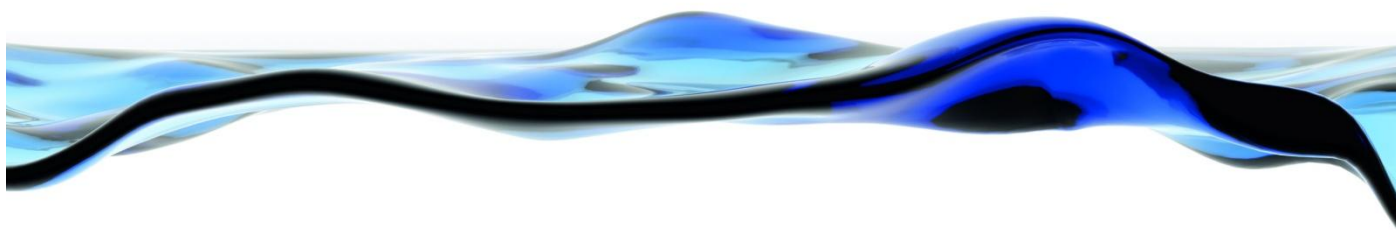


Causes of high pH in South East wetlands

Reid R, Mosley L



Goyder Institute for Water Research
Technical Report Series No. 15/25

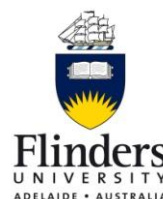


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Goyder Institute for Water Research Technical Report Series ISSN: 1839-2725

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Citation

Reid R, Mosley L (2015) *Causes of high alkalinity in South East wetlands*. Goyder Institute for Water Research Technical Report Series No. 15/25, Adelaide, South Australia.

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Executive Summary

High pH in lakes and wetlands is not uncommon and is variously attributed to microbial activity, predominantly sulfate reduction or ammonification, or to evaporative concentration of waters associated with high concentrations of sodium and magnesium carbonates (Grant 2004). pH in the range 9 – 10.5 has often been recorded in South East wetlands in South Australia and various studies have attempted to understand the main causes of the alkalinisation (Baldwin et al. 2012; Parsons 2013), and whether the high pH is detrimental to the local environments. On the basis of historical records and water sampling data, and from the results of previous investigations, three possible drivers of the high pH were targeted: A: microbial sulfate reduction, B: sequestration of carbon dioxide and bicarbonate by photosynthesising plants, C: evaporative concentration of saline, carbonate rich surface water. Parts A and B were investigated using mesocosms constructed from sediment and water samples collected from three of the wetlands: England's wetland at Taratap, Schofield Swamp and Rocky Swamp. Part C examined historical and newly collected data on water chemistry to model pH changes induced by evaporative concentration.

The mesocosm studies on sulfate reduction measured the pH, sulfate concentrations and redox potential of sediment and water. To test whether sulfate reduction might be carbon limited, plant organic material was collected from a wetland and added to half the mesocosms. The results indicated that sulfate concentrations in the wetlands studied were low or negligible and would be unlikely to generate large increases in pH. The addition of organic matter caused the available sulfate to be reduced but caused an acidification rather than an alkalinisation of both soil and sediment. Thus, we could find no evidence that sulfate reduction was a significant factor in the high pH.

The mesocosms in which dense plant biofilms developed displayed large diurnal changes in pH similar to those recorded in the wetlands. These diurnal rhythms were superimposed on a baseline of increasing pH up to approximately pH 10.5. pH increased rapidly in the light and usually plateaued after approximately 4 h. When the light was turned off the pH decreased gradually over 24h and stabilised at approximately 8.5, the level recorded in mesocosms maintained in continuous darkness. Both the amplitude of the diurnal variations and the minimum pH reached during the night period were affected by exposure to air. When diffusion from the atmosphere into the mesocosm was restricted, the variations in pH were greatly reduced and the night pH remained high. When the mesocosms were aerated, the variations in pH increased and the night pH were much lower. This suggested that the high pH was in part due to high carbon dioxide demand from the growing plants coupled with the slow diffusion of carbon dioxide from the atmosphere which was insufficient to replenish the carbon dioxide sequestered by the plants.

The geochemical modelling based on water analyses established that evapoconcentration could cause moderate increases in pH, and in the case of Little Reedy could explain pH up to 9.5. Higher pH in lakes elsewhere has been shown to be associated with low levels of calcium and magnesium. Analyses of the solutions from the mesocosms showed that in those with healthy plant growth, there were large reductions in calcium and magnesium concentrations and in carbonate alkalinity compared to mesocosms maintained in darkness. One common feature of all of the wetlands examined was the development of a high plant biomass in parallel with the rise in pH of the surface water. Plant material collected from the wetlands contained large amounts of both calcium and magnesium. Based on estimates of plant biomass and measured metal content, it was entirely feasible that a major reason the draw down in divalent metals was due to plant uptake. Evaporative concentration can also reduce dissolved calcium and magnesium when they are in unequal proportion to carbonates.

On the basis of environmental sampling, mesocosm studies and geochemical modelling, we propose that the high pH in the wetlands studied is a natural phenomenon driven by productive plant growth. Despite the high pH, these wetlands support a diversity of plant and animal life and a quick look under a microscope will show that the alkaline water is teeming with small biota. We cannot however rule out the possibility that the geochemistry of the wetlands has not been altered over the longer time

scale of the drainage system. The high pH SE wetlands appear to be unable to maintain sufficient calcium and magnesium carbonate precipitation, the main pH buffer preventing high pH developing in most water systems. The low buffering capacity means that organisms may be able to counter the high pH through the creation of microcosms of more moderate pH by excretion of small amounts of acid, a common phenomenon in plants.

Acknowledgements

We are most grateful to the South Eastern Water Conservation and Drainage Board (Mark De Jong, John Bennett) and EPA South Australia (Ben Hamilton) for part funding and sample collection. We would also like to thank landholders in the South East for access to the various sites.

Introduction

Historical monitoring records of wetlands in the South East of South Australia reveal that many of the water bodies experience periods of high pH, often exceeding pH 10. There is concern that such alkaline conditions could adversely affect biota, or at least reduce the biodiversity, favouring those organisms tolerant of high pH. The possibility that this is a recent phenomenon linked to the engineering of the extensive drainage system in the South East is difficult to establish because of the lack of long term records. The cause(s) of this alkalinisation have been the subject of several investigations, none of which has conclusively identified the main drivers. In a recent report, Baldwin et al. (2012) described the geochemistry of water and sediment samples collected from 15 wetlands in the South East in late summer 2012. Given that the geology of the South East is dominated by limestone, it could be expected that the pH was dominated by calcium carbonate and sodium bicarbonate chemistries. Geochemical modelling of the analysis data from surface water showed that the dissolved carbonate alkalinity was generally much greater than would be expected for a system in equilibrium with calcium carbonate. Many of the wetlands were supersaturated with calcite, in some cases by a factor or more than 10-fold. It was concluded that there must be other processes that drive up the pH. Of several possible options, the reduction of sulfate to sulfides by sulfur reducing bacteria was considered to be the most likely. This was supported by the identification of high levels of sulfides in some, but not all, of the sediment samples. It was proposed that the seasonal nature of the high pH could be explained by a combination of temperature and the supply of organic carbon for microbial metabolism by the breakdown of vegetation that flourishes in the warmer months. Photosynthesis was briefly considered as a driver of the high pH, and historical records show significant diurnal variations in pH, but there was no evidence that this could generate the observed longer term increases in baseline pH. Following consultation with various stakeholders, the current project was initiated with the aim of evaluating the roles of three possible influences on pH in the South East wetlands:

1. Sulfate reduction by sulfur-reducing bacteria
2. Photosynthesis
3. Evapoconcentration

The project was conducted from July 2014 to May 2015 but most of the wetlands only contained water until October or November 2014, which greatly restricted the ability to do field monitoring. Consequently, much of the data were obtained from experimental manipulation of conditions using mesocosms constructed from sediment and water samples collected from two wetlands, England's Wetland at Taratap and Schofield's Swamp, in July and October 2014, and from samples previously collected from Rocky Swamp in February 2014. Field sampling was conducted at weekly intervals from late September 2014 to late October 2012 at Taratap, Schofield Swamp and Little Reedy, while these wetlands still contained water.

Site Locations

The main 4 wetlands mentioned in this report are located north east of Kingston, South Australia (Fig. 1)

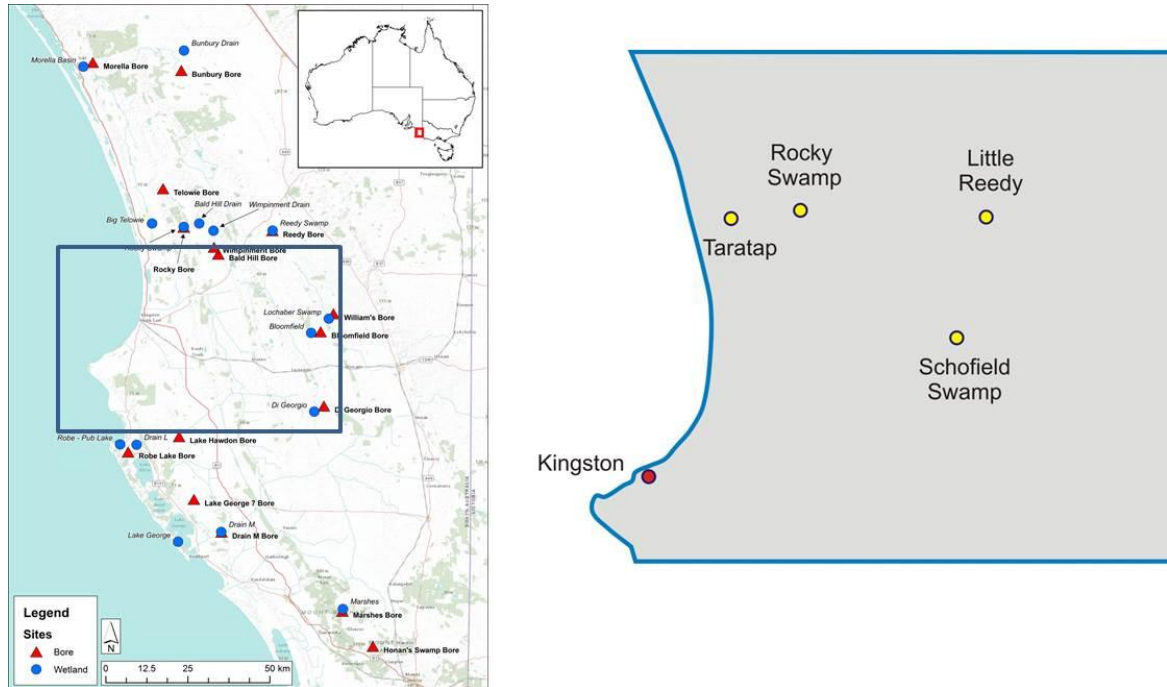


Figure 1. Left: Location of wetlands and bores sampled in Baldwin et al. (2012). Right: Locations of wetlands referred to in this report.

