## EMERGING TECHNOLOGIES FOR NITROGEN AND PHOSPHORUS REMOVAL, AND BRINE MANAGEMENT

David Austin (Jacobs), Jim Bays (Jacobs,) Kate Simmonds (Jacobs), Rafael Vazquez-Burney (Jacobs)

#### ABSTRACT (500 WORDS MAXIMUM)

Treatment wetlands are a sustainable phosphorus and nitrogen removal technology which can provide cost-effective treatment, with low operational costs compared to conventional technologies. A common drawback to their application is the footprint required to support nitrification, denitrification, and phosphorus sequestration.

This paper summarises recent case studies describing four emerging approaches to reducing wetland area through process intensification: super-oxygenation for nitrification, zeolite-anammox media filtration for deammonification, biochemical reactors for denitrification, and geochemical augmentation in surface flow (SF) wetlands for phosphorus removal. These wetland applications can become very effective for application as unit processes within small wastewater treatment plants.

Super-oxygenation recirculates a side stream in SF wetlands through a downflow pure oxygen contactor. A supersaturated recirculation flow (40-80 mg  $O_2/L$ ) boosts nitrification rates by over an order of magnitude compared to passive wetlands. Using this approach, an 800 m<sup>3</sup>/d groundwater remediation wetland located in Michigan USA demonstrates sustained nitrification through winter. A super-oxygenated SF wetland would reduce NH<sub>3</sub>-N from 10 mg/L to 1 mg/L within a wetted area of 5.0 ha, a significant reduction from the 120-ha required for a passive wetland.

Zeolite anammox uses flood and drain (tidal flow) beds of clinoptilolite. Ammonium adsorbs to media during the flooded stage and oxidizes when the bed drains. Nitrification occurs at low ammonium loading and results in complete oxidation. Anammox occurs at high ammonium loading (>120 g  $NH_4^+/m^3/d$ ) and beds are just partially drained. A demonstration system (21 m<sup>3</sup>/d) in Oregon USA reduced ammonia from 1000 mg/L to 300 mg/L after one year of operation and stepping through a nitrification phase. It is currently going through operational optimization to overcome a nitrite limitation without stimulating nitrite oxidation.

Biochemical reactors use compostable media (e.g., wood chips, sawdust, manure) to create saturated anaerobic conditions conducive to denitrification, sulfate-reduction and metal sequestration. Denitrification rates are typically two orders of magnitude greater than SF wetlands. Recent case studies from the USA in RO brine management and mine-water treatment fully demonstrates this technology for application within a wide range of wastewaters.

Phosphorus removal in wetlands is sustained through sedimentation, sorption and predominantly biological uptake and burial. Consequently, passive SF wetland area requirements are typically the largest for wastewater contaminants. For example, treating 10,000 m<sup>3</sup>/d in an SF wetland that polishes wastewater TP from 0.5 mg/L to 0.05 mg/L would require approximately 135 ha. One intensification approach is to add soluble

(non-flocculating) doses of aluminium or iron salts at a concentration below the chronic toxicity threshold. Using this method of geochemical augmentation, removal rates have been shown to increase by approximately an order of magnitude, reducing treatment areas by approximately 90%. The method is in early stages of development. Full-scale pilot projects in Oregon (12,000 m<sup>3</sup>/d) and Georgia (56,000 m<sup>3</sup>/d) USA demonstrate the efficacy of this method.

If traditional passive wetlands are considered low-rate, and conventional wastewater technologies high-rate, these emerging wetland technologies would be considered medium rate. Adopting a medium-rate wetland process strategy appears to show great potential as a nutrient management application for small-flow treatment plants (<10,000  $m^3/d$ ).

#### KEYWORDS

Wetland, nitrification, denitrification, deammonification, phosphorus, reverse osmosis brine

#### PRESENTER PROFILE

David Austin:

David leads Natural Treatment Systems in Solutions and Technology at Jacobs. He has developed wetland treatment technology since 1991. Since 2008, he has completed over two dozen reservoir/lake remediation projects. David is based in the USA, and has worked in Canada, UK, UAE, Israel, Brazil, Australia, and New Zealand.

Kate Simmonds:

Kate has a variety of multidisciplinary experience having worked on projects in New Zealand, the United Arab Emirates and Australia over her 14-year career. Kate was awarded the Australian Water Association Young Water Professional of the Year, Victorian State winner (2012) and National winner (2013).

## **1** INTRODUCTION

Many councils in New Zealand operate Wastewater Treatment Plants (WWTP) which comprise predominantly of pond based treatment and are relatively "small" in size. These WWTP can be followed by wetlands for "polishing", however these wetlands are generally poorly maintained and undervalued. Consent discharge limitations are becoming increasingly stringent, and many councils are experiencing issues with meeting discharge consent limits from pond based systems, particularly Nitrogen (N) and Phosphorous (P).

The benefit of wetlands is that they are simple to build and operate, have high robustness and process stability, can buffer hydraulic and organic load fluctuations, and produce very low volumes of sludge. Although wetland operation has improved over the years, several limitations remain. The most significant limitations are poor nutrient (N and P) removal, large footprint requirements, and oxygen transfer limitations.

Small WWTP can meet rigorous nutrient discharge criteria through innovation. The definition of "small" varies. Those accustomed to large municipal treatment systems may consider WWTP treating flows below 10 MLD as small. On the other hand, flows of 1 MLD or less may be subject to the same discharge standards as a WWTP of 100 MLD.

