annual mean data. In fact, excluding 1996 and 2008 data where TOC and DOC were essentially the same, a strong linear relation (VSS = 7.89 SOC) is established with $R^2 =$ 0.89. Although VSS is commonly intended as a measure of organic solids in water and wastewaters, the loss-on-ignition method employed may result in overestimations due to losses from sources such as inorganic salts, structural water, sulfide oxidation or inorganic carbon compounds (Vereş, 2002). Thus, the VSS measure does not preclude inorganic constituents such as carbonates and hydrated silicates. For example, the presence of inorganic C in minerals such as magnesite ($MgCO_3$), rhodochrosite ($MnCO_3$) or siderite ($FeCO_3$) will evolve CO_2 at temperatures between 425 and 520°C (Vereş, 2002); i.e., less than the temperature (550°C) at which loss-on-ignition (LOI) represents the VSS content. In this present study, from X-Y plots of influent VSS and SOC, distinction could be made between the annual data where volatile inorganic solids (carbonates) were signifi-cant-showing an inverse "VSS"-SOC correla-tion ("VSS" = -5.5SOC + 11.2, $R^2 = 0.82$ (n = 6)) and those more reflective of actual organic

matter-showing a direct strong VSS-SOC correlation (VSS = 8.0 SOC, $R^2 = 0.91$ (n = 13)). The inorganic constituents were dominant in the influent VSS measure in 1996/1997, 2005/2006 and 2008/2009. Mostly, these were years where dominance of mineral content in TSS was also noted (Section 3.3.1).

Theoretically, LOI at 550°C is assumed to be derived from organic material with the formula $(CH_2O)_n$ and hence a conversion factor (CF) of 2.5 is expected to be applied to the organic carbon content (SOC) according to the formula CH_2O/C. This however is not the case in this study, where the CF is 8.0 (*vide supra*); i.e. over three times higher. According to Vereş (2002), the value of CF between LOI and the organic carbon in sediments may depend on the type and chemical composition of the analyzed sediments. We speculate that the higher CF (for the VSS data that correlated directly with SOC) in this study is due to extra LOI from structural water in inorganic com-pounds such as silicates present in clays and fine silts. We further speculate that the "VSS" content which correlated inversely with organic carbon in the influent wastewater is due to LOI derivable from carbonate sources. Thus, a theoretical CF of 5, according to the formula CO_3^{2-}/C, is to be expected (based on assumption that negative errors in SOC estimation is attributable to carbonate presence). Interestingly, the observed CF in this present study is fairly close to this value (i.e., 5.5, which is a deviation only by 10% from the expected value).

Unlike SOC, no significant correlation is found between VSS removal efficiency and TOC or DOC removal efficiency for the full data, although some fair correlation is found with TOC removal efficiency ($R^2 = 0.47$) and weak correlation with DOC removal efficiency ($R^2 = 0.13$) when the post-flood data (2013/2014) is excluded. Nonetheless, similar to TOC removal (Quagraine et al., 2017), two unique and contrasting pH-dependent VSS

removal characteristics occurred during the study period.

The first VSS removal process involved 1994-1997, 1999-2000, 2005-2006, and 2009-2010 (n = 10), which encompasses years with inorganic matter laden VSS fractions (apart from 2008 where some other factors dictate unique behavior (*vide supra*)) and some years of substantial organic fractions, which presumably are of grain size amenable for plant uptake. As a group, the VSS removal was characterized by the following:

a) Favored by decreasing influent pH (i.e., inverse linear relation between VSS removal efficiency (y) and influent pH (x): $y = -109.7x + 959.4$; $R^2 = 0.87$ (n = 10).

b) Favored by decreasing $[NH_3]/[NH_4^+]$ ratio (i.e. inverse linear relation between VSS removal efficiency (y) and $[NH_3]/[NH_4^+]$ ratio (x): $y = -180.9x + 68.5$; $R^2 = 0.68$ (n = 10).

c) Correlates with NH_4^+ removal (i.e., a direct linear relation between VSS removal efficiency (y) and NH_4^+ removal efficiency (x); $y = 2.17x - 150.7$, $R^2 = 0.73$ (n = 10).