Historical Patterns

While many of the wetlands have installed instrumentation and telemetry, very few record pH and calibration of probes is intermittent. As a consequence, our understanding of historical trends in wetland pH is patchy. Figure 2 shows one of the more complete monitoring sets for England's Wetland, Taratap over the past 5 years. The corresponding data for Schofield Swamp are shown in Appendix 1.

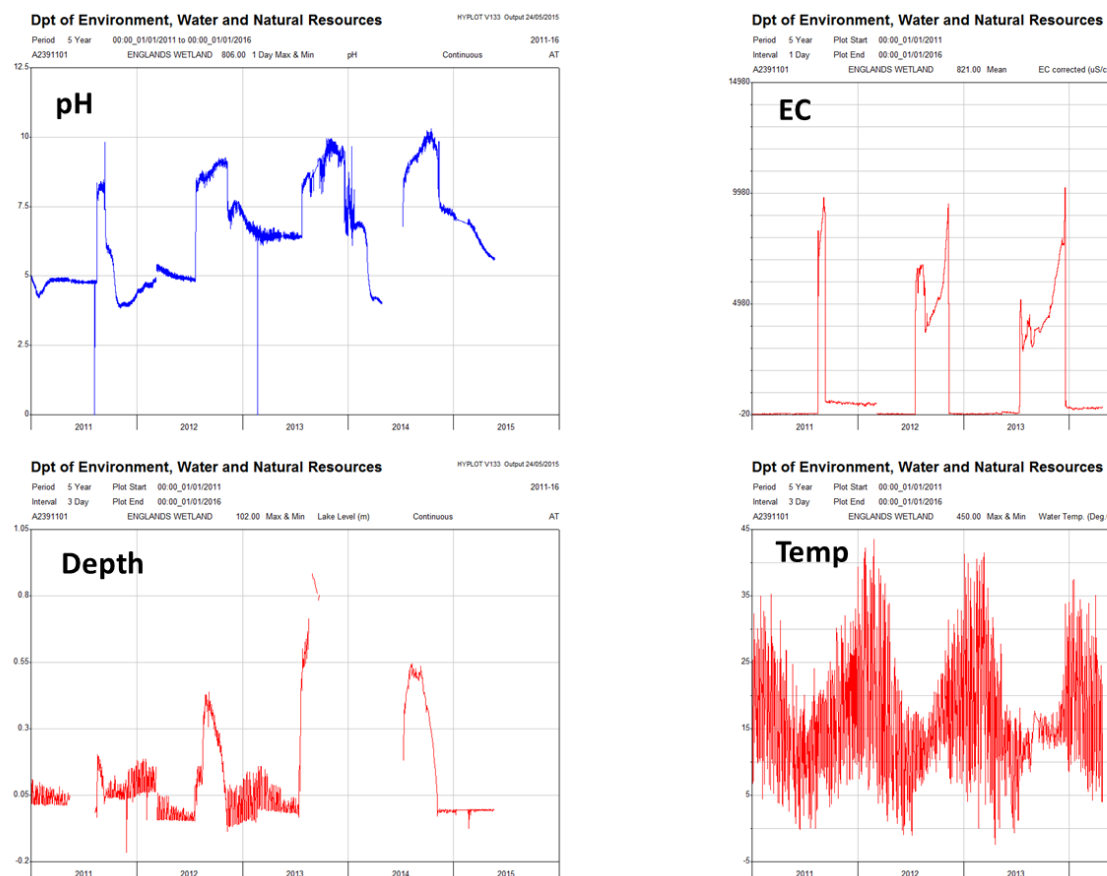


Figure 2. Five year telemetry records for pH, EC depth and water temperature at England's Wetland, Taratap

It is clear from this data that there is a strong seasonal element to the pH, with higher pH during spring-summer when lower water levels, higher EC and higher temperatures also occur. For the wetlands considered in this project, there are long periods in which there is no surface water, most commonly from mid-summer till early winter. During the 'dry periods' the wetlands revert to marshy or saline dryland vegetation, which when eventually inundated, 'drowns' through lack of oxygen or carbon dioxide for photosynthesis, and becomes replaced by aquatic species adapted to surviving under water. It is the transition from dryland to wetland that correlates with the alkalisation that then continues until the wetland dries out again. The seasonal progression can be described as follows:

1. Dryland or marsh conditions dominated by saline tolerant species (e.g *Sarcocornia*, *Wilsonia*, *Selliera*, *Samolus* etc.)

2. Upon inundation, disappearance of terrestrial plant species and growth of aquatic species (e.g. *Myriophyllum*, *Ruppia*, *Triglochin*, *Crassula* and various charophyte species).
3. Vigorous growth of aquatic plants during spring
4. Falling water levels increase salinity.
5. As the wetlands dry out, high light combined with increased salinity and temperature cause plants to die.
6. Decaying aquatic plants provide carbon sources for aerobic microbial species which deplete oxygen and lead to the proliferation of anaerobic organisms, including iron and sulfur reducing bacteria.

In Fig. 3 These phases are superimposed on the changes in pH and water depth for Taratap in 2014. In addition to water depth, the seasonal influences also include increasing day length and light intensity as well as change in the water temperature.

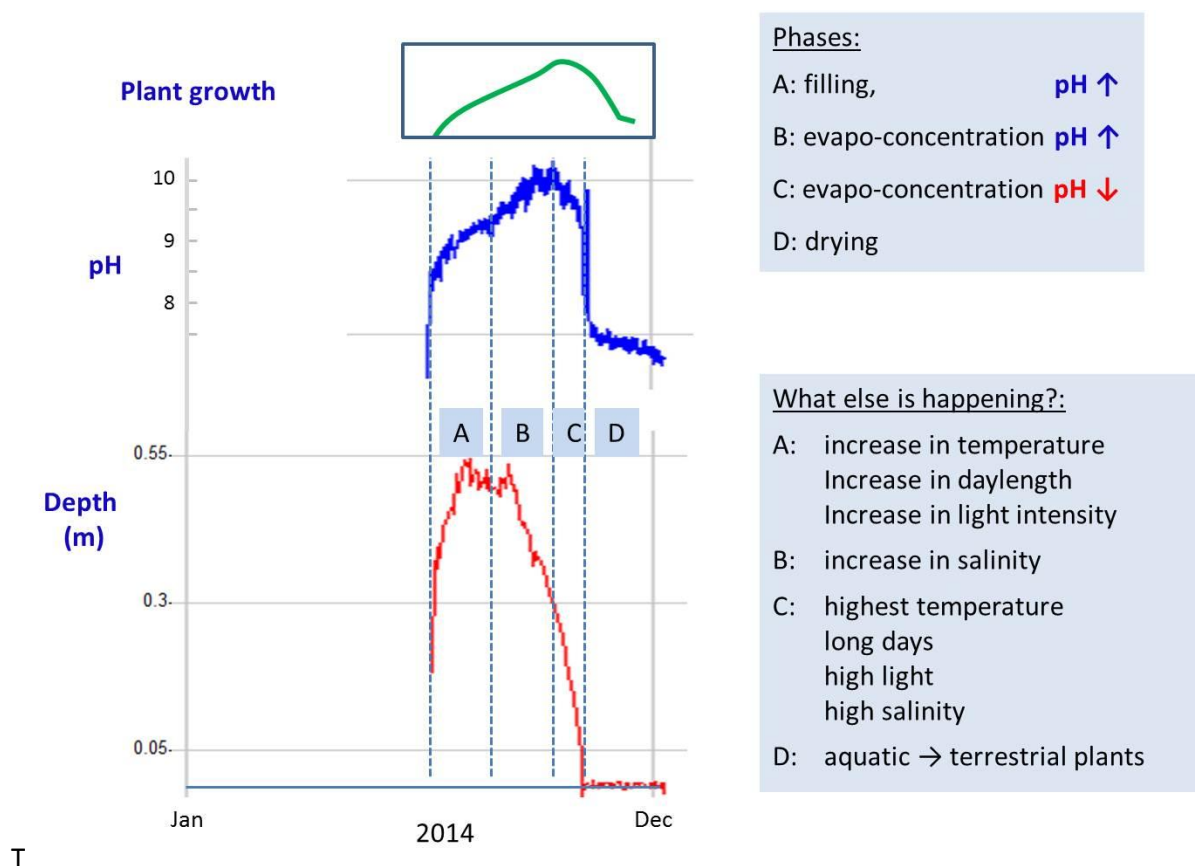


Figure 3. Changes in pH and water depth at England's Wetland Taratap in 2014

Figure 4 illustrates the density of vegetation at Taratap towards the end of spring 2014, while Fig. 5 traces the change in vegetation types during the drying of Schofield Swamp in October 2014.



Figure 4. Image illustrating the high density of aquatic vegetation in some wetlands. The image shows flowering *Ruppia* at England's Wetland Taratap two weeks before it dried out in October 2015.