For the purposes of this paper, a small WWTP is considered as flows from 0.1 to 10 MLD flow. At the lowest range of these flows, discharge may be subsurface. Groundwater protection often demands low discharge concentrations of total nitrogen (TN). Most flows in this range will discharge to surface water. Flows discharging to freshwater typically need to fully nitrify and have low total phosphorus (TP) concentrations. Discharge to coastal areas generally need to have low TN concentration. The technology focus of this paper is on emerging treatment wetland technologies for small municipal wastewater flows which have been proven overseas, and are now rousing the interest of water authorities in Australia and New Zealand. The technologies are suitable for use in New Zealand, and many offer a low-cost passive solution to help meet more stringent N and P discharge limits. WWTPs tend to be outside of heavily urbanized areas where more land is available for treatment technologies, such as membrane bioreactors, successfully scale down to treat small flows to high standards, there are practical limitations.

Upgrading small WWTPs to high-tech wastewater treatment technologies often entails decommissioning of the existing systems, such as lagoons, tricking filters, or simple activated sludge systems. The costs of doing so are high. Even if funding is available to cover capital costs, the cost of operating high-tech systems can be burdensome for smaller municipalities.

Traditional treatment wetland technologies are passive and not well suited to complete nitrification, complete denitrification, and polishing of phosphorus to low concentrations, without impracticably large footprints. Innovative treatment wetland technologies treat at far higher rates than passive systems, significantly reducing the treatment footprint through process intensification. These emerging treatment wetlands offer opportunities to upgrade many small wastewater treatment plants in a cost-effective manner, to allow them to meet the increasingly stringent discharge requirements. This paper reviews recent developments in intensified treatment wetland technologies.

## 2 NITROGEN

### 2.1 SUPER-OXYGENATED WETLANDS FOR NITRIFICATION

For domestic wastewater, the oxygen demand of nitrification is substantially higher than can diffuse passively from the atmosphere into process water (Kadlec and Wallace, 2009). In subsurface flow (SSF) wetlands, dispersed aeration systems underlying treatment media have proven effective at complete nitrification with outflows of  $NH_3$ -N < 1.0 mg/L (Nivala et al., 2013). The key technical innovation with aeration in SSF wetlands has been to use drip irrigation tubing as a low intensity, high density diffuser system. The cost of treatment media and low energy efficiency of shallow water (< 0.5 m) aeration restrict practical application of aerated SSF wetlands to very small flows, probably much less than 1.0 MLD.

At slightly over one third the specific (per hectare) capital cost of SSF wetlands (Kadlec and Wallace, 2009) on average, surface flow (SF) wetlands are a potential alternative to SSF wetlands. Aeration, however, has proven impractical in SF wetlands. Plants will heave up and destroy diffuser systems placed on soil. Aquatic rodents tend to gnaw and destroy diffuser tubing. Aeration of open water zones cannot meet oxygen demand exerted by wetland sediments and process water in shallow, planted zones. Superoxygenation provides an alternative in meeting oxygen demand.

Super-oxygenation injects pure oxygen into a recirculating side stream. A pump withdraws water from a downstream section of the SF wetland, passes process water through a pure oxygen contactor and then injects water supersaturated with dissolved

oxygen (DO) back into upstream sections of the wetland (Figure 1). The DO concentration in the recirculation water is high, typically 40 to 80 mg/L, depending on the water temperature and pressure within the oxygen contactors. Such high DO concentrations are possible because of the enhanced solubility of oxygen in water in contact with a pure oxygen atmosphere (Henry's Law), approximately five times greater than water in contact with air. Mixing DO supersaturated water with ambient water reduces the DO in the process water to saturation or low super-saturated concentration (Speece, 2008) to meet the oxygen uptake rates of wetland biofilms.



*Figure 1:* Super-oxygenation plan schematic. Pumped recirculation water passes through a pure oxygen contactor and the injected into open water, deep (~1.5 m) zones through eductor array to then flow through shallow (< 0.5 m) planted zones (patterned areas).

The super-oxygenated SF wetland concept was first tested on a benchtop (Palmer et al., 2009). The next application was designed to treat 1.5 MLD of ammonium contaminated groundwater in the State of Michigan, USA (Austin et al., 2017b). Treatment started in April 2016. The average flow was 0.9 MLD and the inflow NH<sub>3</sub>-N ranged from approximately 5 to 10 mg/L. Within six weeks, the outflow NH<sub>3</sub>-N was near the method detection limit of 0.2 mg/L (Figure 2). Freezing winter conditions tested the limits of nitrification in cold water. Nitrification began to degrade slowly when water temperatures dropped to  $0.5^{\circ}$ C in December 2016. Injection of 8 L of a commercial nitrification by apparent recolonization of wetland biofilms when water temperatures were less than 5°C.



*Figure 2:* Nitrification performance of super-oxygenated SF wetland. The straight line is the 1 mg/L NH<sub>3</sub>-N permit standard.

