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TECHNICAL ARTICLE

Hydraulic, Chemical, and Vegetation Characteristics of the Corridor Creek Wetland Filter: Implications for Biopolishing Efficiency

B. S. Sherman[1] · C. Drury[1] · G. B. Douglas[2] · G. N. Rees[3] · G. Miller[1] · S. Perryman[3] · J. Gallant[1] · M. G. Trefry[2] · M. Iles[4] · P. Davey[5]

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Abstract

Processing uranium ores into transportable oxide powders produces a stream of wastewaters high in metals, acids, and predominantly nitrogenous nutrients. Conventional water treatment can remove metal ions and buffer acids, but nutrient removal is problematic as it entails both oxidative and reductive steps. Engineered wetlands can achieve nutrient removal by a process of biopolishing, i.e. employing metabolic characteristics of the natural wetland microbiota to carry out the oxidative and reductive steps in series. In this study, we report on the hydraulic characteristics, dissolved oxygen (DO) dynamics, and vegetation of the Corridor Creek Wetland Filter (CCWF) at the Ranger Uranium Mine. Breakthrough curve analysis of dual-tracer test data showed the CCWF to be a highly dispersive wetland system with a dispersion coefficient $\geq \approx 10{,}000$ $m^2\ d^{-1}$. The times for 95% of the tracer to pass through the individual wetland cells were 2–3 times the corresponding cell residence times. DO concentration data suggests that anaerobic conditions are unlikely to occur in the water column. Macrophyte cover in the six cells ranged from 15 to 95% of the cell area and contained 47–96 kg of nitrogen: this compares to an anticipated nitrogen load of 60 kg d^{-1} from the water treatment plant. Our study demonstrated that the CCWF is a complex physical, hydraulic, and biogeochemical system. Operational conditions required consideration of varying, rather than constant, wetland flow conditions in the breakthrough curve analysis used to quantify the dispersivity of the wetland cells. Water column DO dynamics indicated limited scope for denitrification. The high variability of macrophyte and microbial biomass constrained access to parts of the CCWF, largely limiting measurements to the open water regions. Therefore, rather than attempt quantitative biogeochemical modelling of wetland performance, our study focussed on identifying and understanding key processes in the CCWF. Comparable studies of wetland filters may encounter similar challenges in process quantification.

Keywords Denitrification · Stratification · Tracer test · Macrophyte

Introduction

Management of site water inventory is a critical aspect of the environmental compliance strategy for many mine sites. Water accumulates at mine sites through rainfall events and surface water abstractions, and through mining operations that intercept the water table. Water is often used in the primary production process, and the large volumes of water produced at a mine site may exceed water quality guidelines for release to the environment. Therefore, much effort is directed toward establishing water management systems at each mine site. Site-specific factors need to be incorporated into the design of water management systems so that local characteristics are accounted for to ensure consistent regulatory compliance. For example, tropical mine sites may experience very large episodic precipitation events as well as high annual rainfalls, necessitating the provision of sufficient storage capacity and high peak-flow treatment capability. Environmental discharge guidelines must address the specific flora and fauna at risk, and no two mine sites have the same combination of hydrology, climate, biota, and social values. The local regolith geochemistry also strongly

✉ G. B. Douglas
grant.douglas@csiro.au

1 CSIRO Land and Water, Canberra, ACT, Australia

2 CSIRO Land and Water, Perth, WA, Australia

3 CSIRO Land and Water, Albury, NSW, Australia

4 Energy Resources of Australia Ltd, Darwin, NT, Australia

5 CDM Smith, Darwin, NT, Australia

influences the design of the requisite hydrometallurgical processing and water treatment systems.

The Ranger Uranium Mine is unique for its combination of sensitive economic, social, and environmental factors. The mine is situated within the bounds of the Kakadu World Heritage Area in the Northern Territory of Australia (Fig. 1) but is separate from the Kakadu National Park. Kakadu is also a region of cultural significance to the local indigenous peoples who still inhabit the area and regard many local landforms, plants, and animals as sacred. Ranger is in a tropical zone and prone to strong monsoonal rainfall and deluge events that drain to the Arafura Sea via the Magela Creek floodplain and the East Alligator River. The primary uranium orebodies largely resided in a brecciated chloritized schist formation, which required a mineral processing train involving dissolution of the crushed ores via sulfuric acid, then precipitation via the addition of ammonia, and finally drying in a furnace. At the time of the project, the effluent stream (process water) resulting from the mineral processing train displayed a complex hydrochemistry, with low pH, high total dissolved solids (TDS), and significant concentrations of metals, major ions, nutrients, and radionuclides (Douglas et al. 2010; Topp et al. 2003). A separate effluent stream of higher water quality (but also requiring treatment before environmental release) resulted from site run off and secondary operational activities. This inventory of disparate water qualities necessitated a specialized water treatment strategy. For the process water stream, lime addition was used to increase the pH and to precipitate most of the salts and metals. The supernatant from the liming stage was then passed through a reverse-osmosis (RO) plant to remove residual salts. The RO permeate was still high in nutrients (primarily ammonia/ammonium), so a system of engineered wetland filters was designed to remove and mineralize the nutrients via biogeochemical means known as biopolishing (Kadlec 1994; Kadlec and Knight 1996) before eventual release to the Magela Creek floodplain. The biopolishing wetland filters were constructed in the Corridor Creek catchment, a minor sub-catchment of the Magela Creek system.

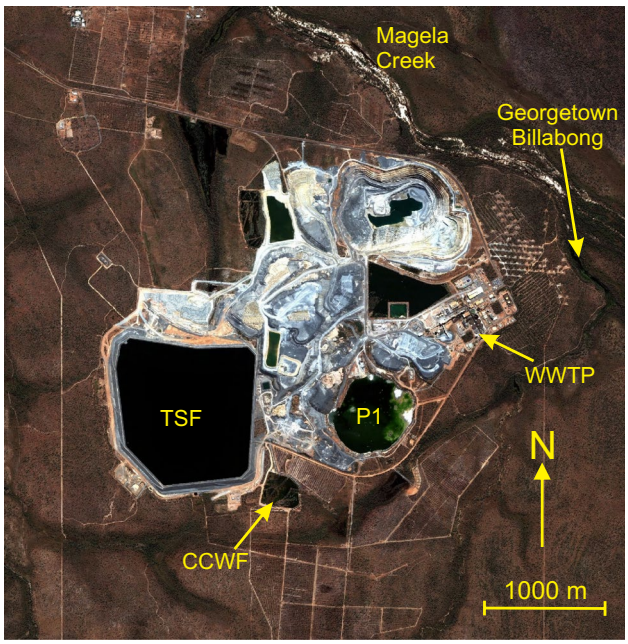

Fig. 1 Aerial view of Ranger Uranium Mine (as operating in July 2008), showing the tailings storage facility (TSF), Pit#1 (P1), the wastewater treatment plant (WWTP), Corridor Creek Wetland Filter (CCWF), Georgetown Billabong, and the Magela Creek drainage system

In this paper, we present the results of research undertaken to quantify the hydraulics and stratification dynamics as well as the chemistry and vegetation of the Corridor Creek Wetland Filter (CCWF) in order to assess its potential for nitrogen removal from the wastewater treatment plant effluent. The approach was multidisciplinary and included topographic and vegetation surveys, remote and on-line monitoring instrumentation, microbiological, geochemical, and hydrochemical sampling, tracer experiments, and hydrodynamic analysis. This analysis identifies several aspects of the CCWF that could be altered to increase the biopolishing performance of the wetland.