d) Correlates with PO_4^{3-} removal (i.e., a direct linear relation between VSS removal efficiency (y) and PO_4^{3-} removal efficiency (x); $y = 1.016x + 7.74$, $R^2 = 0.76$ (n = 10).

e) Correlates with TP removal but to a slightly weaker extent than with PO_4^{3-}(i.e., a direct linear relation between VSS removal efficiency (y) and TP removal efficiency (x); $y = 1.075x + 4.57$, $R^2 = 0.74$ (n = 9). NB: Inclusion of 2010 weakens the relation ($R^2 = 0.45$).

f) Correlates inversely, but only fairly, and on a more restricted data with DOPP removal (i.e. inverse linear relation between VSS removal efficiency (y) and DOPP removal efficiency (x): $y = -1.49x + 147.7$, $R^2 = 0.49$ (n = 8). NB: Inclusion of

1996 and 2006 weakens the relation substantially ($R^2 < 0.10$).

g) Results in increasing pH (i.e., a direct linear relation between VSS removal efficiency (x) and ΔpH (y): $y = 0.0084x - 0.53$, $R^2 = 0.75$ (n = 10).

The correlation results above for this class of VSS removal is consistent with our earlier assertion (Section 3.2.1 and Quagraine et al., 2017) for plant assimilation of NH_4^+ (not NH_3) as N-source, PO_4^{3-} as P-source for growth, and CO_2 and HCO_3 (Eq. 2)- directly from the CW water and/or indirectly from microbial oxidation of TOC/BOD (or in this case VSS) fractions as C-sources to account for the observed increasing pH trend with VSS and other nutrient utilization. In fact, direct VSS uptake is also possible as a complementary C-source for the plant growth. How exactly then does VSS contribute to the plant photosynthetic growth? What is the actual relation between VSS and TOC or DOC during this period of operation? We attempt to provide answers to these and similar questions from the following discussions.

For this first set of data, no correlation existed between the VSS removal efficiency and DOC removal efficiency ($R^2 = 0.01$, n = 10). However, a fair correlation is found between the VSS removal efficiency and TOC removal efficiency ($R^2 = 0.42$, n = 10). Furthermore, a strong correlation is found between VSS removal efficiency (x) and effluent DOC (y_1) ($y_1 = 0.114x + 19.51$, $R^2 = 0.89$ (n = 9)); whilst a slightly weaker correlation is found with the effluent TOC (y_2) ($y_2 = 0.12x + 20.75$, $R^2 = 0.73$ (n = 9)). (Both correlations are weakened with the inclusion of the1997 data: i.e., $R^2 = 0.6$ and 0.48, respectively). These results, together with others above involving VSS removal, do suggest direct plant uptake of VSS and/or its microbial oxidation as CO_2/HCO_3^- source for plant photosynthetic growth with concomitant production of soluble organic compounds. The surfaces of plants in

CW are coated with active biofilm of periphyton which can absorb colloidal and soluble matter (USEPA, 1999). Depending on the nature of the suspended solids, they may directly penetrate into plants (Donnelly et al., 1994) or be metabolized and converted to soluble compounds, gases or biomass, which re-enter the water column (USEPA, 1999).With about half of the annual VSS data in this group dominated by mineral content, which reduces with decreasing pH; the above assertion of CO_3^- as mineral source of C in the suspended solids is also confirmed, which would be converted to HCO_3^-/CO_2 (with pH decline and potentially by some biological metabolism) for plant photosynthetic growth.

The other set of VSS data showed fair direct linear relation between its removal efficiency (y) and influent pH (x) ($y = 41.97x – 307.6$, $R^2 = 0.53$ (n = 10); whilst its removal also led to decreasing pH trend (i.e. an inverse linear relation between VSS removal efficiency (x_1) and ΔpH (y_1); $y_1 = -0.02x + 0.55$, $R^2 = 0.63$ (n = 10). This second VSS removal process, which involved 1996-1998, 2002-2004, 2007-2009, and 2013 (n = 10) is further characterized by the following:

a) Contrary to the first data set, removal is favored, though only fairly, by increasing $[NH_3]/[NH_4^+]$ ratio (i.e. direct linear relation between VSS removal efficiency (y) and $[NH_3]/[NH_4^+]$ ratio (x): $y = 68.3x + 37.0$, $R^2 = 0.45$ (n = 9). (NB: Inclusion of the 2008 completely distorts this correlation ($R^2 = 0.006$)).