Super-oxygenation solves the oxygen transfer problem of nitrification SF wetlands. Outfall DO is consistently near or over saturation. Consequently, nitrification rates in the standard reactors-in-series, first-order model (Kadlec and Wallace, 2009) are intensified by a factor of at least 15. The impact on wetland size is profound. A 10 MLD passive SF wetland treating 10 mg/L NH<sub>3</sub>-N to 1.0 NH<sub>3</sub>-N would require an area of 128 using mediation nitrification rates reported in Kadlec and Wallace (2009). A super-oxygenated wetland would require 7 ha, and could perhaps go as small as 3.5 ha. There is some uncertainty in the observed nitrification rates because most of the effluent NH<sub>3</sub>-N concentrations were below the method detection limit of 0.2 mg/L (SM 4500 NH3 D).

The Michigan wetland was 2.3 ha, of which 2.1 ha was oxygenated. The oxygen contactor (Speece cone) was rated at 267 kg  $O_2/d$ . Nitrification performance analysis reveals that the wetland could treat approximately 6 MLD of inflow in the same area for the same influent concentrations, achieving discharge concentrations of 1.0 mg/L.

For lagoon treatment systems that lose nitrification even in mild winters, retrofit or addition of a super-oxygenated SF wetland would maintain nitrification. For small activated sludge or tricking filter plants that do not nitrify, a super-oxygenated wetland downstream of the clarifier will meet rigorous nitrification standards. As a public domain technology, it is open to development by utilities.

### 2.2 ZEOLITE-ANAMMOX FOR TOTAL NITROGEN REMOVAL

The anammox process begins with ammonia oxidation to nitrite, which then serves as an electron acceptor from an ammonium electron donor (Jetten et al., 2005). Although regarded as a recent discovery, it was actually discovered in 1902 by Dunbar and Thumm in contact beds (Kinnicutt et al., 1919).

Dunbar (1908) emphasized the fundamental importance of ammonium adsorption in ammonium-oxidizing contact beds, which flood and drain several times per day. Rediscovery of contact beds for nitrification in the late 20<sup>th</sup> Century confirm the importance of ammonium adsorption (Tanner et al., 1999, Austin, 2006). When beds flood, ammonium adsorbs to media. When beds drain adsorbed ammonium oxidizes. This process can operate by pumps or gravity for little to no energy (Austin and Nivala, 2009).

It is important to note that contact beds have long been known to be highly effective for nitrification (Kinnicutt et al., 1919, Barwise, 1901, Barwise, 1899), superior in the past to other wastewater technologies until nitrification was perfected in activated sludge in the first decades of the 20<sup>th</sup> Century. Contact beds fell out of favour soon after World War I because tricking filters and activated sludge are far more effective at removing BOD from large flows of wastewater. Rediscovered in the late 20<sup>th</sup> Century for very small flows, generally 1 MLD or less, variations on old contact bed designs are now common in some countries. France, for example, now has approximately 4,000 small flow wetland contact beds (Esser, 2015). A high rate of ammonium oxidation is a distinguishing feature for this technology. The recent discovery of anammox in some contact bed wetlands (Ronen and Wallace, 2010, Sun and Austin, 2007, Dong and Sun, 2007) has sparked interest in the ammonia adsorption capacity of media as a key design parameter, revealing that zeolite, which has an ammonium exchange capacity (AEC) in the order of 1,000 to 2,000 g NH<sub>4</sub><sup>+</sup>/m<sup>3</sup>, appears to stimulate total nitrogen removal through anammox even at low concentrations found in domestic wastewater (Collison, 2010).

Zeolite-anammox contact beds use zeolite media to promote the growth of anammox bacteria for total nitrogen (TN) removal (Grismer and Collison, 2017, Collison and Grismer, 2018). Development of this technology has advanced in continuous flow contact beds without flood and drain (tidal flow) hydraulics. Harder zeolites, such as clinoptilolite or mordenite are a useful media for tidal contact beds. The high media AEC promotes a high rate of nitrification at start-up with inoculation by nitrifying bacteria. Although anammox may be native to zeolite systems for reasons yet to be elucidated, growth of anammox bacteria is very slow compared to nitrifying bacteria. Thus, inoculation with zeolite anammox seed helps speed up conversion of contact beds from nitrification to anammox.

The Roseburg Urban Sanitary Authority in Roseburg (RUSA), Oregon USA treats approximately 15 to 20 MLD of domestic effluent to secondary standards. It runs zeolite-anammox contact beds to remove total nitrogen from excess filtrate produced by the dewatering of biosolids. Most filtrate is used by local farmers as fertilizer.

There are two beds constructed of a 45-cm layer of clinoptilolite over a layer of drain rock (Figure 3). The area of each cell is 124 m<sup>2</sup>. Filtrate passes through a clarifier to remove solids, then into a dosing siphon box that batch loads the zeolite beds. When filtrate reaches the surface of a bed the drain siphon triggers, emptying the bed into a recycle/discharge basin. Filtrate flow to the beds is up to 23 m<sup>3</sup>/d. The ammonia-N concentration is approximately 1,000 mg/L. Recycle flows are set to ensure approximately a dozen flood and drain cycles per bed per day. Approximately half of the zeolite bed drains in each cycle to allow anoxic conditions to prevail in the lower part of the bed. The bottom layer in the zeolite bed was seeded with approximately 12,000 kg of zeolite-anammox media that had treated biosolids filtrate in California.