Methods

Site Description

The Ranger Uranium Mine is a remote mine site located within the Kakadu World Heritage Area, in the tropical north of Australia on a floodplain that is subject to intense seasonal monsoon rainfall events. The CCWF is an engineered wetland just over 5 ha in total area, south of the Ranger mine site's main operations area (Fig. 1). It was constructed in the drainage line of the Corridor Creek system, which drains eastwards towards Georgetown Billabong and ultimately to Magela Creek. The wetland is fed by the treated wastewater stream emitted by the Ranger treatment plant, which consists of three RO units, each with a design flow rate of 0.0172 $m^3\ s^{-1}$, and by waste rock runoff during the wet season. During most of the study, two units were operated at the design flow rate, but for operational reasons, this varied on a few occasions to one or all three units. Where this wastewater stream arises from treatment of high-quality pond water at the mine, there is a relatively low nutrient content, but as the wastewater treatment strategy expands to incorporate lower quality process water, the nutrient concentration may rise to $\approx 20\ NH_4\text{-N}\ L^{-1}$ (ammonia). The intended function of the CCWF was to attenuate the NH_3 concentration to below the environmental regulatory target, which at the time was 1.7 mg $NH_4\text{-N}\ L^{-1}$ for discharge to natural waterways.

Fig. 2 Satellite photograph of Corridor Creek Wetland (CCW). Red line and arrowheads denote the mean flow path between cells, blue rectangles denote the spillways between cells and yellow circles denote the sampling locations located at the downstream end of each cell where discrete water samples for NaBr analysis were collected and fluorometers were collocated to continuously measure rhodamine WT fluorescence. White circles with an "H" denote the location of the ISCO samplers and Hydrolab sondes used for longer term monitoring from May 2007 to May 2008. Also shown are 0.2 m interval contours from the bathymetric survey (refer to SI for details)

Table 1 Bathymetric characteristics of CCWF and the nominal detention time for design flow of 5 ML/d

	Volume (m^3)	Area (m^2)	Mean depth (m)	Detention time (d)
Cell 1	2408	3810	0.63	0.5
Cell 2	1930	4096	0.47	0.4
Cell 3	3211	6019	0.53	0.6
Cell 4	3692	5420	0.68	0.7
Cell 5	17,723	19,821	0.89	3.5
Cell 6	9513	11,734	0.81	1.9
Total	38,477	50,900	0.76	7.7

A bathymetric survey of the CCWF was conducted on 6–7 Sept. 2006 [see supporting information (SI) for method details]. The CCWF contains six cells (Fig. 2, Table 1) defined by bunded walls and connected in series by shallow spillways. Cells 1–4 are shallow, with relatively smaller volumes, shorter residence times, and densely vegetated in places. Cells 5–6 are larger and deeper, with longer residence times. A fundamental design objective of the CCWF was to facilitate nitrogen removal by conversion of ammonia to nitrogen gas through volatilisation and coupled nitrification–denitrification, and by direct biological assimilation of nitrogen into plant and algal biomass.

A simple metric is the nominal detention time, τ_{nom}, which can be expressed for any water body of volume V subject to a flow rate Q as $\tau_{nom} = V/Q$, yielding a nominal CCWF ($V = 38{,}477$ m^3) detention time of 13 d for a WWTP discharge rate of ≈ 3 ML d^{-1}, characteristic of continuous operation of two RO units.

Conceptual Ammonia Fate Model for CCWF

A constructed wetland can remove nitrogen from water passing through it by several processes: volatilisation, incorporation into plant (macrophyte) and bacterial biomass, and denitrification. The first process can be expected to diminish over time as available binding sites are filled. Volatilisation is increased by increases in both cell pH and temperature (Freney et al. 1981). Macrophyte growth is a sink for nitrogen in the wetland and the macrophyte biomass status of CCWF is an important indicator of the wetland's capacity to absorb and assimilate nutrients. Incorporation of nitrogen into biomass may saturate, in theory, as the system approaches an equilibrium condition in which nutrient assimilation into fresh biomass equals nutrient regeneration from the decay of old biomass. Harvesting of plant biomass can increase the assimilative capacity of the wetland via new growth and associated epiphytic bacterial colonisation on macrophyte leaf surfaces. The supply by macrophytes of substrate, organic carbon, and nutrients is an important modifier of the microbial ecology of the wetland. Denitrification offers a sink for nitrogen that does not saturate as the consumed nitrogen is subsequently released to the atmosphere. Provided there are adequate nutrients (especially labile carbon and phosphorus) to supply the microbial community, denitrification can be expected to operate in a near-continuous fashion. These processes will all remove nutrients as a function of contact surface area, residence time, and concentration as approximately:

$$F_i = -k_i \times A_{si} \times C_i \times \Delta t \quad (1)$$

where F is the load of nutrient removed over the residence time, C is the concentration (or relevant concentration change) of the nutrient, A_s is the contact area, k_i is a rate constant, Δt is the residence time, and the subscript i simply denotes the different nutrient processes.

The overall nutrient removal performance of the wetland is given by the sum of all nutrient removal loads, $\sum F_i$, and we wish to maximise this value. Assuming the inflow nutrient concentration is fixed, wetland performance is maximised by ensuring maximum contact area (a function of vegetation and morphometry) and residence time (a function of the hydraulic characteristics) and ensuring sufficient

resources are available to support microbial processes that influence the relevant rate constants, k_i, (a function of vegetation, microbial, and physical hydrodynamic and chemical characteristics).