b) A fairly good correlation is found between % VSS removal (y) and % NH_3 removal (x) ($y = 3.98 x – 321.3$, $R^2 = 0.57$ (n = 9)); inclusion of 2013 data completely distorts the correlation ($R^2 = 0.07$). (NB: Similar correlation for the first data set was weaker for a similar number of data (n = 9): i.e., $y = 3.67 x – 323.5$, $R^2 = 0.28$.

c) Unlike the first set of data, correlation between % VSS removal (y) and % NH_4^+ removal (x) was absent for the full set of data ($R^2 = 0.02$, n = 10); although on a more limited subset data (n = 6) a good linear relation is eminent ($y = 0.32x + 40.7$, $R^2 = 0.82$).

d) Contrary to the first set of data, VSS removal correlates inversely with PO_4^{3-} removal (i.e. an inverse linear relation between VSS removal efficiency (y) and PO_4^{3-} removal efficiency (x); $y = -1.27x + 63.1$, $R^2 = 0.65$ (n = 9). Inclusion of the 2008 data (n = 10) significantly worsens the correlation ($R^2 = 0.21$)

e) Contrary to the first set of data, VSS removal correlates inversely with TP removal (i.e. an inverse linear relation between VSS removal efficiency (y) and TP removal efficiency (x); $y = -1.73x + 73.1$, $R^2 = 0.59$ (n = 9). Inclusion of the 2008 data (n = 10) significantly worsens the correlation ($R^2 = 0.16$).

f) Contrary to the first set of data, direct correlation between VSS removal and DOPP removal exists (though only fairly and on a restricted data) (i.e. direct linear relation between VSS removal efficiency (y) and DOPP removal efficiency (x): $y = 0.25 x + 39.6$, $R^2 = 0.44$ (n = 8). NB: Inclusion of 2003 and 2007 weakens the relation substantially ($R^2 = 0.01$).

The contrasting results between the two differing yearly groups of VSS removal clearly suggests two different dominating VSS, ammonia, and phosphorus (PO_4^{3-} and DOPP) metabolic processes for these group periods, which impact pH in contrasting way. The results for the second group are consistent with microbial oxidation of organo-phosphorous and N matter in the solid form as VSS (see Eq. 5; though P is excluded in the equation) as being a predominant process.

$$C_nH_aO_bN_c + \left(\frac{2n+0.5a-1.5c-b}{2}\right)O_2 \rightarrow nCO_2 +$$

$$cNH_3 + \frac{a-3c}{2}H_2O \tag{5}$$
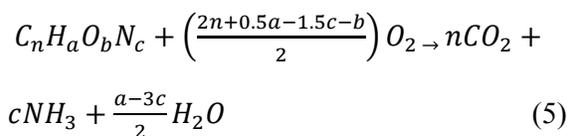
where: n = %C/12T, a = % H/T, b = %O/16T, c = %N/14T; and T = %C/12 + %H + %O/16 + %N/14.

The results further suggest suspended particulate form of phosphorus (PP) as a significant portion of DOPP for the periods covering this mechanistic class of VSS removal. In fact, a significant correlation was found between the influent VSS and DOPP for this group of data (R^2 = 0.51, n = 9). The annual mean influent DOPP for this group of data was 0.20 ± 0.13 mg/L. Unlike the first data group where algal photosynthesis dominates, NH_3 (and not NH_4^+) seem to be the dominating ammonia specie of uptake by microorganisms for growth. Furthermore, decreasing effluent DOC concentration (y) is observed with increasing removal of VSS (x) (i.e., y = -0.17x + 29.47; R^2 = 0.4; n = 8) suggesting favorability for heterotrophic utilization of DOC with VSS metabolism.