*Figure 3: Section schematic of zeolite-anammox system.* 

Start-up began in November 2016 at low flow of 4 m<sup>3</sup>/d. With water temperatures approaching 10°C, and subsequent slow growth of anammox bacteria, the initial process goal was to establish nitrification and pH control (>7.0) with addition of alkalinity. Initially, the entire zeolite bed flooded and drained. With rising water temperatures in the spring, flows were ramped up with pH control to reach a loading rate over 120 g NH<sub>3</sub>-N/m<sup>3</sup>/d in order to suppress activity of nitrite oxidizing bacteria through ammonia toxicity (Third et al., 2002).

Nitrification was established at start up (Figure 4). The drainage level was set to half of the zeolite bed in July 2017. In September 2017 the loading threshold of 120 g/m<sup>3</sup>/d was crossed at a flow of 11 m<sup>3</sup>/d. Alkalinity demand dropped to zero. Dissolved inorganic nitrogen (DIN) removal reached 70% in November 2017.

The RUSA zeolite anammox system successfully demonstrated first nitrification and then DIN removal. There was no measurement of organic-N. It is notable that either there is near complete nitrification with modest total DIN removal, or there is substantial DIN removal with an NH<sub>3</sub>-N residual of about 30% of influent NH<sub>3</sub>-N. Apparent DIN loss at start-up is temporary as zeolite adsorption and absorption saturates with ammonium. Effluent DIN was greater than influent DIN from April through October as a function of this adsorption lag.

The RUSA system demonstrates the practicality of tidal flow contact beds for nitrification and DIN removal. Ramp-up to anammox took the best part of a year. A more aggressive approach to ramp-up with tight control of pH through alkalinity addition may have succeeded in reaching anammox activity sooner, but the cold water during the first four months of operation may also have been an insuperable obstacle to such a strategy. As the first such system in operation, there is a learning curve.



Figure 4: Zeolite-anammox ramp-up data.

The zeolite-anammox process is public domain technology. There is a great deal of design engineering information available in early 20<sup>th</sup> Century textbooks that can be downloaded from Google Books. For small treatment works needing nitrification or DIN removal with simple, open-source technology zeolite-anammox contact beds may be an attractive technical option. Although the 19<sup>th</sup> Century contact beds treated primary effluent, it should be noted that contact beds are sensitive to clogging from excessive BOD and TSS loading. Consequently, zeolite-anammox should be downstream of a clarifier or receive very light hydraulic loading rates.

## **3 PHOSPHORUS**

Phosphorus (P) removal can be challenging for small WWTP. Biological P-removal requires tight process controls in activated sludge systems that may be impractical due to variability in flows and loads, or entail high labour costs. Conventional flocculation and sedimentation with metal salts is less complicated. Both approaches require attention to solids management. Effluent total P (TP) less than 0.5 to 1.0 mg/L is impractical for small WWTPs without a secondary TP removal unit process.

Phosphorus removal is a common design goal for constructed surface flow (SF) wetlands (Kadlec and Wallace, 2009). Long-term removal of TP is a process of accretion in which biogeochemical cycles entomb a fraction of inflow P in organic residuals or minerals in wetland soils (Kadlec, 2005, Kadlec, 2006). Phosphate adsorption sites skew performance for the better in the early life of treatment wetlands in an early stage of the life-cycle. In the long term there must be process attention to mineral sequestration, either natural or engineered, to ensure sustained design treatment performance.

Geochemical augmentation uses non-flocculating doses of metal salts to sequester phosphate in insoluble minerals in SF treatment wetland sediments. Wetlands are not clarifiers. Rather, negatively charged biofilms in plant thatch and sediment surfaces serve as attachment sites for aluminium or ferric hydroxide complexes. In turn these complexes adsorb negatively charged phosphate and dissolved organic carbon (DOC). The chemistry is complex and poorly characterised, but there empirical results indicate that removal of 0.2 to 1.0 mg/L TP is feasible in storm water ponds (Osgood, 2012, Austin et al., 2017a) and treatment wetlands (Austin et al., 2018).

An ongoing study for Clayton County Water Authority, Georgia USA is testing the capacity of geochemical augmentation for TP polishing in a 108 ha SF treatment wetland receiving flows of 57 MLD. In the Phase 1 full-scale pilot reported here, aluminium chlorohydrate (ACH) was injected from September to December 2017 into the discharge from the W.B. Casey Water Reclamation Facility, which then flows into the wetland complex.

Influent and effluent TP samples were collected as grab samples taken four or five days per week. Doses of ACH were conservative, to avoid exceeding chronic toxicity limits for aluminium (USEPA, 2017). The maximum ACH dose was approximately 4.0 mg/L.

In 2016, median wetland inflow TP was 0.5 mg/L, during the pilot 0.57 mg/L (Figure 5). There was no statistically significant difference (p=0.12) between median inflow values. Median outflow TP in 2016 was 0.39 mg/L, but 0.19 mg/L during the pilot. The median outflow difference was significant to p<0.0001.



Percent of TP values less than or equal to indicated concentration

*Figure 5: Total phosphorus influent and effluent values during the pilot and the prior years (2016).* 

The minimum calculated chronic toxicity threshold, based on wetland pH, DOC, and hardness (USEPA, 2017), was 444  $\mu$ g/L. The maximum observed AI concentration in the wetland was 11  $\mu$ g/L.

Injection of ACH improved TP removal rates over the 2016 by a factor of about 5, from an area rate removal coefficient of 3 m/y to an average area rate removal of about 20 m/y at the maximum ACH dose. See Kadlec and Wallace (2009) for discussion of TP rate removal coefficients. Their median reported removal rate coefficient of a survey for TP removal in SF wetland is 10 m/y.