The hydraulic characteristics of a wetland influence A_{si}, C_i, and Δt in Eq. (1). Using a simplified one-dimensional model, and ignoring local sinks and sources, nutrient transport through any cell, j (= 1.6), of the wetland is controlled by advection and diffusion. The change in concentration over space and time is given by:

$$\frac{\partial C_j}{\partial t} = D_j \frac{\partial^2 C_j}{\partial x^2} - \frac{Q}{A_{xj}} \frac{\partial C_j}{\partial x} \tag{2}$$

where D_j is the effective dispersion coefficient ($m^2\ s^{-1}$), A_{xj} is the cross-sectional area of the cell normal to the direction of flow, and Q is the flow rate through the cell (assumed to be approximately equal for all cells, i.e. evaporation and leakage were assumed to be negligible). Dispersion spreads the flow along the axial and transverse dimensions. Higher transverse dispersion increases mean residence time and increases the potential contact area, A_s, across which reactions take place. The existence of preferred flow paths with little transverse mixing (often called short-circuiting) reduces both D_j and A_s. Note that D_j is also a function of A_s, where A_s depends on the density (shoots m^{-2}) of rooted macrophytes and their diameter. Other obstructions to local flow, e.g. boulders, logs, etc. may also be lumped into the effective D_j value of each cell.

This simple model identifies key hydraulic parameters that are important in estimating biopolishing efficiency. Effective cell cross-sectional areas, A_{xj}, and dispersion coefficients, D_j, are required to model ammonia breakthrough curves, so that ammonia removal rate constants, k_i, can be quantified. Thus, in order to understand the chemical and biological functioning, it is necessary to understand the hydraulics of the wetland. Flow determines the transport of the contaminants to the reactive surfaces present in the biofilms located on the macrophytes, sediment surfaces, and sediment pore spaces (in the case of hyporheic flows).

The CCWF study was designed to elucidate and quantify the relative potential contributions of the different nutrient removal processes. To achieve this, we used a combination of hydraulic characterisation of the system using a dual-tracer method and groundwater sampling, vegetation surveys, and monitoring and measurement of water chemistry with special emphasis on pH, temperature, and dissolved oxygen (DO). Integration of these elements allowed a more holistic understanding of individual wetland cell and aggregate wetland function including: solute mixing efficiency, the rate and extent of nutrient assimilation into macrophyte and algal biomass (biological N sinks), and the potential for nitrification and denitrification to directly remove nitrogen. Together, these processes governed the likelihood that discharge from the wetland would comply with environmental release criteria. This type of detailed, integrative analysis allowed for retrospective recommendations for design improvements to improve wetland biopolishing performance.

Breakthrough Curve Analysis

Breakthrough curve analysis following Kadlec (1994) (see SI for details) was used to determine the mean residence time and the dispersivity of each wetland cell and of the whole wetland from the time series of tracer concentration, C, measured at the exits of each wetland cell, and discharge, Q, measured at the treatment plant and assumed to apply throughout the entire wetland. For any wetland cell, the tracer mass flux, M_0, is given by:

$$M_0 = \int_0^{t_f} QCdt \tag{3}$$

where the tracer initially enters a wetland cell at time = 0 and has fully passed through the cell at time = t_f. The effective tracer residence time, τ_a, of a wetland cell is:

$$T_a = \frac{\int_0^{t_f} tQCdt}{\int_0^{t_f} QCdt} \tag{4}$$

The dispersion coefficient, D, for a wetland context is discussed by Kadlec (1994). It is conveniently determined from tracer breakthrough curves using statistical moment analysis (see SI for details).

Tracer Test

Dual Tracer Test for Hydraulic Characterisation of CCWF

A dual-tracer test was conducted to characterise the fundamental hydraulic properties of the CCWF. Bromide (as NaBr) and rhodamine WT (RWT) were selected as the two tracers. Care must be taken with both tracers in natural systems to avoid undue ecological disturbance. Of the two, NaBr has a more conservative nature, as RWT is known to adsorb onto organic surfaces and to decay photolytically (Dierberg and DeBusk 2005; Wilson et al. 1986). Because Br is typically used in trace (low mg/L) concentrations and is invisible to the human eye, accurate measurement in the field is problematic, so fluid samples must be collected for later analysis. Given the analytical costs, there is a need to identify those samples that must be analysed to minimize costs. In comparison, RWT is easy to measure accurately using in situ fluorometers and is therefore the better tracer for providing high temporal resolution.

Selection of water samples for Br analysis based on continuous RWT fluorescence data allows accurate characterisation of the NaBr breakthrough curve while minimising the total number of NaBr samples analysed and the associated costs. The conservative nature of Br allows quantitative measurement of tracer loss through groundwater seepage, adsorption onto surfaces, etc., while the very high temporal resolution of the fluorescence data allows accurate breakthrough curve analysis.

RWT Measurements

RWT concentrations were measured using 2 Turner Cyclops-7 rhodamine fluorometers. The fluorometer data were logged using Datataker 505 and Datataker 85 dataloggers. Secondary temperature standards (Thermometrics CSP) were attached to each of the fluorometers to provide accurate (± 0.01 °C) measurements of in situ water temperatures. All fluorometers were calibrated against stock dye solutions. Fluorescence measurements during the tracer test were corrected for background fluorescence and thermal effects. The thermal sensitivity and temporal decay of RWT fluorescence were determined from the on-site data. All RWT fluorescence data presented in this report are adjusted to a standard temperature of 25 °C (see SI for details). In situ fluorescence data that were obviously contaminated by either the presence of bubbles within the fluorometer measurement volume or by sunlight (which produce large spikes in the fluorometer signal) were discarded prior to analysis.

The data loggers and battery were housed in protective cases (Pelican) with environmental seals to allow unattended operation in the field. The data loggers were programmed to sample the fluorometer output voltage and the temperature sensor every 2 s and record the average values of 15 samples every 30 s. The fluorometer systems were deployed in the exits to adjacent wetland cells (Fig. 2). Shortly before the tracer was expected to arrive at the next unmonitored downstream cell, the most upstream system was redeployed (leap frogging) into the exit of the next unmonitored cell.

Br Samples

Water samples for Br (and RWT) analysis were collected using ISCO automated samplers. No ISCO sampler was deployed at the exit to Cell 3 because of relatively difficult access. Each sampler pumped samples from the spillways between wetland cells at the same location as where the fluorometers were deployed. The frequency of sample collection varied between 1 and 4 h, typically, with a higher sampling frequency employed during periods when tracer concentration changes were most rapid and longer periods used to sample the tails of the concentration time series. The sampling period was increased to 8–12 h for Cells 5 and 6 towards the end of the experiment as fluorometer readings confirmed very slow changes in concentration following the passage of the concentration peak. Br analysis was performed by the Northern Territory Environmental Laboratory using inductively coupled plasma mass spectrometry (ICP-MS).

Tracer Stock Concentrations and Injection

To ensure a high signal to noise ratio, 5.24 kg of NaBr was dissolved into ≈ 50 L of permeate water on 7 May 08. The corresponding mass of Br was 4.07 kg. The fluorescent tracer was made by adding 2 L of RWT concentrate (20%) to permeate water to make up a total volume of ≈ 50 L, approximating a RWT total mass of 0.4 kg. Concentrations of both tracers were selected to comply with prevailing environmental regulations while providing the highest possible signal to noise level (see SI for details).