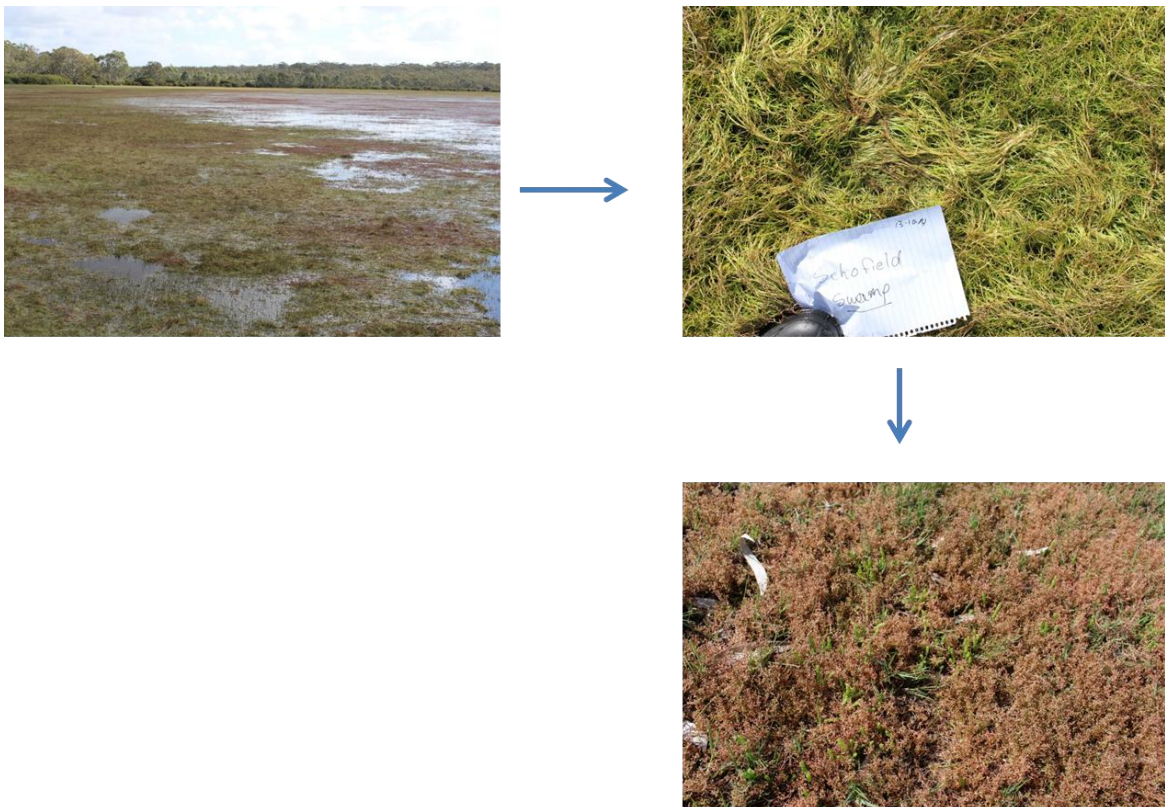


Figure 5 Transition from submerged vegetation to terrestrial plant species during the drying of a wetland. (images from Schofield Swamp 13/10/2015). Note the density of plant material in all of the stages.

Closer examination of the hourly records from all 4 sites reveal significant diurnal variations in pH, and where measured, in dissolved oxygen. Figure 6 shows daily recordings from Taratap during early filling and 6 weeks later when the maximum water depth was achieved. The pH baseline rises quite steeply early in the season then stabilises. pH variations with a similar amplitude were observed at both stages.

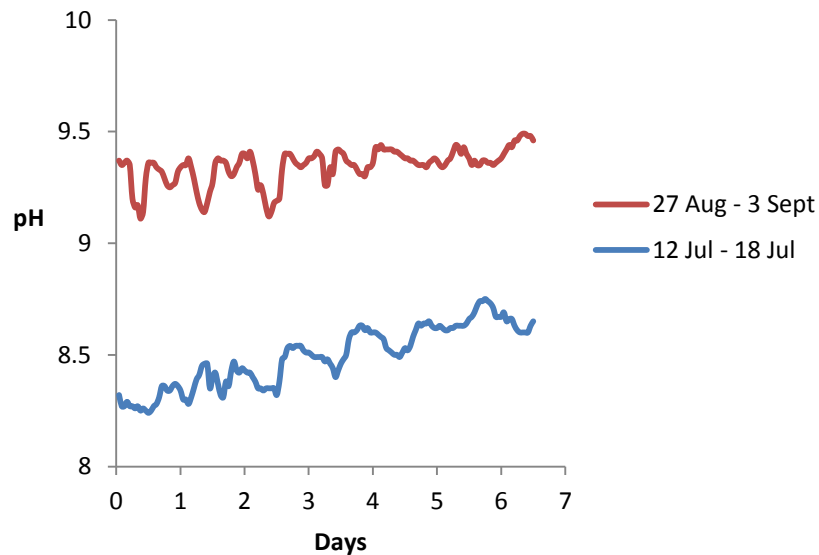


Figure 6. Diurnal variation in pH at England's Wetland Taratap 2015

HYPOTHESIS A: That sulfate reduction causes wetland pH to rise

The oxidation of soil sulfides to sulfuric acid is a spontaneous process in the presence of adequate water and oxygen. In aquatic systems, sediments containing high concentrations of sulfides remain stable due to the lack of oxygen in the water column. However, when these sediments are exposed by falling water levels, the pH falls. The drought in SE Australia between 2006 and 2010 uncovered large areas of normally submerged sulfidic soils in the lower lakes causing the development of severe acidity (Fitzpatrick et al. 2008). On reflooding, the sulfates become reduced back to sulfides by the action of sulfur reducing bacteria. For this to happen, three conditions need to be met, 1) a redox potential lower than 0 mV, 2) a supply of free sulfate and 3) a source of organic carbon. Equation 1 shows a typical conversion using acetate as the carbon source.



In the wetlands considered in this report, large amounts of organic matter accumulate as water levels fall and the sediments dry out. Thus there is abundant organic carbon for sulfur reducing bacteria when the wetlands become re-inundated. Michael et al. (2015) showed that decaying leaves of *Phragmites* could stimulate sulfur reducing bacteria to raise soil pH from less than 4 to more than 8 over several months. Baldwin et al. (2012) concluded that this was the most likely cause of the alkalisation in these wetlands, and therefore further investigation was warranted.

Methods

Mesocosms

Small mesocosms were set up using 200 g of moist sediment from Taratap, Schofield Swamp and Rocky Swamp, and overlaid with surface water from the same location. For comparison, a sulfidic soil with residual high sulfate content collected from the Finniss River was included. In order to emulate the input of organic matter, aquatic vegetation collected from a water depth of 25 cm at Taratap in late October 2014 was dried and 5 g was added to half of the mesocosms by incorporation into the sediment. Some of this organic matter floated into the overlying solution but most remained within the sediment.

Analyses

The mesocosms were incubated at 22°C under 14h/10h light dark cycles for 4 weeks before measurements of pH, Eh and sulfate content of the sediments and surface water were made. pH and Eh electrodes were either suspended in the middle of the water column or inserted 4 cm into the sediment. Readings were recorded after 10 mins. Eh values were corrected for the offset of the Ag/AgCl reference electrode compared to the standard hydrogen electrode. Soluble sulfate was determined as described in Michael et al. (2015). The method used for extraction of sulfate from soil is described in Hoeft et al. (1973).

Results

Sulfate concentrations

The surface water from Taratap and Rocky Swamp mesocosms contained moderate concentrations of sulfate. Upon addition of organic matter, the sulfate concentrations of these mesocosms was reduced by approximately 75% (Table 1). Despite the obvious sulfide odour, water from Schofield Swamp was found to contain negligible amounts of sulfate. The control sulfidic soil contained much higher concentrations of sulfates and all of this was consumed following addition of organic matter, presumably by reduction to sulfides. Likewise, the high sulfate concentration of the sulfidic soil sediments was strongly reduced by addition of organic matter (Table 1). Neither Taratap nor

Schofield Swamp had significant concentrations of sulfate in their sediments, while Rocky Swamp had a moderate level of sulfate that disappeared following addition of organic carbon.

Table 1 Sulfate concentrations in surface water and sediments in mesocosms with or without added organic matter after 4 weeks incubation

Surface water			Sediment		
	Sulfate (mM)			Sulfate $\mu\text{mol/g dwt}$	
	no mulch	+ mulch		no mulch	+ mulch
Taratap	4.40	1.10	Taratap	-0.18	-0.10
Schofield	-0.06	-0.04	Schofield	0.58	0.18
Rocky Swamp	3.56	0.77	Rocky Swamp	7.31	-0.63
Sulfidic soil	11.93	0.02	Sulfidic soil	30.38	10.03

pH changes in solution and sediments

For the 3 wetland samples, the pH of both the solutions and sediments declined following addition of organic matter (Fig. 7). In the case of Rocky Swamp, the changes were more than 1 pH unit. The trend was opposite in the sulfidic soil where the pH increased by 0.7 in the solution and 0.3 in the sediment.

Redox of solutions and sediments

Conversion of sulfate to sulfides requires strongly reducing conditions, generally with an Eh less than 0 mV (Fig. 7). For surface water, this condition was only met at Schofield Swamp, which may explain the lack of measurable sulfate at this site. All of the sediments except Rocky Swamp had Eh values less than 0 mV.