Results from the pilot study indicate that a more aggressive ACH dosing strategy could potentially sequester a greater fraction of TP (phosphate fraction) permanently in aluminium salts. The attainable TP outflow concentration via geochemical augmentation is unknown. Two storm water pond studies suggest a concentration in the 0.04 to 0.06 mg/L range. However, the phosphorus sequestration entails not only binding of inflow TP, but also whatever fraction in wetland sediments that may solubilize. The latter is a dynamic process dependent on temperature, the organic carbon pool in sediments, and other site-specific factors. Thus, the favourable results of this study encourage continued investigation in this technology, but should not be regarded as definitive of a performance standard.

Although flows in this study are not small, lessons for small flows apply directly. Large municipalities rarely have land available for TP removal. In fact, the study wetlands were never designed for TP removal, but rather are being investigated for their potential to remove TP. Small flows often are in areas which have land available for treatment wetlands. The low removal rates of passive SF wetlands for TP polishing render them impractical for most municipal applications. At an extremely conservative ACH dosing rate TP removal rates were greatly increased in this study. A similar pilot study done for a flow of 11 MLD using alum had an observed TP area removal rate coefficient of 193 m/y without causing flocculation (Austin et al., 2018). That observed rate likely represents a maximum because the calculated aluminium concentration in the wetland exceeded chronic toxicity criteria. Based on currently available data, geochemical augmentation for TP polishing (inflow TP < 1.0 mg/L) will reduce the wetland size by at least 50%, but potentially as much as 90%.

## 4 **REVERSE OSMOSIS BRINE**

With increasing pressure on the supply of potable water worldwide, the advent of increasingly cost-effective membrane (e.g. reverse osmosis [RO]) treatment has enabled new water sources for public, industrial and agricultural uses. Typically, ions and compounds rejected by the membranes in the fluid separation process are concentrated to levels greater than naturally occurring in the raw water. Management and disposal of the RO concentrate (ROC) requires special consideration given the elevated salinity, metals and toxicity. Untreated or improperly managed concentrate can result in adverse environmental effects, due to high salinity, nutrients (typically phosphorus and nitrogen), organic contaminants including pharmaceuticals and personal care products, and trace amounts of inorganic compounds (Joo and Tansel, 2015). Small volumes may be disposed of through dilution in sanitary sewers but large flows typically require oceanic or riverine discharge, deep well injection, pond evaporation, or mechanical crystallization, at significant cost of capital and operation.

Over the past fifteen years, pilot projects and literature reviews have given increasing credence to the concept that constructed wetlands may provide a more natural alternative to concentrate disposal. The possible beneficial reuse of concentrate for wetland treatment, creation and enhancement was first described conceptually by the WateReuse Foundation (2006). Brackish wetlands occurring naturally in estuaries or

inland saline lakes have been found to process and remove nutrients, metals, and inorganic ions. By constructing wetlands planted with native species tolerant of and adapted to brackish waters, these natural processes can be harnessed for passive improvement of water quality and creation of new wetland habitat.

Multiple pilot studies conducted in the United States and Australia (Kepke et al. 2009) have demonstrated significant reductions in nitrate-nitrogen, selenium, and metals in concentrate treated in constructed wetlands. Anaerobic wetlands constructed of peat or compostable organic material were found to be particularly effective in removal of oxidized contaminants. These findings supported a conceptual foundation of utilizing constructed wetlands to remove contaminants followed by dilution with other waters to create a water source for surface discharge, infiltration or wetland restoration. Recent publications have documented either continuations of early pilots (Chakraborti et al. 2015), parallel activities by other researchers (Liu, 2012; Perez-Gonzalez et al., 2012; Xu et al., 2017), or extensions of the concept to new or refined applications (Bays et al. 2013; Bays et al. 2017). Selected recent concentrate wetland treatment and related projects are provided an overview in the following subsections.

# 4.1 WETLAND TREATMENT OF CONCENTRATE FROM GROUNDWATER AND RECLAIMED WATER

For the City of Oxnard California, a pilot study conducted by CH2M compared the efficacy of six wetland technologies in treating groundwater-derived ROC from 2003-2005, and determined that anaerobic wetland treatment of ROC significantly removed nitrate, selenium and other metals, thereby creating a brackish water suitable for coastal wetland restoration (Kepke et al 2009).

A subsequent 2008 pilot study of a subsurface flow constructed wetland conducted by CH2M for the City of Oxnard receiving ROC produced from reclaimed wastewater achieved significant reductions in nitrate, nitrite and total nitrogen concentration and mass consistently with literature expectations (Chakraborti et al. 2015). A 0.4-ha wetland system constructed in 2012 at the City's Advanced Water Purification Facility is now poised to begin receiving ROC as a full-scale demonstration.

#### 4.2 ANAEROBIC WETLANDS FOR ENHANCED METAL REDUCTION IN RO CONCENTRATE

The US Bureau of Reclamation and the City of Goodyear Arizona constructed and operated a pilot system designed by CH2M consisting of seven large (18 m<sup>2</sup>) fibreglass up flow anaerobic wetlands receiving groundwater-derived ROC from the City's Bullard Water Campus (US Bureau of Reclamation 2012; Bays et al. 2014a). The pilot program, which has operated continuously since 2010, has provided information useful for planning full-scale systems.