3.4   Major inorganic constituents

The dominant inorganic constituents in the CW influent included HCO_3^-/CO_3^{2-}, SO_4^{2-}, Na^+, Cl^-, Ca^{2+}, Mg^{2+}, and K^+. Earlier, we had discussed the HCO_3^- and CO_3^{2-} behavior and hence details of their uptake or export are excluded in this section. Generally, the effluent quality in terms of these parameters were higher than in the influent for both when the latter was of facultative lagoon treated standard (1994-95) and when improved to a conventional secondary treated standard (Table 2).

For most of these constituents, the increase in concentration would be due to evaporation losses leading to ion concentration. K, an essential plant nutrient, however behaved differently; it showed about 31% removal at the juvenile stages of the CW vegetation,

which reduced to an annual % average removal of only ~ 2% at the latter stages of the CW operation. In fact, consistent but decreasing net uptake of K lasted only for the first 4 years (21.5 ± 11.3%), after which smaller but erratic uptake or export occurred although the unique uptake in 2005 - 2006, 2010 and 2014 were notable. Even under the erratic uptake conditions, K was generally most efficiently utilized or least exported amongst the other major inorganic constituents.

Despite these notable general trends, there were some unique occurrences with respect to major ion uptake or release which deserve some comments. In 1999, net uptake of all the major ions (except HCO_3^-) occurred. In contrast, in 2013 (i.e., first year of operation after the flood) significant net export of all the major ions occurred (except CO_3^{2-} of 20% removal); i.e. ≥ 45% export of these ions except K where the export was lower at ~16%. We attribute this to the washing off of exposed top sediment after the flood occurrence. Significant exports also occurred in 2009 and 2014, which may not be solely due to evaporation. For example, ~446% export of Mg occurred in 2014, which may be attributed to top sediment washing; in fact a disproportionate export of Mg had earlier being observed in 2009.

3.5   Trace Elements

Most of the measured trace elements were below detection limits of the measurements and hence are not discussed here. Though present at low levels, Arsenic was one unique trace metal which was consistently measured at the μg/L level, but the CW was incapable in its removal (Table 2). Copper (Cu) was also present at μg/L level, but the measure were too close to the detection limit and hence could not be scrupulously monitored although there seem to be some removal by the CW.

Table 2 Mean inflow and outflow concentrations, and mean % reduction (+) or increase (-) of major inorganic constituents and trace elements in MWW across the CW in 1994-1995, when inflow quality was of facultative lagoon standard and in 1996-2014, when the quality was of a conventional secondary effluent standard. Values in parenthesis are standard deviation values for the corresponding mean data. All inflow/outflow concentration units are in mg/L, except for some trace metals marked in asterisks which is μg/L and total alkalinity and total hardness which is as mg/L $CaCO_3$

Parameters	1994 - 1995			1996 - 2014		
	Inflow	Outflow	% Removal	Inflow	Outflow	% Removal
CO_3^{2-}	3.3 (4.0)	8.1 (0.3)	-931 (1276)	39.7 (25.9)	6.9 (6.2)	70.0 (47.37)
HCO_3^-	550 (10)	533 (15)	3.0 (4.6)	363 (74)	472 (74)	-32.4 (17.5)
T-Alkalinity	459 (11)	455(19)	0.8(8.9)	351 (54)	395(65)	-13.0 (13.0)
Ca^{2+}	94.7 (7.8)	102.9(11.1)	-8.5 (2.7)	95.2 (11.5)	100.0 (17.3)	-4.9 (11.5)
Mg^{2+}	78.0 (11.8)	81.4 (8.9)	-4.7 (4.4)	70.5 (10.6)	96.9 (87.1)	-34.1 (107.3)
T-Hardness	558 (68)	592 (64)	-6.3 (1.4)	532 (74)	564 (111)	-5.9 (13.6)
K^+	26.8 (1.6)	18.5 (2.5)	30.9 (5.2)	28.7 (4.9)	28.1 (5.2)	2.2 (6.8)
Na^+	435 (56)	432 (15)	0.2 (9.3)	363 (58)	392 (71)	-8.3 (14.6)
Cl^-	236 (4)	223 (7)	5.7 (4.5)	201 (31)	217 (40)	-7.8 (13.5)
SO_4^{2-}	716 (155)	745 (98)	-5.1 (8.9)	687 (114)	709 (150)	-3.2 (15.3)
Al	-	-	-	0.11 (0.05)	0.08 (0.07)	29.3 (61.9)
As[*]	5.71 (1.26)	6.24 (0.05)	-12.0(25.5)	3.73 (2.42)	3.85(2.62)	- 14.9 (51.4)
B	1.40 (-)	1.06 (-)	24.5 (-)	1.28 (0.57)	1.23 (0.54)	5.5 (11.4)
Cu	0.003(.002)	0.003(.001)	5.6(7.9)	0.06 (0.19)	0.10 (0.35)	34.2 (46.3)
Fe	-	-	-	0.62 (1.42)	0.68 (1.34)	-66.2 (142.1)
Mn	0.20 (0.15)	0.12 (0.12)	50.3 (21.6)	0.12 (0.08)	0.40 (0.42)	-394 (599)
Si	-	-	-	4.19 (3.26)	3.37 (2.38)	14.5 (63.5)
Sr	1.09 (0.09)	0.97 (0.10)	11.1 (2.2)	0.85 (0.26)	0.85 (0.25)	2.6 (22.6)