The density of the RWT-Br tracer stock concentration is affected by temperature; it is denser than water by an amount roughly equivalent to ≈ 0.7 °C difference (colder). It is desirable to minimise this density difference to ensure that the tracer mixes as completely as possible with the receiving water rather than forming a density current that moves through the wetland differently from the main water mass. Midday timing of the injection reduced the risk of incomplete mixing of the tracer in the wetland.

The tracer was injected into the permeate discharge pipeline beginning at 11:00 h on 8 May 08 and continued until the pump was turned off at 11:15 h with ≈ 12 L of stock solution remaining. The tracer first arrived at the wetland at 11:50 h and was virtually exhausted by 12:03 h. The discharge of permeate from the water treatment plant during the tracer study was maintained as close to 0.0343 $m^3\ s^{-1}$ as possible. Wetland water sample collection commenced on 8 May 2008 and ceased on 6 June 2008 in Cell 5 and 10 June 2008 in Cell 6 (note that groundwater sampling continued until February 2009).

Vegetation Survey

A baseline vegetation survey was performed during 19–22 Sept. 2006 to identify macrophyte and algal species, and their areal distribution in order to provide a reference for biomass trends throughout the operational life of the wetland. Percentage macrophyte cover was estimated using a quadrat-based harvesting method as was plant biomass since the cells either had well defined patches of macrophytes or near-total cover. Some cells contained large amounts of dead material and, where possible, the biomass of this material was included in the cell estimates. Small amounts of vegetation were removed from the wetland and their dry weight

measured. This allowed estimation of the approximate total macrophyte biomass in the CCWF.

Dissolved Oxygen Survey

Snapshot Profiles

Vertical profiles of water column temperature and DO concentration were taken at three locations along Cell 6 on the afternoon of 5 Sept. 06 using a Yeokal 612 sonde to assess the extent and strength of stratification within the water column during this time of year. Profile locations were chosen to ensure the deepest regions of Cell 6 were measured.

Diurnal Oxygen Dynamics

Diurnal oxygen dynamics were monitored using Hydrolab Minisonde 4 instruments in Cells 5 and 6 on 6 Sept. 2006 and 7 Sept. 2006, respectively. In each cell, one sonde was placed 30–40 cm below the water surface and the other ≈10 cm above the bottom. The sondes recorded DO, temperature, electrical conductivity, and pH, every 10 min for 24 h.

Continuous Monitoring

Water Quality

Continuous monitoring systems were deployed at the outlets of Cells 2, 4, 5, and 6 (Fig. 2). Each system consisted of an ISCO autosampler to collect water samples for subsequent chemical analysis and a Hydrolab Minisonde for high frequency, in situ measurement of temperature, DO, pH, turbidity, and conductivity. The sondes were deployed by attaching them to star pickets and orienting the sondes vertically in the water at a depth of 30–40 cm. Campbell CR10X data loggers were configured to regularly interrogate the water quality sondes and to control the ISCO autosamplers. The systems were configured to log water quality data every 10 min and to allow remote interrogation through the CDMA network.

Routine data collection commenced in May 2007 and concluded in May 2008. Apart from consistent poor performance of Sonde 2 (Cell 5), the performance of the overall system was good through October 2007, but subsequently became more variable due to problems experienced with communication between the data loggers and the sondes, which could only be addressed through on-site inspection.

Treatment Plant Discharge

Treatment plant discharge, monitored by the plant operators, was recorded every five minutes from 0700 on 5 Aug 2008 to 1000 on 15 June 2008. For all practical purposes, the WTP discharge ceased on 13 June 2008.

Results

Tracer Test

Treatment plant discharge during the study is shown in Fig. 3. During the first 2 weeks of the tracer test, by which time nearly all the tracers had passed through Cell 4 (see Fig. 4), two RO units were operating; the discharge averaged 0.033 $m^3\ s^{-1}$. Notably, the WTP discharge was reduced by roughly 50% from 1500 on 10-5-08 to 0900 h on 11-5-08 due to the loss of a RO unit, and subsequently increased by operation of all three RO units from 1300 on 12-5-08 to 1300 h on 13-5-08, at which point the cumulative mean WTP discharge (dashed line in Fig. 3) had recovered to the longer-term average.

The reduction in discharge early in the experiment had the potential to affect the breakthrough curve analysis. Because water levels were not monitored in each of the wetland cells, the variable discharge introduced some uncertainty into the tracer calculations due to ambiguity regarding the exact propagation of the flow perturbation through the wetland. A simple model (see SI) of the propagation of the flow perturbation was used to adjust the time-dependent discharge through each of the cells. The model predicted a time lag of ≈6 h for a perturbation to reach the exit of Cell 4. No data were available to validate the accuracy of this simple model, but the values used were consistent with observations of approximate flowing depths over the spillways separating the wetland cells. Incorporation of the lagged discharge data had an inconsequential effect on flux calculations for Cells 2 and 3, where flow perturbations were negatively correlated with

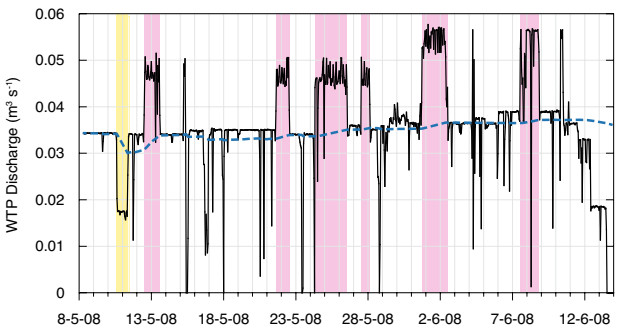

Fig. 3 Permeate mean hourly discharge from WWTP during the tracer study. Throughout most of the study, two RO units were operational. The yellow shading denotes a period when only one RO unit was operating. Purple shading denotes operation of 3 RO units. Heavy dashed line denotes the cumulative mean discharge entering the wetland commencing 8-5-08

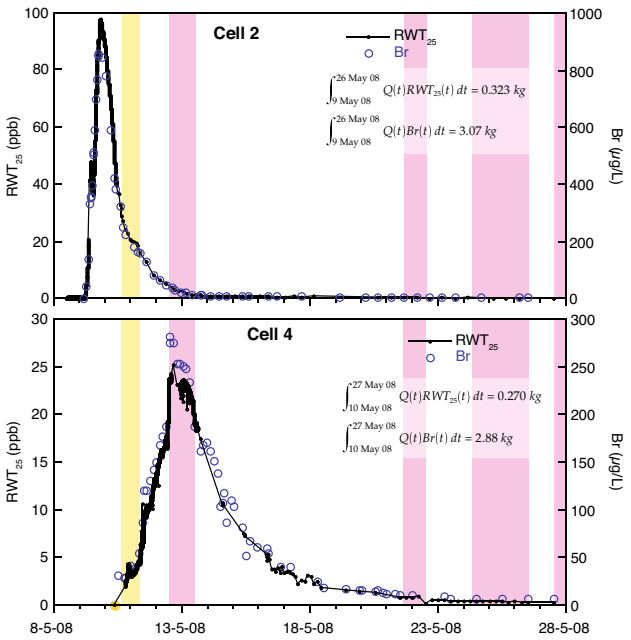

Fig. 4 Tracer test breakthrough curves measured at the exits to Cells 2 and 4 of CCW. The yellow band denotes a period when only one WTP RO unit discharged into Cell 1 and purple bands denote when 3 RO units were discharging into Cell 1

concentration but increased the mass flux by 8% for Cell 4 where the perturbations were positively correlated with concentration (i.e. periods of higher discharge were shifted to coincide with higher measured tracer concentrations).