Fundamentally, the pilot documented that that three native brackish marsh plants (saltgrass [*Distichlis spicata*], Olney's bulrush [*Schoenoplectus olneyi*], and cattail [*Typha latifolia*]) grew vigorously in the ROC, strongly suggesting that brackish marsh plants native to a region could be similarly trialled to determine feasibility. Water balance analysis indicated that evapotranspiration of ROC caused by the extremely arid location increased from 7.1 mm/d to 18.6 mm/d over three years as the plant cover matured. During this period, average total dissolved solids content increased from approximately 8 g/L to 11 g/L.

Organic substrates consisting of compostable organic materials (e.g., wood waste, manure) achieved the greatest reductions in ROC contaminants to less than state water quality standards, with nitrate-nitrogen decreasing from 55 mg/L to <2 mg/L, selenium

from 22  $\mu$ g/L to <2  $\mu$ g/L, arsenic from 24  $\mu$ g/L <10  $\mu$ g/L, and chromium from 42  $\mu$ g/L to 8  $\mu$ g/L.

Testing established that the wetland effluent could pass invertebrate fecundity test when diluted to 50-75% reclaimed water. The treated wetland product water, blended with treated reclaimed water, or other similarly dilute water supply, could then be used as a source of water to restore riparian habitat in the Salt River, which has a total dissolved solids content of approximately 3.5 g/L. A preliminary design of a 1-ha demonstration wetlands modelled after the pilot was completed in 2016 and funding is being sought to carry the project to completion.

# 4.3 INTEGRATED PASSIVE BIOLOGICAL TREATMENT OF CONCENTRATE USING BIOCHEMICAL REACTORS

In Centennial, Colorado, the Cottonwood Water & Sanitation District completed a pilot study in 2016 designed and supervised by CH2M of an integrated passive biological treatment system (BTS) combining an anaerobic biochemical reactor with aerobic polishing to treat concentrate from the Joint Water Purification Plan (JWPP) to meet multiple regulatory water quality criteria (Bays et al. 2017). Where feasible, anaerobic organic media reactors create conditions favourable to dissimilatory reduction, adsorption and volatilization of selenium at a lower cost compared to active biological treatment systems (Bays et al. 2014b).

CH2M constructed a BTS pilot at the JWPP comprised of two parallel trains, each receiving 85 mL/min of concentrate. Water in each train flowed passively through passive vertical downflow anaerobic biochemical reactors (BCRs) comprised of wood chips, sawdust, straw, horse manure, and limestone chips for primary removal of Se, followed by a sequence of organic and inorganic media cells designed to polish Se, sulphide, organic matter, iron and phosphorus. The BTS was operated and monitored under the direction of CH2M in three phases from January through December 2016. Daily measurements of dissolved oxygen, temperature, redox potential, pH, and specific conductivity confirmed that the BTS established and sustained anaerobic conditions in the initial units and aerobic conditions in the final polishing units. Samples were collected weekly and laboratory analyses performed using US EPA methods.

Inflow selenium averaged 68, 47 and 37  $\mu$ g/L and outflow selenium averaged 4, 3.4, and 3.3  $\mu$ g/L for Phases 1, 2 and 3, respectively. Substrate analysis showed selenium sequestered as predominantly adsorbed selenite, elemental and organic selenium. Total phosphorus, nitrogen, oxidized metals, divalent inorganic cations, micro-pollutants, and toxicity exhibited consistent and significant reductions through the BTS. The BTS pilot effectively met the 30-day average discharge criterion of 4.6  $\mu$ g selenium/L, as well as criteria for phosphorus and key water quality parameters, demonstrating the benefit of following an anaerobic process sequence with aerobic cells. Sizing criteria agreed closely with original models used to establish system size, and confirmed that the BTS could be constructed within available area.

A full-scale system has been designed through the 60% completion phase and is anticipated to begin construction in 2018.

### 4.4 FULL-SCALE WETLAND BLENDING AND TREATMENT OF CONCENTRATE

In addition, other projects have implemented important full-scale or pilot constructed wetland projects for treatment of groundwater-derived ROC. In Indian River County Florida, the 28-ha full-scale Spoonbill Marsh project constructed in 2009 as a constructed surface flow marsh that receives up to 5.7 MLD of ROC and up to 15 MLD of naturally saline water pumped from the adjacent Indian River Lagoon (TCPalm 2015). The blend of

concentrate and saline lagoon water in the wetland undergoes 66% reduction of total nitrogen and 80% reduction of total phosphorus before passive discharge through natural mangrove wetlands back to the Lagoon.

## **5** CONCLUSIONS

Recent developments in treatment wetland technologies add to the menu of technologies appropriate to small wastewater treatment plants in need of nutrient removal. A key feature of these technologies is increased treatment rates that translate to radical reductions in treatment footprints compared to conventional treatment wetlands. As practical matter, it is more probable for a small regional or district council to have 1 ha to available for a treatment wetland than 10 ha.

In looking across the suite of technologies featured in this paper, there are potential changes to process diagrams. One possibility for small wastewater treatment plants to meet both low N and P, or to nitrify if P removal is done upstream of the clarifier. In small activated sludge plants meeting an effluent P of 0.5 to 1.0 mg/L through biological P removal is possible, especially with injection of iron or aluminium salts into process water at concentrations low enough to not interfere with dewatering of solids. With compact, nitrifying wetlands using super-oxygenation, it is possible to ignore nitrification upstream of the clarifier and still meet the most stringent ammonia-N discharge standards. Polishing of phosphorus to very low concentrations is also possible in compact wetlands.