Boron (B) and strontium (Sr) were removed to a reasonable extent (~11.1 - 24.5%) at the early years of the CW operation, but declined to only about 2.6 - 5.5% in the latter stages of operation. Aluminum and silicon were not monitored during the early stages of operation, but the CW demonstrated ability to remove these elements, though only moderately and quite erratically (mean net annual removal of 29.3 ± 61.9 and $14.5 \pm 63.5\%$, respectively).

The CW showed ability to remove manganese (Mn) during the first two years of operation; removing as much as 50% of the influent Mn. In fact, consistent but decreasing net uptake of Mn lasted only for the first 3

years of operation ($35.5 \pm 29.8\%$), after which mostly large exports occurred (Table 2). Though to a lesser extent, significant exports of iron (Fe) were also released since the early first 2 years of operation.

3.6 Bacteriology

The bacteria measures were monitored only as fecal and total coliforms. The reported coliform (fecal and total) counts were quite erratic. For example, the fecal and total coliform counts in the first two years of operation were respectively $3,607 \pm 5,057$ and $26,072 \pm 6,060$ CFU/100 mL. Despite the variability, the respective reduced bacteria

counts of 17 ± 14 and 711 ± 983 CFU/100 mL in the effluent would suggest the CW process as very effective, at least during the initial stages of operation, in removing bacteria: i.e. removing on an annual average of ~56 and 98%, respectively. The coliform removal efficiency of the CW however became inconsistent in later years, although total coliform removal was less irregular. In fact, apart from the post flood data (i.e. 2013 and 2014) when net export of total coliform was realized, consistent removal averaging $77 \pm 19\%$ occurred after the initial two years of operation. The 2013 and 2014 average increase in total coliform was ~75% and ~397%, respectively. The increase in total coliform for these years is reflective of vegetation loss after the flood with many patched areas of uncovered vegetation. Plants play a vital role in coliform and TSS removal processes. Submersed plant parts and their associated sticky biofilms form trap for particles, including all sizes of microorganisms (Kadlec and Wallace, 2009).

Consistent with bacteria clumping together in aggregates and/or attaching to suspended particles, coliform removal have been found to be mainly due to physical separation of suspended particles (Kadlec and Wallace, 2009; Ng and Gunaratne, 2011). In this study however, no obvious relation was found between TSS removal and coliform removal for the full data; albeit some relation was identified on some limited data ($n \leq 14$), but the correlations were negative and weak (i.e., $R^2 = 0.24$, $n = 14$) to moderate for about half of the study period ($R^2 = 0.63$, $n = 9$). These results suggest that sedimentation is not likely a dominant mechanism by which coliform was removed from the CW. Microbial metabolism of TSS was earlier implicated. In fact, the processes involved in reducing bacteria in FWS CW are many and in complex interactions. Apart from settling and filtration, the removal processes include also UV

disinfection, predation by nematodes, rotifers, protozoa etc., "natural" mortality and regrowth (Kadlec and Wallace, 2009). Organisms associated with suspended particles are far less susceptible to UV and solar disinfection, presumably because of shielding effect. Reductions of coliforms are also noted to be more efficient at higher pH (Ng and Gunaratne, 2011).