Breakthrough curves measured at the exits of Cells 2 and 4 are shown in Fig. 4 along with the calculations of the tracer mass fluxes (data for all cells are in the SI). Nearly 15% of each of the tracers was lost from the wetland between these two locations. It was not possible to apportion the loss between Cells 3 and 4. Note, however, that the results from Cell 3 gave a tracer mass flux of 0.28 kg of RWT, which would suggest most of the leakage occurred in Cell 3. Tracer mass was conserved from the exit of Cell 4 to the exit of Cell 6.

Residence Times

Residence time distributions were quantified for all cells individually and tracer mass balances were calculated. The results of the breakthrough curve analysis are reproduced in Table 2. Tracer observations and analyses show that the 95% of the input tracer pulse had exited CCWF within 30 days of the initial injection. The observed mean residence time was 11–15 days for the whole wetland, compared with a nominal mean residence time of 14 days (based on volume divided by mean flow rate).

All cells of the wetland were extremely dispersive (dispersion coefficient, $D, > 9000\ m^2\ d^{-1}$) situating CCWF towards the more dispersive end of the range of free water surface wetlands described by Kadlec (1994). This means that there was significant lateral mixing in the wetland, including Cells 1, 2, and 3, which were intended to be aerobic and possess dense stands of macrophytes that would be expected to provide a large surface area to support N removal during the first 5 days as the water passed through these cells. The concentration peak took roughly 3 days to pass through Cells 5 and 6, whereas the mean residence time through the two cells was a fortnight.

Figure 5 summarises the tracer breakthrough and residence time data, showing generally increasing residence times for successive CCWF cells, with Cells 5 and 6 exhibiting largest residence times overall. This is consistent with

Table 2 Tracer results for CCWF

Cell	Start time	End time	Peak time	RWT (kg)	Br (kg)	Travel time (h)	Tracer residence time (d)	Dispersion coefficient D (m^2 d^{-1})	95% time (d)
Inject	8 May11:51	8 May 12:03:34							
1	8 May 20:00	13 May 13:00	8 May 21:54	0.34	3.4		0.6	10,673	1.9
2	9 May 04:00	26 May 12:40	9 May 19:50	0.32	3.1	22	1.6	n.d	5.7
3	9 May 15:13	27 May 12:45	11 May 02:20	0.28	n.d	30	2.8	n.d	8.0
4	10 May 12:00	27 May 12:30	12 May 13:00	0.27	2.9	35	3.8	32,910	9.4
5	12 May 22:00	5 June 17:00	17 May 09:00*	0.20	2.7	116	8.8	16,524	20.0
6	14 May 22:00	6 June 07:28	24 May 00:00*	0.14	2.4	159	11.4	9267	21.0
5 ex	12 May 20:00	14 June 18:40		**0.27**	**3.0**		**10.9**	30,461	22.5
6 ex	14 May 00:00	15 June 02:10		**0.27**	**2.8**		**15.2**	17,811	28.5

Start and End times correspond to the period of overlapping data records for both tracers except for Cell 3 where only RWT sample times are used due to incomplete Br data sampling record. (ex) = extrapolated value, * = estimated value, n.d. = not determined. Bold figures for Cells 5 and 6 denote results of calculations after adjusting RWT fluorescence for decay. Travel Time is the time for the peak concentration to traverse the cell. 95% Time is the time when 95% of tracer mass had passed out of the cell

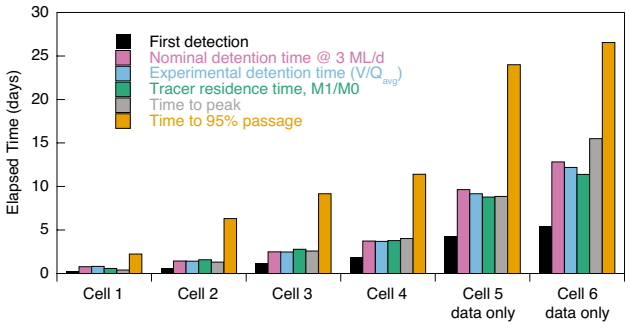

Fig. 5 Results of the tracer test showing residence times as tracer fluids pass through each wetland cell. All data reflect the cumulative performance of the wetland from the WWTP discharge to the end of the cell shown

the design goal of ensuring a long and slow denitrifying phase in the (intended) carbon-rich waters of Cells 5 and 6.

Vegetation Survey

The dominant two *Eleocharis* species present in the wetland cells were *Eleocharis dulcis* and *E. sphacelata*. In addition, a third species of *Eleocharis* (tentatively identified as *E. gracilis*) as well as a *Juncus* species (*Juncus usitatus*) were observed. The latter two species were in very low numbers and occurred on the fringes of the wetland cells so likely only make a very small contribution to the ecological status of the wetland cells. A common floating water lily, *Nymphaea violacea*, was also prevalent in the wetland.

Macrophyte Cover

Vegetation cover and macrophyte density were highly variable amongst the cells and ranged from an insignificant contribution in Cell 6, to nearly complete cover in Cell 1 (Table 3). Cell 1 had the greatest density of living and total material, with most of the dead stems having already fallen into the water column. Cell 2 contained similar levels of standing living and standing dead material (see Fig. 6), but large masses of algae covering the submerged dead stems prevented their measurement.

The macrophyte dry mass measurements were scaled by the areal coverage, yielding an estimated total dry biomass of 3000 kg for the entire wetland. If one multiplies this by the mean nitrogen content reported across several surveys (avg 15.6 mg-N (g dry wt)$^{-1}$, max 31.7 mg-N (g dry wt)$^{-1}$) the total amount of nitrogen bound in macrophyte biomass is in the range 47–96 kg-N. This compares with a design nitrogen load from the water treatment plant of roughly 60 kg-N d^{-1} (3 ML d^{-1} at 15 mg-NH_4^+ L^{-1}). Clearly, assimilation into macrophyte biomass represents only a relatively small sink for the anticipated nitrogen load and microbial processes (assimilation and denitrification) must play a major role in nitrogen removal for the wetland to achieve its designed performance.