The zeolite-anammox process offers a purely passive means of nitrification that will grow into TN removal as anammox bacteria mature. Demonstration projects are necessary before this technology can be widely applied to small domestic wastewater flows. The choices in this regard are low-rate systems taking raw wastewater, such as the systems in France mentioned previously, or higher rate systems taking clarified effluent. The potential for clogging is a central design concern with any type of contact bed.

Finally, the technology profile for reverse osmosis systems, which may be necessary in small drinking water or reuse plants is modular and can be fit to almost any treatment flow. What to do with RO brine is a key sticking point for implementing RO systems. Salinity by itself may be an issue, but it is more common for excessive nitrate or toxic concentrations of metals to be the key issue. Biochemical reactors offer an effective, passive means of removing nitrate or toxic metals, leaving a clean saline wastewater treatment that is often simpler to manage. The studies cited here demonstrate that wetlands have the capacity and versatility to provide effective and economically viable ROC treatment which can improve the sustainability of RO-based water treatment or create a beneficial use, as brackish wetland creation or restoration.

#### ACKNOWLEDGEMENTS

The authors acknowledge the following clients: The Dow Chemical Company, Roseburg Urban Sanitary Authority, Clayton County Water Authority, the City of Oxnard, the City of Goodyear, the US Bureau of Reclamation and Indian River County for supporting innovative approaches to problem solving.

#### REFERENCES

AUSTIN, D., JOHNSON, E. & PARTINGTON, H. 2017a. Geochemical augmentation with aluminium salts for control of internal nutrient loading and algae blooms in reservoirs, lakes, and ponds. *North American Lake Management Society.* Denver, Colorado.

- AUSTIN, D., MADISON, M., CHAKRABORTI, R., MECHAM, J. & BAIRD, J. 2018. Improving phosphorus removal in a surface flow wetland and land application system by geochemical augmentation with alum. *Science of The Total Environment*, 643, 1091-1097.
- AUSTIN, D. & NIVALA, J. 2009. Energy requirements for nitrification and biological nitrogen removal in engineered wetlands. *Ecological Engineering*, 35, 184-192.
- AUSTIN, D., VAZQUEZ-BURNEY, R., DYKE, G. & KING, T. 2017b. Nitrification and total nitrogen removal in a side-stream oxygenated, surface flow wetland. *WETPOL.* Big Sky, Montana.
- AUSTIN, D. C. 2006. Influence of cation exchange capacity (CEC) in a tidal flow, flood and drain wastewater treatment wetland. *Ecological Engineering*, 28, 35-43.
- BARWISE, S. 1899. *The Purification of Sewage,* London, England, Crosby Lockwood and Son.
- BARWISE, S. 1901. *Bacterial Purification Of Sewage,* Derby, England, United Kingdom, Crosby, Lockwood & Son.
- BAYS, J.S., J. TUDINI, B. T. THOMAS, D. EVANS, AND T. HARRISON. 2013. Advances in the Use of Passive Wetland Systems for Selenium Treatment of Mine-Impacted Water. Proc. SME Annual Meeting, Feb. 24 - 27, 2013, Denver, CO.
- BAYS, J., POULSON, T., HWANG, M., RHOADES, R. 2014a. Goodyear Concentrate Management Wetlands Pilot Study: Summary and Application. American Water Works Association ACE 2014, Boston MA. June 14 2014.
- BAYS, J.S., R.C. THOMAS, D. EVANS. 2014b. Integrated Biochemical Reactor Wetland Systems for Passive Treatment of Selenium. Pp. 454-363 in Proc. 14th Intl. Conf. on Wetland Systems for Pollution Control, 12-16 October 2014, Shanghai, China. Conference organized by Tongji University and Chongqing University. Prof. Qi Zhou and Prof. Jun Zhai (Eds).
- CHAKRABORTI, R.K., J. BAYS, J. THIEN, NG, BALDERRAMA, L., KIRSCH, T. 2015. A Pilot Study of a Subsurface Flow Constructed Wetland Treating Membrane Concentrate Produced from Reclaimed Water. *Wat. Sci. Technol.* 72(2), 260–268.
- COLLISON, R. S. 2010. *Effects of porous media and plants in the performance of sub surface flow treatment wetlands.* Ph.D., University of California, Davis.
- COLLISON, R. S. & GRISMER, M. E. 2018. Upscaling the zeolite-anammox process: Treatment of secondary effluent. *Water*, 10, 236.
- DONG, Z. & SUN, T. 2007. A potential new process for improving nitrogen removal in constructed wetlands—Promoting coexistence of partial-nitrification and ANAMMOX. *Ecological Engineering*, 31, 69-78.
- DUNBAR, W. P. 1908. *Principles of Sewage Treatment,* London, Google Books. Original Charles Griffin & Company, Limited.
- ESSER, D. 2015. 25 years of treating raw sewage with vertical downflow treatment wetlands in France a personal history of lessons learned. *IWA Specialist Group on Wetland Systems for Water Pollution Control*, 16-26.
- GRISMER, M. E. & COLLISON, R. S. 2017. The Zeolite-Anammox Treatment Process for Nitrogen Removal from Wastewater—A Review. *Water*, 9, 901.
- JETTEN, M., CIRPUS, I., KARTAL, B., VAN NIFTRIK, L., VAN DE PAS-SCHOONEN, K., SLIEKERS, O., HAAIJER, S., VAN DER STAR, W., SCHMID, M., VAN DE VOSSENBERG, J., SCHMIDT, I., HARHANGI, H., VAN LOOSDRECHT, M., GIJS KUENEN, J., OP DEN CAMP, H. & STROUS, M. 2005. 1994-2004: 10 years of research on the anaerobic oxidation of ammonium. *Biochem. Soc. Trans.*, 33, 119-123.
- JOO, S. H., TANSEL B. 2015. Novel technologies for reverse osmosis concentrate treatment: A review. J. Env. Management. 150, 322-335.
- KADLEC, R. 2006. Free surface wetlands for phosphorus removal: The position of the Everglades Nutrient Removal Project. *Ecological Engineering*, 27, 361–379.
- KADLEC, R. & WALLACE, S. 2009. *Treatment Wetlands*, Boca Raton, Florida, CRC Press.