In this study, apart from the early stages of CW vegetation establishment (1994-1996) and during the first year of re-vegetation after the flood (2013), a reasonable positive correlation ($R^2 = 0.52$) existed between influent pH(x) and total coliform $\log_{10}$ reduction (y): $y = 2.03x - 16.99$, $n = 15$. On the contrary, for the periods associated with vegetation establishment or re-establishment a strong inverse relation ($R^2 = 0.94$) is observed between influent pH(x) and total coliform $\log_{10}$ reduction (y): $y = -4.03x - 34.89$, $n = 4$. The results suggest two contrasting processes dominating coliform removal during these distinct periods of operation (i.e., during the plant establishing and established periods). In the case of the former (with un-vegetated sections of the CW), plant establishing growth required essentially an unlimited amount of NH_4^+ and hence decreasing pH (favoring NH_4^+ uptake over NH_3) promoted better growth providing more vegetative surface area to trap bacteria from the water column. With full vegetative coverage of designed sections of the CW and full growth of plants after the vegetative establishment period, annual distinction in vegetative surface area becomes less relevant and so is the external demand for N sources. However external factors such as temperature, pH, etc. would significantly influence the ability of the vegetative surfaces to adsorb not only microbes but organic matter.

With upgrade of the city's WWTP, the influent fecal coliform improved, but its removal in the latter years became inconsistent, showing some large net exports

($-189 \pm 324\%$). Net average exports of fecal coliform occurred for half the number of years of investigation and mostly at the later stages of operation. In fact, apart from 1997 where only ~4.6% export occurred; consistent net fecal coliform removal by the CW was maintained till 2001, after which mostly exports occurred. Reductions in the latter years were realized only in 2004, 2006 and 2009. The reintroduction of fecal coliform into the CW water would originate from many different warm-blooded animals that inhibit or frequent the CW including large duck population in the storage pond (the CW outlet).

CONCLUSIONS

As observed in the second paper involving N species, TOC, BOD, and others (Quagraine et al., 2017), pH was confirmed as a key indicator for the main biological activities involved with the removal (or release) of P species by the CW: i.e. microbial respiration (with co-uptake of these speciated forms of nutrients)as mainly responsible for pH reduction, whilst algal/plant photosynthetic growth counteracted against such pH depression from the likely utilization of CO_2 and co-uptake of any or all these P species with other nutrients such as NH_4^+ and/or NO_3^- In fact, the relative amount and uptake of the various speciated forms of P (i.e. PO_4^{3-}-P, organic-P, and particulate-P) and organic carbon (as DOC or SOC (VSS)) seemed to have influenced the dominance of one of these two main processes over the other and in dictating the resulting effluent pH. The relative composition of inorganic and organic constituents in suspended solids in the water (measured as TSS or VSS) also played a significant role in influencing the predominance of any one of the above two biological process over the other. For example, suspended solids of significant mineral contents or organic fractions of, presumably, particular grain size

amenable for plant uptake seemed to promote photosynthetic activity from co-uptake of C (of both inorganic and organic sources) and P (typically as PO_4^{3-}). VSS removal was implicated to involve either co-uptake of NH_4^+ and PO_4^{3-} in plant photosynthetic growth or co-uptake of NH_3 (not NH_4^+) and non-phosphate P-DOPP and (not PO_4^{3-}) in microbial oxidation to promote relative pH increase in the former and pH decrease in the latter.

A fairly strong negative correlation was also observed between influent pH and TP as well as PO_4^{3-} removal efficiency. The CW generally was ineffective in removing major inorganic species and trace elements although K^+ ($31 \pm 5\%$) and Mn ($50 \pm 22\%$) removal were realized in the early 2-years of operation. Effective reduction of both total coliform (56% average) and faecal coliform (98% average) was demonstrated in the early two years of the CW. However, whereas the total coliform removal was maintained or improved till a flood incidence in 2011 (77% average reduction), the faecal coliform removal became inconsistent, showing some large net exports which is attributed to the different warm-blooded animals that inhibit or frequent the CW including duck population in the storage pond (the CW outlet).

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