Algae

Extensive algal mats were present throughout many of the cells, either attached to bottom sediments or to macrophytes as epiphytic biomass (see Fig. 6). Many types of algae were present within the benthic mats; however, the algal populations were dominated by desmids. Desmids are members of the *Chlorophyta* (green algae) and are common in freshwater systems, but seldom occur to the extent observed in CCWF. The very high density is consistent with elevated nutrient levels in the wetland waters. Qualitative observation of vegetation cover during the tracer test in 2008 suggested a substantial increase in in both macrophyte and algal cover and density.

Dissolved Oxygen Survey

Snapshot Profiles

Weak stable temperature stratification was observed (data not shown), which allowed a DO gradient to become

Table 3 Macrophyte survey (Sept 2006) results

Cell	Percentage areal cover	Areal coverage (m^2)	Dry mass (g m^{-2})			
			Live stems	Standing dead material	Fallen dead stems	Total
1	95	3620	542 (268)	0	42 (25)	584
2	15	610	94 (52)	71 (69)	n.d	n.d
3	30	1810	71 (51)	94 (43)	123 (63)[a]	288
4	15	810	79 (25)	16 (27)	100 (44)	195
5	20	3960	31 (20)	0	0	31
6	Insignificant	Insignificant	Insignificant	Insignificant	Insignificant	Insignificant

n.d. not determined

[a]Includes some algal biomass. Brackets indicate standard deviations

Fig. 6 Dense macrophytes beds in Cell 2 (left) and submerged dead material from Cell 3 including algal mass (right)

established. The DO concentration was supersaturated (125%) near the bottom at two of the three sites and decreased to just over-saturated near the surface. Conspicuous algal mats were likely responsible for the oxygen production at the bottom at these sites. No algal mat was present at the third site and the DO concentration was appreciably lower there. Nevertheless, the water column was saturated to supersaturated everywhere at all three sites with a total temperature change of about 1 °C. These profiles were taken at the time of day when diurnal temperature stratification would be expected to be the strongest. Therefore, it is extremely likely that these cells mix completely every day due to natural convection. Because the water column is no deeper than 2.2 m in Cells 5 or 6, persistent (longer than 1 day) stratification is unlikely at any time of year.

Diurnal Oxygen Dynamics

The sondes recorded strong diurnal temperature variations with maximum temperature differences of 0.7 (Cell 5) and 1.5 °C (Cell 6) at ≈4 pm (Fig. 7). There were also vertical gradients in DO concentration, pH, and electrical conductivity, although the magnitudes of the gradients varied in time, and for some ranges of the diurnal cycle, the magnitudes were zero. In Cell 5, which has a flatter bottom than Cell 6, the water column appeared to be well mixed for two thirds of the diurnal cycle. Cell 6 displayed more persistent stratification in the water column with evidence of lateral advection of cooler water at depth, probably driven by differential cooling in shallower parts of the cell.

Maximum thermal stratification occurred at 1600 h. Notice that DO concentration at the bottom was greater than at the surface during mid-afternoon and never drops below 70% saturation. Convergence of top and bottom tracers denotes complete mixing to the depth of the bottom sensor, e.g. the water column in Cell 6 (panel a) mixes just before 0400 h due to penetrative convection.

In Cell 6, respiratory demand lowered DO concentrations to only 70% of saturation. There seems little chance of anoxic conditions developing at the sediment–water interface, although the presence of black material below the sediment–water interface suggests anoxic conditions several millimetres below the interface. In this cell, the pH was well correlated with the DO concentration.

Despite deeper cell bottom sediments displaying dark colour indicative of reducing conditions, the observed diurnal mixing and high oxygen production at the bottom of the water column make it unlikely that anoxic conditions occur at the sediment–water interface in Cells 5 and 6.

Continuous Monitoring

Near-surface DO concentrations in Cells 2, 4, 5, and 6 during 2007–2008 were consistent with the DO survey results from 2006.

Discussion

The results indicate that the CCWF operates hydraulically largely as intended. That is, volumes, mean depths, and mean residence times are low in the shallow Cells 1–3 and are much longer in the deeper Cells 4–6 (see Tables 1 and 2). There is some evidence of tracer mass loss (≈15%) in the vicinity of Cell 3, but, apart from that, CCWF retained most of the tracer mass. Thus, leakage from CCWF was regarded as being acceptably low.

Assessing the biopolishing performance of CCWF is less straightforward. Although it would be simple to compare the

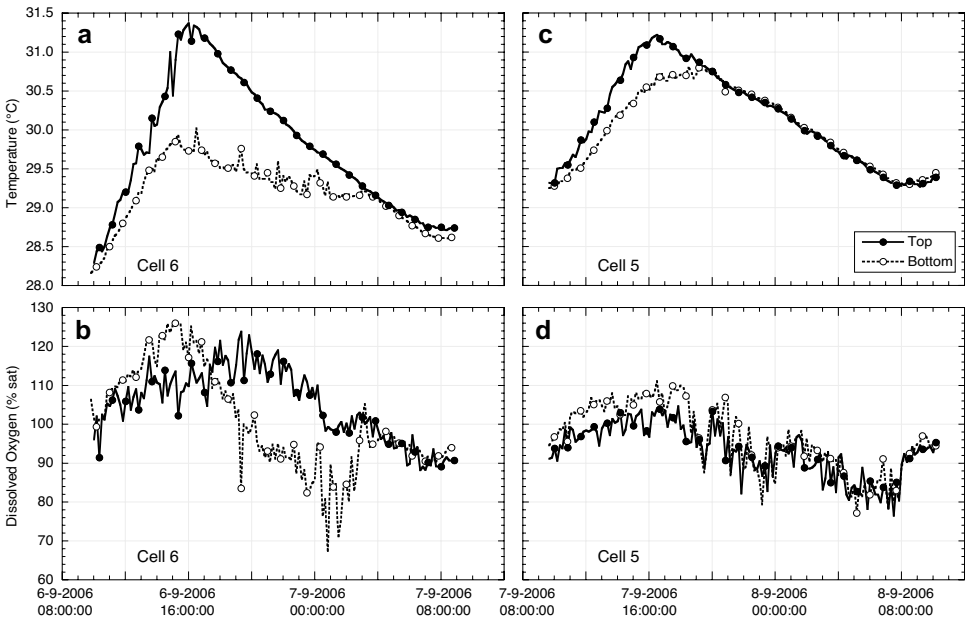

Fig. 7 Diurnal temperature and oxygen dynamics in CCW: **a**, **b** Cell 6 during 6–7 Sept 2006; **c**, **d** Cell 5 during 7–8 September 2006. Solid circles denote upper measurement at 30–40 cm below water surface. Hollow circles denote measurements approximately 10 cm above the bottom at a depth of roughly 1.6–1.7 m

influent ammonia concentration (at the WWTP discharge pipe entering Cell 1) with the effluent concentration (at Cell 6 outflow), such comparisons do not shed light on the mechanisms and rates of the various potential nitrification/denitrification pathways involved. The likely ammonium removal pathways are:

- direct assimilation into bacterial, macrophyte, and algal biomass
- transformation to nitrate through nitrification, which requires exposure to oxic conditions
- conversion to ammonia at elevated pH and loss to the atmosphere through ammonia volatilisation

Further nitrogen removal can occur through:

- direct assimilation into bacterial, macrophyte, and algal biomass
- loss to the atmosphere following transformation to N_2 gas through denitrification, which requires exposure to anaerobic conditions.