- KADLEC, R. H. 2005. Phosphorus Removal in Emergent Free Surface Wetlands. *Journal of Environmental Science and Health, Part A*, 40, 1293 1306.
- KEPKE, J., BAYS, J., LOZIER, J. 2009. Concentrate Treatment Using Wetlands. Water (J. Australian Water Association), 36(7): 57-63.
- KINNICUTT, L., WINSLOW, C. E. & PRATT, R. W. 1919. *Sewage Disposal,* New York, New York, Google Books, Original John Wiley and Sons.
- LIU, J. 2012. Sulfate, Nitrate and Selenium Reduction in Mining Wastewater Brine using Anaerobic Bacteria. M.S. Thesis, University of British Columbia, Canada.
- NING R.Y, TARQUIN A, TRZCINSKI M., PATWARDHAN G. 2006. Recovery optimization of RO concentrate from desert wells. Desalination, 201(1–3):315–322.
- NIVALA, J., WALLACE, S., HEADLEY, T., KASSA, K., BRIX, H., VAN AFFERDEN, M. & MÜLLER, R. 2013. Oxygen transfer and consumption in subsurface flow treatment wetlands. *Ecological Engineering*, 61, 544-554.
- OSGOOD, R. A. 2012. Controlling Wolffia using alum in a pond. *Lake and Reservoir Management*, 28, 27-30.
- PALMER, H., BEUTEL, M. & GEBREMARIAM, S. 2009. High Rates of Ammonia Removal in Experimental Oxygen-Activated Nitrification Wetland Mesocosms. *Journal of Environmental Engineering*, 135, 972–979.
- PEREZ-GONZALEZ, A., URTIAGA, M., IBANEZ, R., ORTIZ, I., 2012. State of the art and review on the treatment technologies of water reverse osmosis concentrates, Water Res., 46, 267-283.
- RONEN, T. & WALLACE, S. TAYA– Intensive Wetland Technology facilitates the treatment of high loads of organic pollutants and ammonia. 12th International Conference on Wetland Systems for Water Pollution Control, 4-9 October 2010 Venice, Italy. IWA.
- SPEECE, R. 2008. Superoxygenation applications in wastewater collection and treatment systems. *Water21*, , 25-30.
- SUN, G. & AUSTIN, D. 2007. Completely autotrophic nitrogen-removal over nitrite in labscale constructed wetlands: Evidence from a mass balance study. *Chemosphere*, 68, 1120-1128.
- TANNER, C., D'EUGENIO, J., MCBRIDE, G., SUKIAS, J. & THOMPSON, K. 1999. Effect of water level fluctuation on nitrogen removal from constructed wetland mesocosms. *Ecological Engineering*, 12, 67-92.
- TC PALM. 2015. https://www.tcpalm.com/media/cinematic/gallery/34563623/spoonbillmarsh-built-to-filter-brine-after-drinking-water-production/. (Accessed July 8 2018).
- THIRD, K., SLIEKERS, A., KUENEN, J. & JETTEN, M. 2002. The CANON System (Completely Autotrophic Nitrogen-removal Over Nitrite) under Ammonium Limitation: Interaction and Competition between Three Groups of Bacteria. *Systematic and Applied Microbiology*, 24, 588-596.
- US BUREAU OF RECLAMATION. 2012. Regulating Wetlands Pilot Study for Concentrate Management. Science and Technology Program Report No. 3699.
  - https://www.usbr.gov/research/projects/download\_product.cfm?id=520.
- USEPA 2017. Draft Aquatic Life Ambient Water Quality Criteria for Aluminium. *In:* WATER, O. O. (ed.). USEPA.
- WATEREUSE FOUNDATION. 2006. *Beneficial and Non-traditional Use of Membrane Concentrate*. Prepared by CH2M HILL and Mickley Associates, Inc., for the WateReuse Foundation. Project 02-006b-01. Alexandria, Virginia.
- XU, J., ZHAO, G., HUANG, X., GUO, H., LIU, W., 2017. Use of horizontal subsurface flow constructed wetlands to treat reverse osmosis concentrate of rolling wastewater, International Journal of Phytoremediation, 19:3, 262-269, DOI: 10.1080/15226514.2016.1217392.