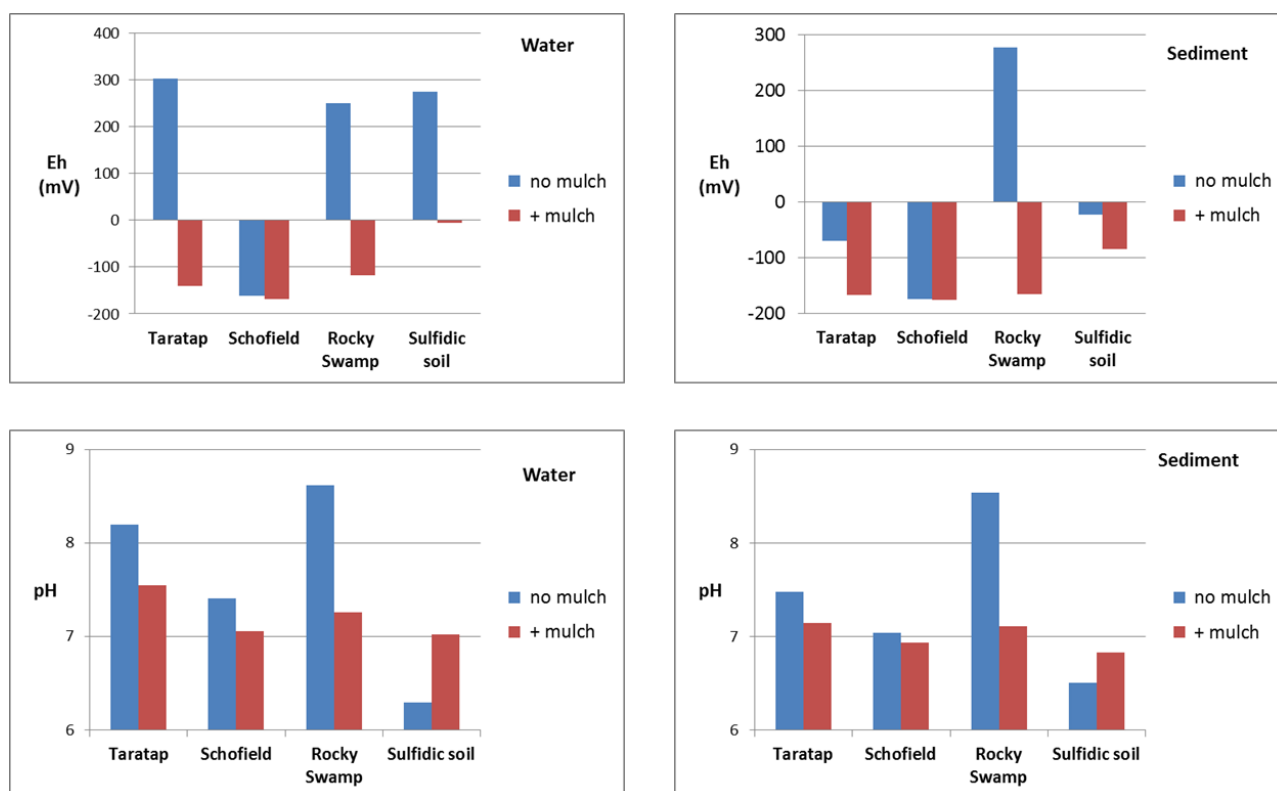


Figure 7. Redox potential (Eh) and pH of surface water (left panels) and sediments in mesocosms with or without incorporation of organic matter. Incubation time was 4 weeks.

Discussion and Conclusions

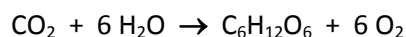
The surface water from Taratap and Rocky Swamp contained moderate concentrations of sulfate but had redox potentials in the aerobic range, which would not favour sulfate reduction. Addition of organic matter greatly reduced the Eh to less than 0 mV with a corresponding reduction in sulfate content. Similarly, the sediment from Rocky Swamp had significant amounts of sulfate and an aerobic Eh, both of which decreased upon addition of organic matter. It is not clear whether the sediment or the surface waters were carbon limited at this site, or whether the Eh was unfavourable for sulfate reduction. The lack of sulfate in either sediment or solution from Schofield Swamp, combined with the obvious smell of sulfides suggests that reduction of all available sulfate was complete, and therefore not carbon limited.

The large reduction in sulfate concentration in the sulfidic soil mesocosms is strong evidence for the action of sulfur-reducing bacteria, yet the pH changes were relatively small. In the wetland mesocosms the reduction in pH rather than an increase probably indicates that the acidity released by the breakdown of inorganic matter exceeds the alkalinising effect of the small amount of sulfate reduction. In summary ***we conclude that sulfur reducing bacteria do not have a major influence on pH in these wetlands.***

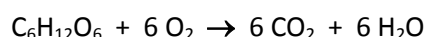
HYPOTHESIS B: That CO₂ removal by photosynthesising plants causes wetland pH to rise

Aquatic plants can modify the carbonate alkalinity through exchanges of CO₂ during photosynthesis and respiration, the overall equations for which are as follows:

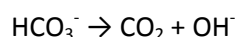
Photosynthesis



Respiration



The removal of CO₂ during photosynthesis typically causes the pH to increase during the daytime, and CO₂ production from respiration causes the pH to decrease during the night time. Carbon dioxide is the preferred source of inorganic carbon for plants but under alkaline conditions, free CO₂ becomes limiting for photosynthesis. Many aquatic plants have adapted by using HCO₃⁻ accompanied by the release of hydroxyl ions:



In the presence of sufficient alkalinity this process can drive the pH up by several units, typically reaching pH 10.5 (Cavalli et al. 2012). Although plants produce CO₂ during respiration, photosynthetic CO₂ fixation in aquatic plants can exceed respiratory CO₂ production by more than 10-fold during the day (Cavalli et al. 2012; Hyldgaard et al. 2014). At night, only CO₂ release during respiration occurs but even taking this into account, consumption of CO₂ by actively growing plants may greatly exceed its production. If CO₂ is not replaced by diffusion from the surface, then increasing pH should result unless other compensatory reactions occur (e.g. precipitation of Ca and Mg carbonates). However, if divalent metals are limiting, photosynthesis may result in pH increases up to 12.6 (Baas Becking et al. 1960).

The influence of aquatic plants on solution pH was investigated using mesocosms. This permitted a range of variables to be examined under reproducible and controlled conditions.

Methods

The mesocosms were glass, 26 cm in height with a volume of 2 litres. They were prepared from sediment and water samples collected from the wetlands. The sediment layer was approximately 8 cm thick. Mesocosms were incubated under a 14h/10h light regime at a controlled temperature of 24°C/20°C (light/dark) which induced a range of plant species to grow (Fig. 8). After 4 months, most mesocosms had healthy biofilms (Fig. 9). To identify mesocosms, they were designated M followed by a unique identifier (e.g. M17) which related to the origin and date of establishment.



Figure 8. Development of biofilms in mesocosms. M14 and M26 were maintained in the dark and no biofilm developed. M13 and M25 were exposed to 14h/10h light dark cycles for 6 months.



Figure 9. Variation in mesocosm plant composition, and probes for continuous monitoring of pH, Eh, EC and temperature.

Diurnal changes in pH did not occur in solution removed from the mesocosms, indicating that the changes observed in the complete mesocosm were due to benthic vegetation rather than

phytoplankton. Cultures of *Ankistrodesmus* did display diurnal variations and high pH, and it is highly likely that phytoplankton may contribute to pH changes in nutrient rich wetland conditions.

Results and Discussion

The pH in mesocosms kept in the dark remained low and was virtually constant with time (Fig. 10). In contrast, and in agreement with the field-based monitoring, mesocosms maintained in light/dark cycles displayed diurnal changes in pH (Fig. 10) and dissolved O₂ (data not shown). The maximum pH, in some cases up to pH 10.7, was generally reached after approximately 4 h of light (300 $\mu\text{mol m}^{-2}\text{s}^{-1}$, 25 °C). In contrast to the rapid stabilisation of pH in the light, the fall in pH following the onset of darkness was much more gradual, often taking 20 – 24 hours to reach a steady low value (Fig. 11).

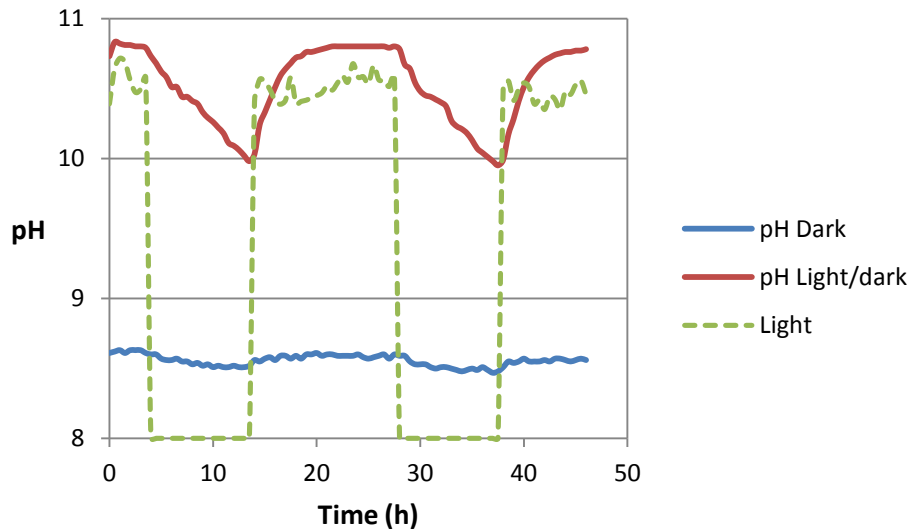


Figure 10. Diurnal variation in pH of mesocosms maintained in light or darkness.

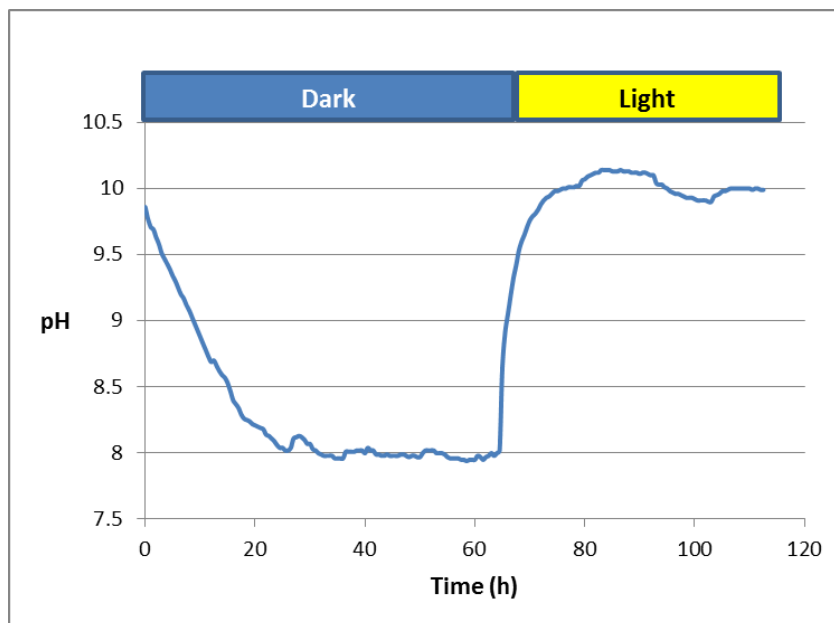


Figure 11. pH transitions in prolonged light and dark in a mesocosm with established biofilm.