Literature reports of total nutrient removal efficiency in wetlands are widely variable. Fisher and Acreman (2004) provide condensed summaries of nitrogen and phosphorus removal in 57 wetlands around the world, including wetlands from temperate and tropical zones in northern and southern hemispheres. Whilst ≈80% of the wetlands surveyed exhibited net nutrient removal, there were several cases where the outlet concentration of nitrogen and/or phosphorus species was equal to the inlet concentration or even higher (net production). Averaged over all the nitrogen-retaining wetlands, the mean nitrogen species removal efficiency was ≈70% with a standard deviation of 27%. Given the water quality objective for CCWF at the time was 2 mg NH_4^+ L^{-1} (< 2 mg N L^{-1}), an input concentration of ≈10–12 mg N L^{-1} to CCWF operating at the mean nitrogen removal efficiency would leave ≈3.0–3.6 mg N L^{-1} in the outlet stream. The global mean reported by Fisher and Acreman (2004) is likely biased to lower values by the inclusion of temperate wetlands where seasonal temperature variations would give rise to wintertime falls in removal efficiency. Confining attention to tropical Australian wetland performance provides a more relevant picture of wetland performance.

In a summary of Australian wetlands, Greenway (2005) reports values that would indicate significant decreases in nitrogen concentrations may be achievable across the range of operational parameters of CCWF, and that the reductions in concentration may potentially be sufficient to achieve the water quality objective for Ranger. It is noteworthy that the lowest ammonia removal performance occurred with the lowest retention time, as might be expected, given the slow metabolic rates of nitrifying bacteria. We note that the estimated residence time for CCWF is ≈8 days, based on an assumption of perfect mixing within each cell, a flow rate of 5 ML d^{-1}, and the total wetland volume reported in Table 1. If short-circuiting occurs, the effective residence time in CCWF may be < 8 days.

In general, the size of the direct assimilation sink may saturate and approach a quasi-steady state because it is ultimately limited by the available substrate (surface area) to support bacterial and epiphytic/benthic algae, and there is a maximum density of rooted macrophytes than can be supported. Regular harvesting of macrophyte and algal

biomass could increase the effective amount of nitrogen assimilation. During the 2006 surveys at CCWF, 20% of the wetland was covered by *Eleocharis* sp. and the estimated total nitrogen content of this biomass was in the range of 50–100 kg-N. The design discharge ammonium load to the wetland is ≈60 kg-N d^{-1}, so even if the entire wetland was 100% vegetated, the assimilated nitrogen is only likely represents < 9 days of ammonium load.

Some loss of nitrogen through conversion of NH_4^+ to NH_3 followed by volatilisation may be expected given the observed range in pH in some of the wetland cells. The year-long sonde deployment data showed that it is relatively common for primary production by the aquatic vegetation and algal biomass to increase pH diurnally to 9–9.5. At this level, some conversion of NH_4^+ to NH_3 might be expected, which allows the possibility of volatilisation of some of the NH_4^+ load. Estimation of the net volatilisation rate has not been attempted as it depends on a variety of parameters, including water chemistry, temperature, wind stress, surface area, and surface tension.

The implication of the limited scope for direct assimilation and incorporation into biomass is that effective nitrogen removal must rely on bacterial processes. Nitrification (plus a contribution from volatilisation of ammonia) will have to suffice to transform the ammonium load into nitrate such that the wetland can meet its design target of reducing ammonium in the discharge from Cell 6 to < 2 mg-NH_4^+ L^{-1}. This will require ensuring a suitable supply of carbon, oxygen, and physical habitat to support an adequate population of nitrifying bacteria. All the DO data collected so far suggest that maintaining oxic conditions will not be a problem. Seldom does DO fall below 50% of saturation and the water column can be expected to mix diurnally due to penetrative convection. It seems likely that the extensive vegetation in Cells 1–4 should provide the necessary substrate to support the nitrification process.

To facilitate compliance with water quality criteria for direct discharge from CCWF to Magela Ck, it would be beneficial for the CCWF to completely remove nitrogen (rather than just reducing the concentration of NH_4^+). This would require microbially mediated denitrification, i.e. coupled nitrification–denitrification of the ammonium load. As with facilitating nitrification, adequate carbon, nutrients, and physical habitat must be provided for the denitrifying bacteria. In this case, however, anaerobic conditions are required by the denitrifying bacteria. The large macrophyte and algal biomass in Cells 1–3 can potentially provide an ample supply of carbon. The sonde data suggest that DO concentration seldom falls below 50% of saturation and that supersaturated conditions can be produced near the sediment interface where there are algal mats. Decomposition of algal cell material from the mats will provide carbon for denitrification; however, the oxygenation generated by the algae will be a major constraint on the rate of denitrification. The dark appearance of the sediment in Cells 5 and 6 suggest that anaerobic conditions exist below the sediment–water interface, but for denitrification to occur, nitrate will have to diffuse through the surficial sediments to be accessible by denitrifying bacteria. Note that sediment oxygen dynamics was not included in this study, and we do not know how the anoxic interface might migrate through the sediment on a diurnal basis in response to local primary production and respiration.

Should any subsequent investigation find undesirably high concentrations of dissolved inorganic nitrogen in Cell 6, it would be worthwhile to consider modifications to Cells 5 and 6 to facilitate the availability of anaerobic environments. This could take the form of introducing substrate to entrap flocs and/or support the growth of biofilms and increase the surface area that the water is in contact with, for example by adding cobble to the beds. A completely subsurface flow regime that would decrease photosynthetic oxygen production and increase the surface area: volume ratio would be desirable from a denitrification perspective. Alternatively, provision of alternative disposal options, such as diversion to additional on-site storage facilities for further treatment, may be required.

The experiment's initial design included monitoring of nitrogen concentrations in each wetland cell to provide a direct top-down measurement of the overall performance of the wetland. Operational conditions at the water treatment plant at the time of the field experiment prevented the discharge of a highly nitrogen-enriched permeate, which led to the abandonment of the nitrogen measurement component of the project. Consequently, we were limited to a more qualitative assessment of overall performance of CCWF based on our quantification of the hydraulic and vegetation properties known to affect wetland performance from a bottom-up perspective through application of Eq. 1.