With increasing plant density, the maximum pH tended to increase and the amplitude of the diurnal pH changes decreased. Figure 11b shows the pH in three mesocosms at different stages of biofilm development.

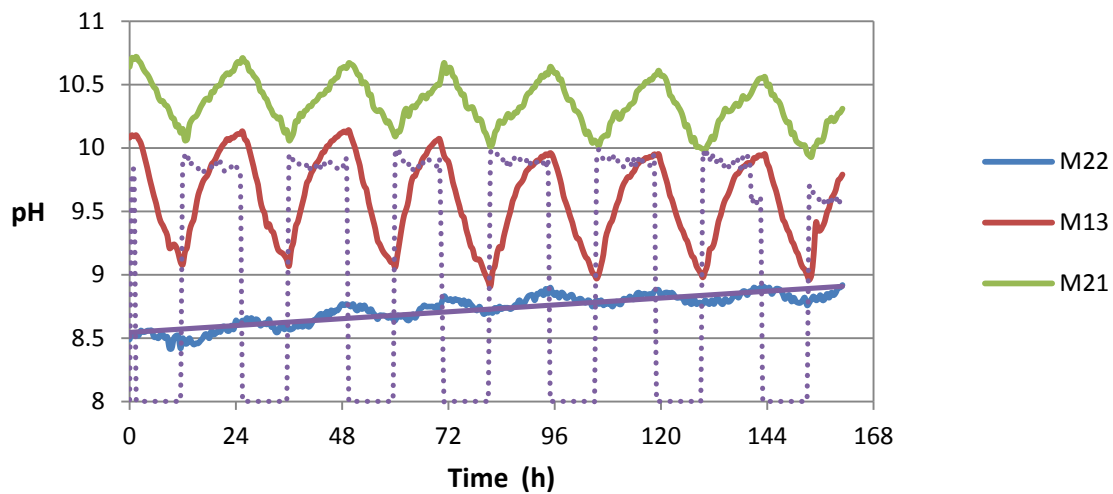


Figure 11b. Changes in pH and diurnal variation in pH during development of biofilms. M21 had a dense mat of filamentous algae after 4 months, while M13 was colonised by a lower density of more varied aquatic species (see Fig.9). M22 was kept in darkness until 1 week before the commencement of pH recordings. The trace for M22 shows the development of diurnal changes in pH superimposed on a gradual rise in baseline pH, corresponding to increasing plant development in the mesocosm. The dashed line traces the light on/off transitions.

Figure 12 shows the steady light and dark pH from a range of mesocosms containing sediment and water from Taratap, Schofield Swamp and Rocky Swamp. These all show a similar pattern of high pH in the light and much lower pH in the dark.

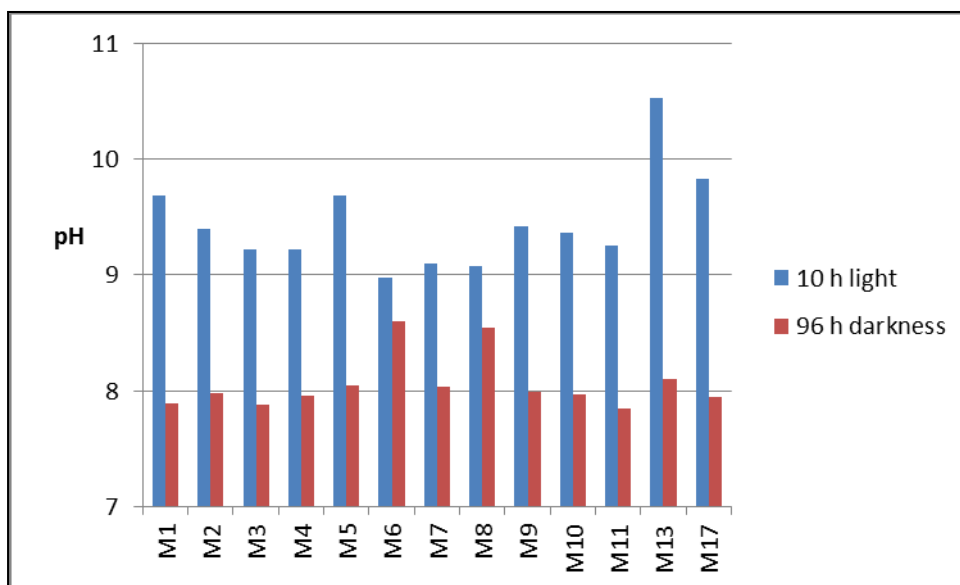


Figure 12. Maximum pH in the light in mesocosms with established biofilms, and the corresponding pH after 4 days of darkness.

The amplitude of the diurnal variation in pH appeared to depend on exchange of gases with the air. When this was restricted by floating a plastic film on the surface, the pH changes were quite small (Fig. 13). Conversely, when the mesocosm was aerated, the maximum pH was lowered and the pH in darkness fell more rapidly, reaching values observed in mesocosms in continuous darkness (Fig. 14).

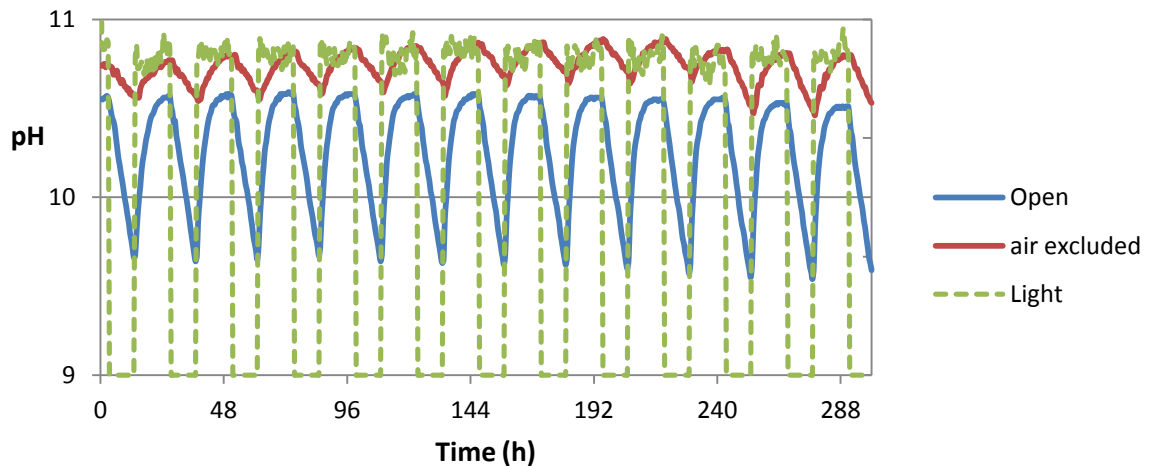


Figure 13. The effect of air exclusion on the amplitude of diurnal pH changes in mesocosms with established biofilms. M13 was open to the air while M21 had a plastic film floating on the surface to reduced gas exchange.

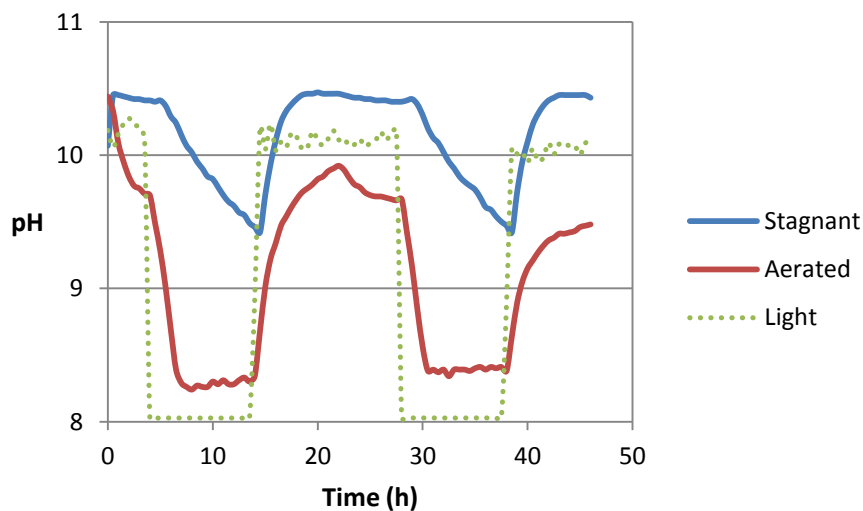


Figure 14. Diurnal variation in pH in mesocosms without (M13) and with (M21) aeration.

It is clear that in the mesocosms, the dominant influence is light. In darkness the pH does not reach 9 whereas in the light, the pH can exceed 10. This strongly points to plant growth and metabolism as the primary driver of the pH increase. The diurnal changes of around 1 pH undoubtedly reflect the removal of CO_2 from the water column, and the reduced amplitude of these changes when access of atmospheric CO_2 was restricted is consistent with this. But can reductions in CO_2 alone account for the observed seasonal increase in the pH baseline? It is known (Baas Beeking et al. 1960) that high pH conditions can be generated under conditions of low Ca and Mg, in combination with low

alkalinity. The analyses of solutions from high pH mesocosms with developed biofilms show that Ca, Mg and alkalinity are all strongly reduced compared to mesocosms without healthy plant material (Table 2).

Table 2. Analysis of water samples from mesocosms maintained for 6 months in 14 h/12 h light dark cycles (M21) or continuous darkness (M22). Major differences are highlighted.

	Units	M21 Light	M22 Dark
Bromide	mg/L	5.55	6.7
Calcium	mg/L	12.5	37.5
Chloride	mg/L	1930	2060
Fluoride	mg/L	0.71	0.87
Potassium	mg/L	52.5	53.1
Magnesium	mg/L	5.05	62.9
Sulphate	mg/L	96	104
Silica - Reactive	mg/L	9	42
Alkalinity as Calcium Carbonate	mg/L	78	487
Bicarbonate	mg/L	23	551
Carbonate	mg/L	35	21
Hydroxide	mg/L	0	0
pH	pH units	10.6	8.4
Ammonia as N	mg/L	0.032	0.02
Sodium	mg/L	1350	1250

Table 3 shows the mineral element composition of submerged vegetation from Taratap. From this it is possible to estimate the extraction of Ca and Mg as a result of plant growth. The difference in Ca concentration between the light and dark mesocosm was 25 mg/L. Reference to Table 3 shows that the submerged vegetation would sequester 8.8 mg g^{-1} Dwt or approximately 0.88 mg g^{-1} Fwt (assuming Fwt:Dwt ratio of 10). To account for the difference between the mesocosms maintained in light with abundant plant biomass and the mesocosms not receiving light, the plant biomass would need to be approximately 29 g L^{-1} , which seems highly plausible based on the images of plant density recorded from the wetlands. For Mg, the corresponding valued would be 51 g L^{-1} , which again would represent a significant draw down of Mg in the water column. Taken together with the net consumption of CO_2 and the limits imposed by the diffusion of CO_2 into the water column, the sequestration of Ca and Mg would intensify the alkalinising effects due to the growth of plants.

Table 3. Analysis of submerged vegetation sampled from Taratap Oct 2014

	mg/kg Dwt
Na	29000 ± 390
K	12800 ± 153
Mg	11267 ± 273
Ca	8833 ± 393
S	5700 ± 153
P	2600 ± 58
Mn	94 ± 3
Fe	89 ± 10
B	58 ± 2
Zn	16 ± 0
Cu	7 ± 0

Why does CO₂ not equilibrate in the water column?

There appear to be two major influences on water chemistry due to plant growth. The first is the reduction in alkalinity which suggests that carbonates are not being replenished from the substrate, and that resupply of CO₂ by diffusion from air down the water column is too slow to compensate for the high photosynthetic demand, especially during late spring and summer where days are long and nights are short and therefore photosynthesis is dominant. Additionally, the dense network of submerged plants would tend to baffle any stirring effect of wind and waves, further reducing the rate of downward diffusion of CO₂. Figure 11b compared the pH changes from two mesocosms differing in plant density. In M21 there was a dense network of filamentous plants which would have greatly restricted CO₂ influx whereas in M13 the canopy was more open. The main differences in the pH responses of these two mesocosms were that higher plant density was associated with higher pH and smaller diurnal variations, some of which is likely to be due to restricted CO₂ access. The fact that oxygen bubbles developed in the plant mass is also evidence for limitation of gas exchange. Upward movement from the sediment may also be restricted. Although the wetlands overlie limestone minerals, they are separated from the surface water by a thick organic layer, and dissolution and diffusion into the overlying water column may be very slow.

The second consequence of increasing plant biomass is the reduction in concentrations of divalent metals, which would otherwise trap inorganic carbon species and act as a buffer against large increases in pH.

It is concluded that high pH in the wetlands occurs as a result of removal of CO₂ or HCO₃⁻ from the surface water by photosynthesis, coupled with the sequestration by plants of Ca and Mg.

HYPOTHESIS C: That evapoconcentration causes wetland pH to rise

Our third hypothesis was that high pH values in wetlands are created by evapo-concentration of highly alkaline, but low Ca and Mg, input water leading to development of a “soda” (sodium-carbonate) water type (Grant, 2004). This part of our study aimed to understand the geochemical drivers of this condition by examining historical data and new data collected during evaporation cycles in Little Reedy, Taratap, Schofield and Rocky Swamp wetlands. Geochemical modelling was used to calculate the speciation of solution, solids and gases in the water for samples collected in the field and wetland evaporation scenarios.

Methods

Historical data

Historical data was obtained from the SECWB and EPA from 2010–2014 for: pH in field and laboratory; conductivity and total dissolved solids (by calculation); temperature, major ions (calcium, Ca; magnesium, Mg; sodium, Na; potassium, K; chloride, Cl; sulfate, SO₄, alkalinity and carbonate, CO₃²⁻, and bicarbonate, HCO₃⁻, by calculation; bromide, Br; fluoride, F; and ammonia). The dataset contains over 100 samples for most parameters from 58 sites. All laboratory analyses were undertaken at the Australian Water Quality Centre (AWQC), a NATA accredited laboratory using standard methods (APHA, 2005). Field measurements were undertaken using calibrated handheld meters.

Sampling and analysis of an evapo-concentration time series in 2014

Water samples were collected in late summer-autumn 2014 from two South East wetlands (Rocky Swamp and Little Reedy) that were undergoing evapoconcentration and that have been previously susceptible to developing high pH conditions. Only limited samples were collected from Rocky Swamp as it dried shortly after sampling commenced. Hence only the time series from Little Reedy is presented here although the samples from Rocky Swamp were included along with the analyses of historical data.

pH, specific electrical conductivity (μS/cm at 25°C), and dissolved oxygen were measured in the field at the time of sample collection using a calibrated instrument.

Water samples were immediately chilled and transported for analysis at AWQC as noted above.

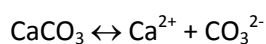
Total alkalinity was measured by titration to a pH 4.5 end-point. Major ions (SO₄, Ca, Mg, Na, K) were measured by ICP-MS and a Ferricyanide method (APHA, 2005; method 4500-Cl- E) for chloride (Cl).

pH was measured again using a calibrated electrode.

Additional “scrapings” of precipitates observed on the dried wetland margins were analysed at CSIRO for their mineral composition using X-Ray diffraction.

Geochemical theory and modelling

The solubility of a particular mineral (e.g. calcite, CaCO₃) constrains the maximum concentration of its dissolved components (Ca²⁺ + CO₃²⁻) in water. When evaporation occurs in a water body, concentrations of dissolved components increase, sometimes to a point where mineral precipitation occurs. Different minerals precipitate at different stages of evaporation. If this ‘saturation’ point is reached, any additional dissolved components added to the pond will tend to precipitate as the mineral form and settle out of solution. The likelihood of a particular mineral precipitating or dissolving can be predicted using knowledge of the relevant dissolved ion concentrations and mineral solubility products (K_{sp}). For example, for calcite dissolution we may write:



With the solubility product:

$K_{\text{calcite}} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] = 10^{-8.48}$ at 25°C. This represents the calcium and carbonate ion activities at equilibrium. For the ion activities in the actual sample, an Ion Activity Product (IAP) is calculated:

$$\text{IAP}_{\text{calcite}} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}]$$

and saturation conditions may be expressed as the ratio between IAP and K which can be used to calculate a saturation index (SI):

$$\text{SI} = \log(\text{IAP}/K)$$

For SI = 0, there is equilibrium between the mineral and the solution. SI < 0 reflects subsaturation (no new precipitation but potential for dissolution if mineral already present), and SI > 0 supersaturation (mineral precipitation likely). These calculations can be most conveniently performed using a geochemical speciation program which can simultaneously consider other mineral precipitation reactions. In this study, chemical speciation and solubility calculations were undertaken using the computer program PHREEQC (interactive version 3, Parkhurst and Appelo, 2013). The measured pH, temperature, alkalinity and major ion concentrations were used as inputs. Charge balancing was undertaken using Cl in the model but calculated charge balance errors in the laboratory data were less than <5%. The Pitzer database in PHREEQC was used as recommended for modelling of high salinity solutions.

Results

Analysis of 2010–2014 water chemistry dataset

The entire laboratory water quality dataset collected in the South East from 2010–2014 was analysed to determine if there were correlations and/or regional patterns in water composition that could explain the high pH conditions.

Summary statistics for the entire dataset are shown in Table 4. On average, the waters of the South East can be characterised as a sodium-chloride dominated water composition with high alkalinity and pH, well oxygenated with low chlorophyll and ammonia levels, and moderate conductivity and dissolved organic carbon levels.

The major ion concentration of the whole 2010–2014 South East dataset versus pH is shown in Fig. 15. Higher pH conditions almost always occur when Ca, Mg and SO₄ concentrations are low. In contrast there is no clear relationship between alkalinity, Na, and K with pH (although note there was a more limited dataset available for Na and K, Table 4).

Table 4. Summary statistics for the South East regional water quality data from 2011–2014. The statistics are the median, 25th and 75th percentiles, minimum, maximum and number of samples (n) including in the analysis.

Statistic	Unit	Median	25th perc.	75th perc.	min	max	n
Alkalinity as CaCO ₃	mg/L	309	258	421	9	669	127
Ammonia as N	mg/L	0.041	0.017	0.081	0.005	0.110	15
Bicarbonate (calc.)	mg/L	359	269	462	3	685	120
Bromide	mg/L	4.4	3.5	5.2	2.4	10.4	23
Calcium	mg/L	77.5	49.6	107.5	2.8	758.0	127
Carbonate (calc.)	mg/L	18.0	0.0	40.0	0.0	125.0	119
Chloride	mg/L	1460	724	3705	30	56900	127
Chlorophyll a	µg/L	2.0	1.0	5.9	0.0	93.1	104
Conductivity (EC)	µS/cm	4650	3055	11250	123	128000	127
Dissolved Organic Carbon	mg/L	14.4	7.4	28.2	2.6	55.5	104
Fluoride	mg/L	0.8	0.8	0.9	0.7	1.0	15
Magnesium	mg/L	111	80	254	2.2	3030	127
pH lab	pH units	8.6	8.2	8.9	5.5	10.5	127
pH field	pH units	8.5	8.2	8.9	5.0	10.7	114
Potassium	mg/L	35.6	25.3	41.6	16.5	66.1	23
Sodium	mg/L	722	609	1009	372	2180	23
Sulfate	mg/L	218	118	545	2.7	8730	127
Total Dissolved Solids (by EC)	mg/L	3000	1575	7475	67	100000	104
Temperature	C	16.5	15.0	18.4	10.7	24.7	99
Dissolved Oxygen	mg/L	8.1	6.2	10.4	0.7	17.2	99

The ratio between the concentrations of cations (Ca²⁺, Mg²⁺) and anions (HCO₃⁻, CO₃²⁻) which precipitate in carbonate minerals can be useful in predicting which waters will develop high pH values during evaporation (Jones and Deocampo 2003). Low ratios (insufficient Ca and Mg relative to carbonate/bicarbonate) is considered indicative of risk of developing high pH conditions and this appears quite consistent for the ratios found during high pH conditions in the South East (Fig. 15).