Considering the impact of measurement uncertainties on our assessment, the most important sources of uncertainty in the application of Eq. 1 are: errors in the effective detention time, Δt, microbial rates of nitrification and denitrification, and the rate of ammonia volatilization. The detention time is pivotal in the calculation of nitrogen fluxes through microbial and volatilisation pathways.

Tracer test results yielded effective detention times within ± 10% of the nominal detention times for all cells except for Cell 1. Notably, the bathymetric survey data for Cell 1 was spatially constrained by the existing dense stand of Eleocharis that prevented access to more than 50% of the area of the cell. The volume occupied by the Eleocharis would have reduced the water volume of Cell 1, thereby reducing the residence time for a given permeate discharge rate. This was the only cell for which the tracer residence time was substantially less than the nominal residence time

and is consistent with the vegetation-caused reduction of the cell volume calculated from the bathymetric survey data.

Errors in either the measurement of macrophyte and algal biomass or DO measurement are of lesser importance. Assuming a DO measurement uncertainty of ± 10% would not affect our conclusion that anaerobic conditions are unlikely to occur in the water column.

Because only a single inventory of macrophyte and algal biomass was undertaken, it is not possible to express biomass assimilation of nitrogen as a rate. Given that the measured biomass nitrogen was only 50% more than the designed daily nitrogen loading, we suggest that biomass accumulation is unlikely to provide a substantial contribution to the overall wetland performance based on the assumption that the measured biomass would have taken months to years to accumulate. A more accurate bottom-up estimate of wetland efficiency would require more emphasis on in situ measurements of volatilisation and coupled nitrification–denitrification rates.

Conclusions

The study described here quantified the residence time distributions of the six cells in the CCWF and the overall residence time distribution of the wetland itself. The use of a dual tracer technique allowed efficient sampling and analysis to be performed, reducing costs considerably whilst also reducing uncertainty in the estimation of tracer breakthrough curves and fluid residence times. Concentration attenuation processes for the RWT tracer were studied and quantified.

For the flow conditions during the tracer study, the mean residence time for the wetland was 19–20 days. Cells 1–3 had dense stands of macrophytes and filamentous algae, which would be expected to provide a large surface area to support N removal during the first five days as water passed through those cells. Passage through Cells 5 and 6 took place through mainly open water over ≈ 14 days and sediment contact is expected to be the dominant mechanism for nitrogen transformation.

Several observations together support the view that denitrification is unlikely to be occurring to a great extent within the last two cells of the wetlands. Water quality profiles show that the bottom waters of Cells 5 and 6 were highly oxygenated; the oxygen levels at depth were consistent with the observed proliferation of benthic algal communities. Although only cursory examinations of the sediment were carried out, the observations suggest that an oxic cap overlays highly reduced sediments. Most microbial activity will occur within the uppermost (oxic) layers of the sediment, supporting the notion that under the physico-chemical conditions observed in this study, denitrification is likely limited. Experimental examination of the water column and sediments would be required to confirm actual and potential levels of denitrification in Cells 5 and 6.

Options available to achieve enhanced nutrient removal are likely to follow two potential courses. One option is to develop the systems so that vegetation becomes the major mechanism for nitrogen removal, while the other is to modify the current structure of Cells 5 and 6 to promote microbial-based nitrogen removal, i.e. a conventional nitrification/denitrification design. Each option has certain advantages and disadvantages. For the first, high vegetation densities would mean that considerable recycling of carbon and nutrients would occur within the wetland cells as plants go through their natural life cycles. Any suggestion of using vegetation as a long-term mechanism for nitrogen removal would require additional management, including optimising nitrogen uptake and periodic removal of plant and associated epiphytic biomass to minimize nitrogen recycling. For ease of harvesting, floating macrophytes and epiphytic biomass attached to woven, permeable substrates such as shade cloth that can be easily retrieved may be preferable to emergent macrophytes for compartmentalizing nitrogen. Further study of relative nitrogen uptake rates of different macrophytes would inform this.

For the second option, increasing the potential for denitrification in Cells 5 and 6 would require that photosynthetic activity be reduced at depth. Given the low turbidity of the treatment water, several metres of additional depth would be required before light is sufficiently attenuated to limit growth of benthic algae. Increasing the amount of sediment organic matter will enhance oxygen consumption at depth, but reliable management of DO may be difficult. Increasing the surface area available for anoxic biofilm development may be a further option and could possibly be achieved by adding rocks or cobbles to the cells. Rapidly decaying carbon sources (e.g. harvested reeds and plants) could also be added to increase DO consumption. Alternatively, an artificial substrate such as shade cloth or similar material could be emplaced vertically within one or both cells quickly and at low cost. This would increase shading, provide an additional biofilm substrate, and increase the cell circulatory path length and tortuosity and hence effective residence time and nitrogen removal efficiency, prior to discharge. The added potential for nitrification and denitrification will, however, be offset by changes to the flow patterns and may require additional management considerations.

There is still much work to be done to achieve a quantitative understanding of the operational biogeochemical dynamics in the CCWF under seasonal and interannual cycles. Comprehensive understanding may not be fully achievable with current technology and available investment and workforce levels. Despite the many operational distractions within an active mine site, the prime consideration is to assess and manage the time-dependent balance between

nitrification and denitrification capacity in the evolving wetland system. The present study has highlighted multidisciplinary techniques to evaluate the key physical and biological processes that contribute to overall wetland biopolishing performance. These lessons are readily transferrable to other field settings and provide a documented basis for improved experimental design and efficient data collection methods to support the future construction and operation of biopolishing wetland filters.

In summary, the assessment of key processes involved in the operation of a wetland filter requires a multidisciplinary approach. Here we have reported on a field campaign to measure simultaneous hydrodynamic, biological, and geochemical variables to understand the operating parameters of the CCWF as it was originally constructed. The field campaign was onerous and was only achieved through close cooperation between site managers and researchers. Important outcomes of the data analysis included: (i) the need to improve the anoxic water-biofilm contact area in Cells 5 and 6, where maximum denitrification of the water flow was intended to occur, and (ii) the need to reduce photosynthetic activity at depth in these latter cells to minimise the formation of benthic algal mats. This is useful feedback for water managers who may be contemplating the use of wetland filters in their waste management strategies. Simply designing and constructing a wetland to support desired wastewater flow rates and residence times is unlikely to be sufficient because these wetlands become biological systems with time-dependent feedbacks to hydrodynamics and geochemistry. Successfully achieving reliable and consistent performance inevitably requires multidisciplinary skills in monitoring and ecosystem optimisation.

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