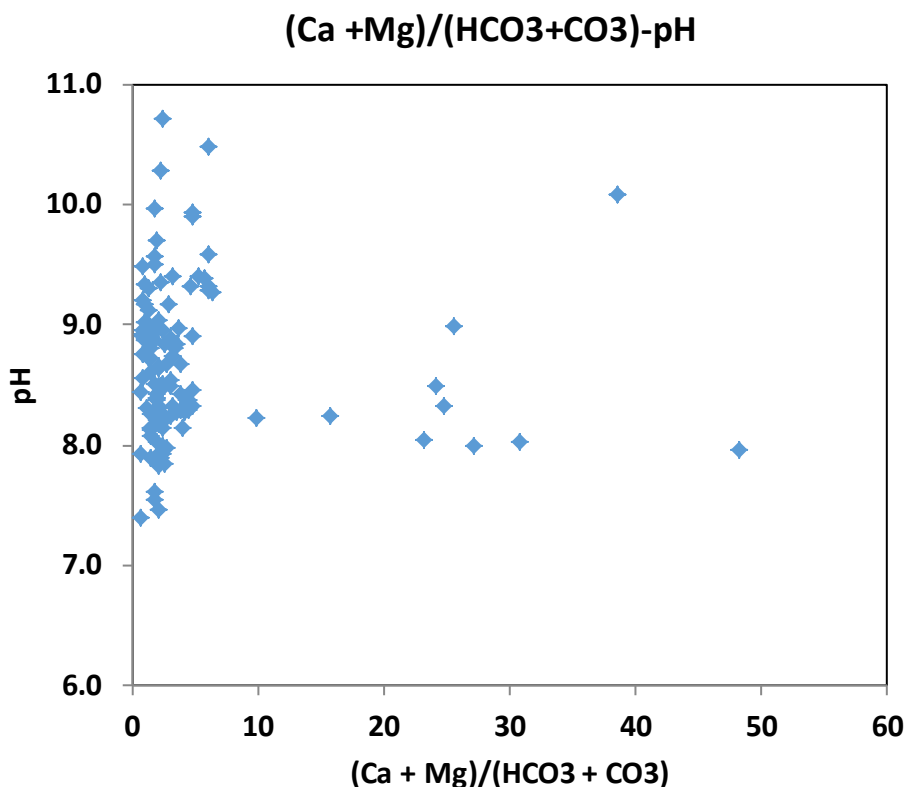


Figure 15. Plot of the sum of dissolved calcium and magnesium divided by the sum of bicarbonate and carbonate concentrations (in meq/L) versus pH

The relevant mineral saturation indices, calculated using PHREEQC for each sample, are shown in Fig. 16. Three carbonate minerals (calcite, CaCO_3 ; magnesite, MgCO_3 ; and dolomite, CaMgCO_3) are supersaturated in the majority of samples ($n > 100$ over 4 years) while gypsum (CaSO_4) is unsaturated. These results indicate that carbonate minerals likely play a significant role in the geochemistry of these waters. The calculated CO_2 gas concentration in the water samples is also shown in Fig. 18 along with the atmospheric CO_2 concentrations. Most samples are near or above (supersaturated) equilibrium with the atmosphere.

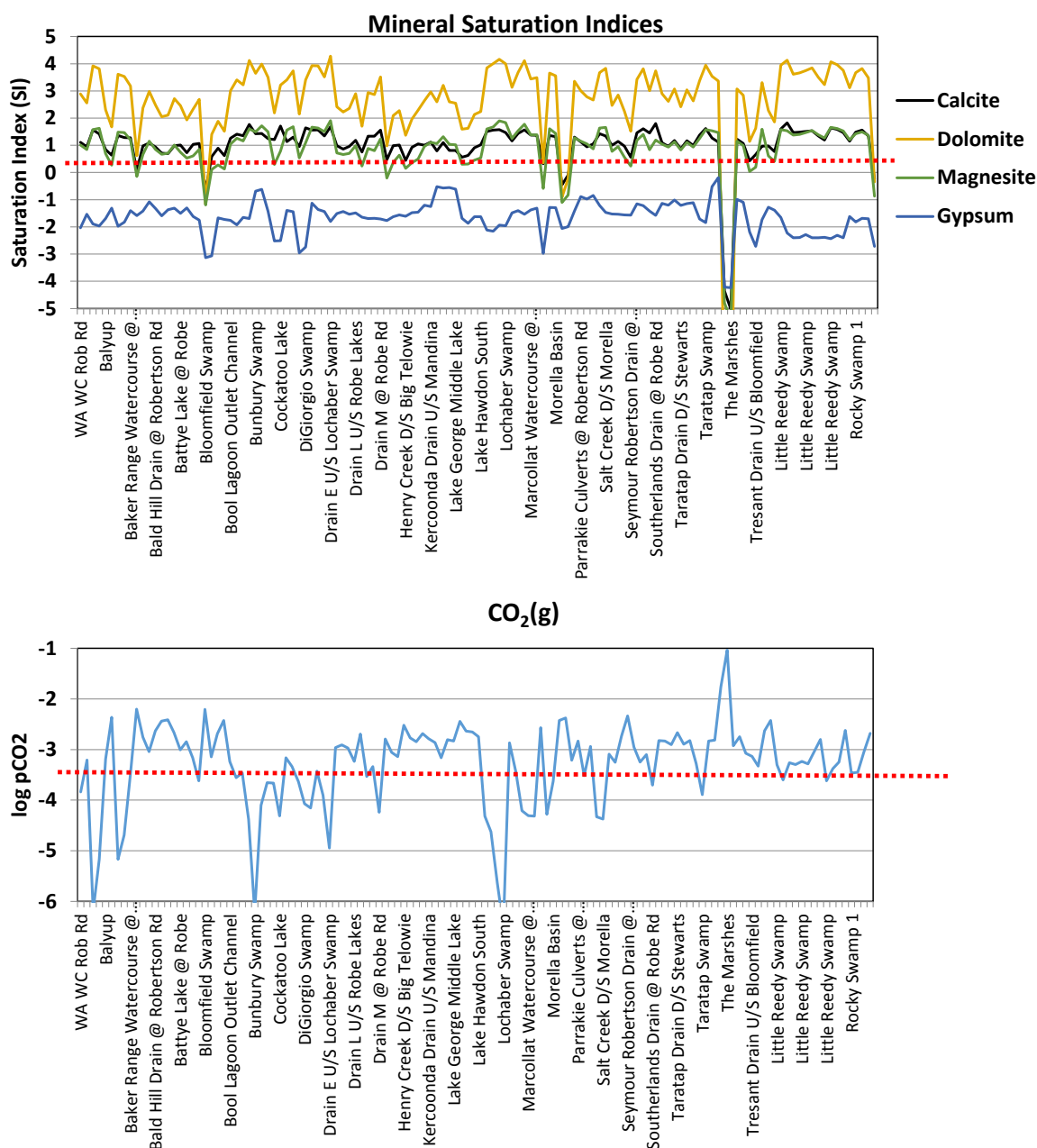


Figure 16. (top) selected mineral saturation indices (SI), the SI for calcite and dolomite is greater than 0 indicating supersaturation, the SI for gypsum indicates undersaturation, and (bottom) pCO₂ concentration in the water as calculated using PHREEQC from the measured pH and alkalinity. The pCO₂ is close to the atmospheric level (horizontal dashed line) in most samples

Trends in major ion concentration and pH in wetlands in 2014-2015

The time series of alkalinity (HCO_3^- , CO_3^{2-}) and major ions at Little Reedy wetland is shown in Fig. 18. The concentrations of chloride, sodium and alkalinity increase as the wetland dried. This is typical of evaporation-driven processes where the water evaporates and the ions concentrate. What is atypical is that the calcium, magnesium, sulfate and potassium do not concentrate. Initially these ions decrease and then remain relatively stable and the reasons for this are discussed further below. pH is high but shows some variation.

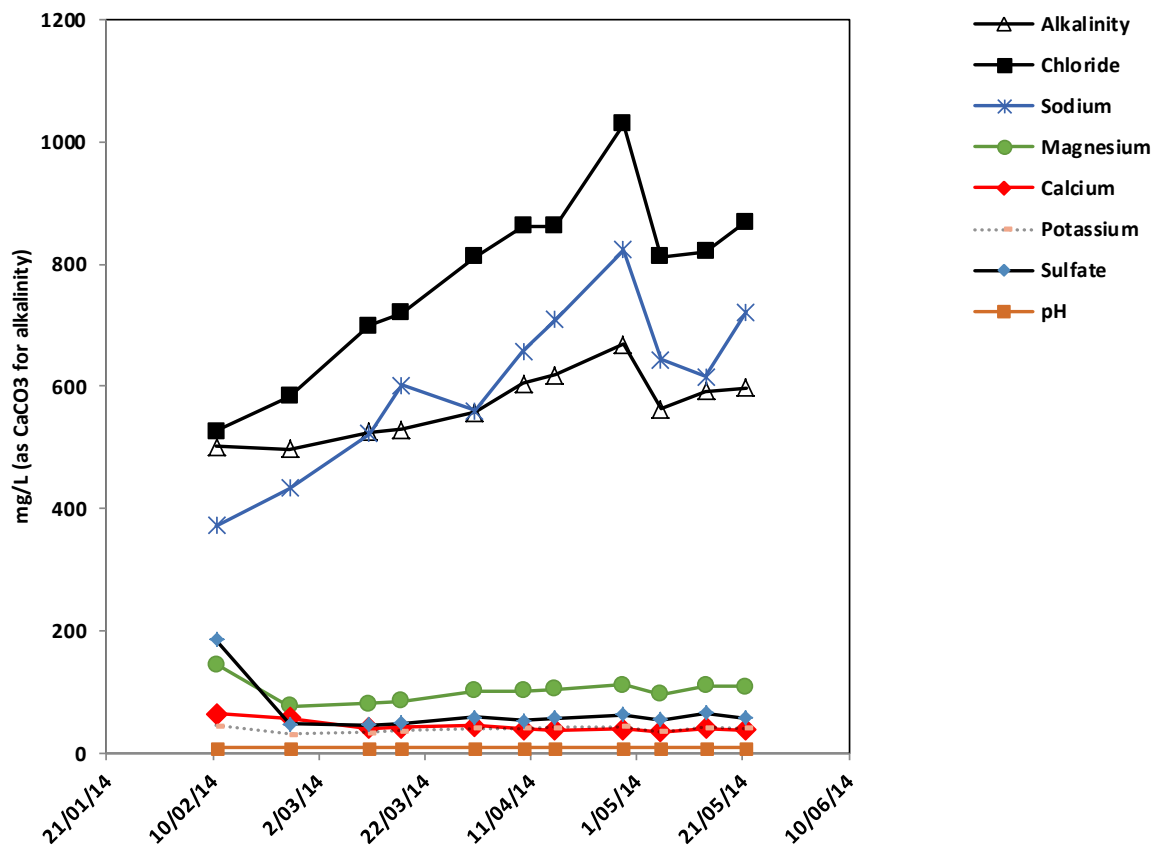


Figure 17. Time series of alkalinity (HCO_3^- , CO_3^{2-}), major ion concentrations, and pH in Little Reedy wetland from Feb-May 2014.

The next winter-spring had low rainfall and very little water entered SE wetlands. Hence the drying cycle was complete by November 2014. Despite a very limited evaporative period high pH values were observed, particularly in Little Reedy and Taratap wetlands (Fig. 18). Consistent with above observations for the preceding summer, there was a trend of increasing alkalinity and low Ca and Mg concentrations. All high pH wetlands appear to have a predominantly Na-Cl-CO_3^{2-} water chemistry.

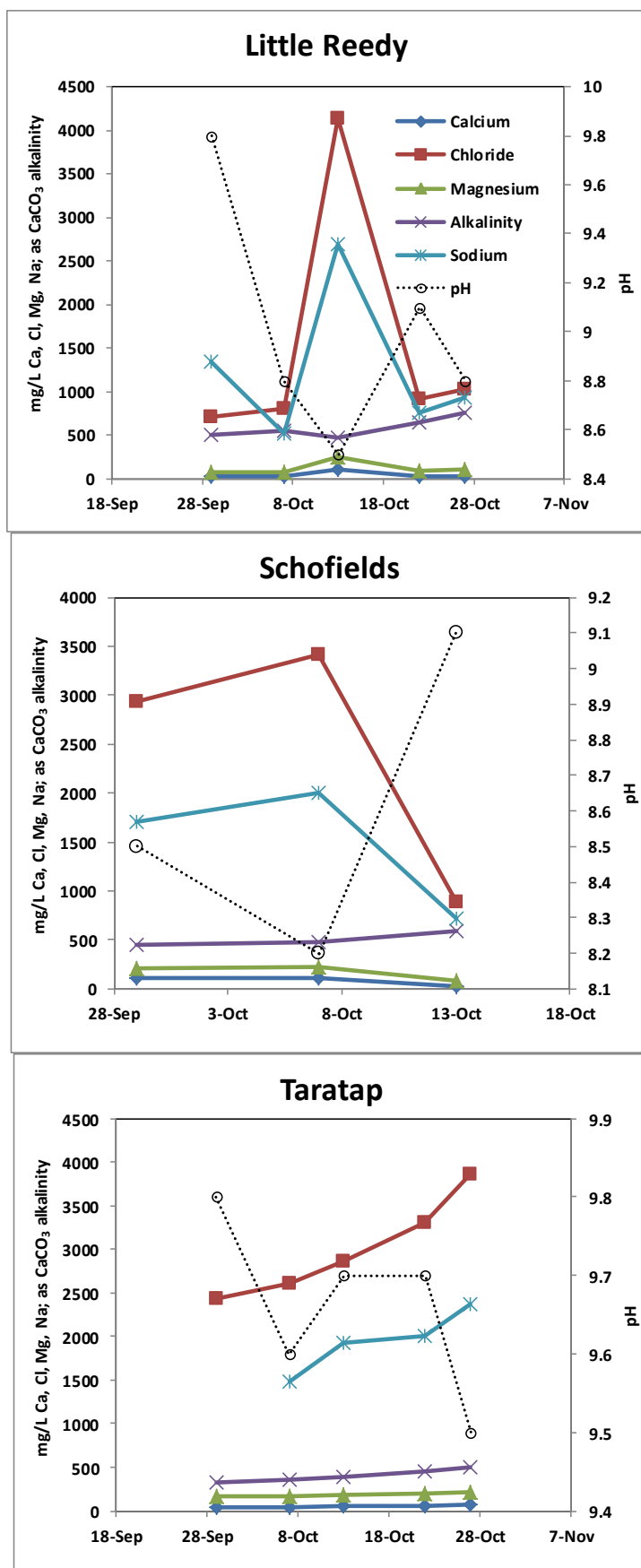


Figure 18. Time series of alkalinity (HCO_3^- , CO_3^{2-}), major ion concentrations, and pH in Little Reedy, Schofields and Taratap from Sep-Nov 2014.

Calcite, dolomite and magnesite are all supersaturated in the above field samples, consistent with the historical dataset (Fig. 18). X-Ray Diffraction analysis of the mineralogy of dried precipitates on the margins of Little Reedy, Rocky Swamp and Taratap (EPA/CSIRO data not shown) showed a range of minerals present. Common findings were calcite (CaCO_3), magnesium-substituted calcite, gypsum (CaSO_4) and halite (NaCl). This suggests these minerals were precipitating during evaporation. For the carbonate minerals this is consistent with above findings for historical dataset of carbonate mineral saturation (Fig. 17 top, note dolomite is similar composition to Mg substituted calcite).

Evapoconcentration in a mesocosm

Changes in pH were monitored during the drying down of a mesocosm with a dense biofilm. The depth decreased from approximately 13 cm to 2 cm over 7 weeks, with a concurrent 6-fold increase in EC. Figure 19 shows the daily minimum and maximum pH values. For the first 6 weeks the maximum pH remained constant, but then began to fall, most probably due to a combination of toxic salinity levels and tissue being exposed above the water line. The minimum pH decreased at a relatively constant rate for the duration of the drying process, which may reflect a shortening of the distance for atmospheric CO_2 diffusion into the water column.

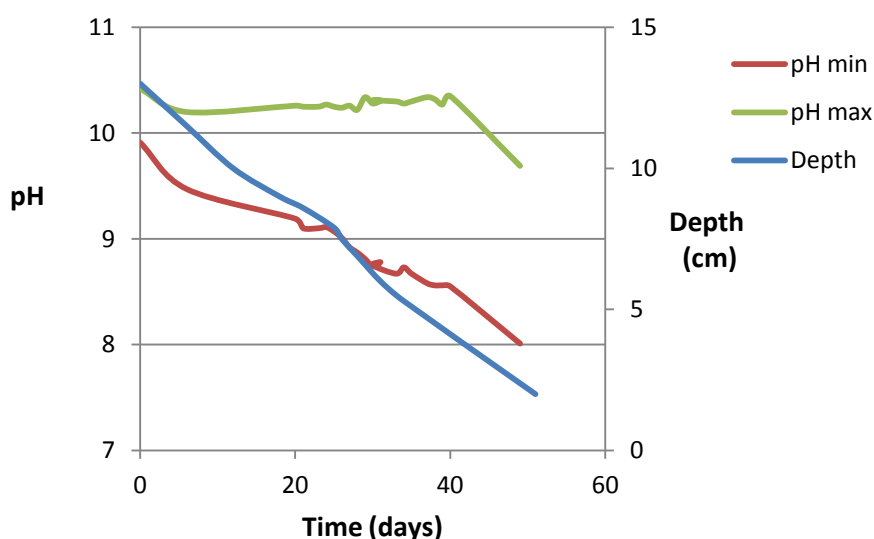


Figure 19. Time course of changes in daily minimum and maximum pH and depth in a mesocosm during evaporation. The initial EC was 4,200 and the final EC was 25,500. The initial composition of the solution when the depth was 26 cm is shown in Table 2 as Mesocosm 21.

Geochemical modelling

pH and water chemistry during evaporation was simulated in PHREEQC for the median South East drainage waters (Table 4) and the Little Reedy water at the start of the sampling period. High pH (9–9.5) developed during the modelled evapo-concentration of both these waters (Fig. 20). This occurred at relatively low concentration factors (1–10 times). These simulations were undertaken with equilibrium with atmospheric levels of CO_2 . When lower CO_2 ($10^{-4.5}$ atm) was simulated in the model, as may occur when high photosynthetic activity in the water removes CO_2 , the pH went over 10 (not shown).

As noted above the Ca/carbonate ratio appears particularly important for determining whether high pH conditions develop during evaporation (Fig. 15). The two simulations described above (top two plots in Fig. 20) had an initial $\text{Ca}/(\text{HCO}_3 + \text{CO}_3)$ ratio of 0.65 and 0.32 for the median SE drainage and Little Reedy water composition respectively. To test the sensitivity of the model to this parameter we also simulated evaporation of a water with a $\text{Ca}/(\text{HCO}_3 + \text{CO}_3)$ ratio of 1.0 (bottom plot in Fig. 20).

The pH showed only a minor initial increase in the model and then decreased slightly at high evapo-concentration factors.

The speciation predominance (zone of stability of major species) diagrams for the Na-Cl-Carbonate system at an equal and low Ca/alkalinity ratio are shown in Figure 21. With low Ca there is an inability to maintain calcite as the dominant species and carbonate builds up in the water. This is consistent with observations of alkalinity increasing during evaporation (Fig. 17). When Ca and dissolved inorganic carbon are approximately equal and the carbonate mineral saturation index is greater than zero, calcite precipitation is dominant and carbonate does not build up in the water. The consequence of this is that sodium carbonate dominated high pH systems cannot form when calcium and carbonate are in equal proportions and calcite is precipitating (ie any concentration of carbonate results in calcite/Mg-calcite precipitation rather than increasing carbonate/alkalinity in the water column).

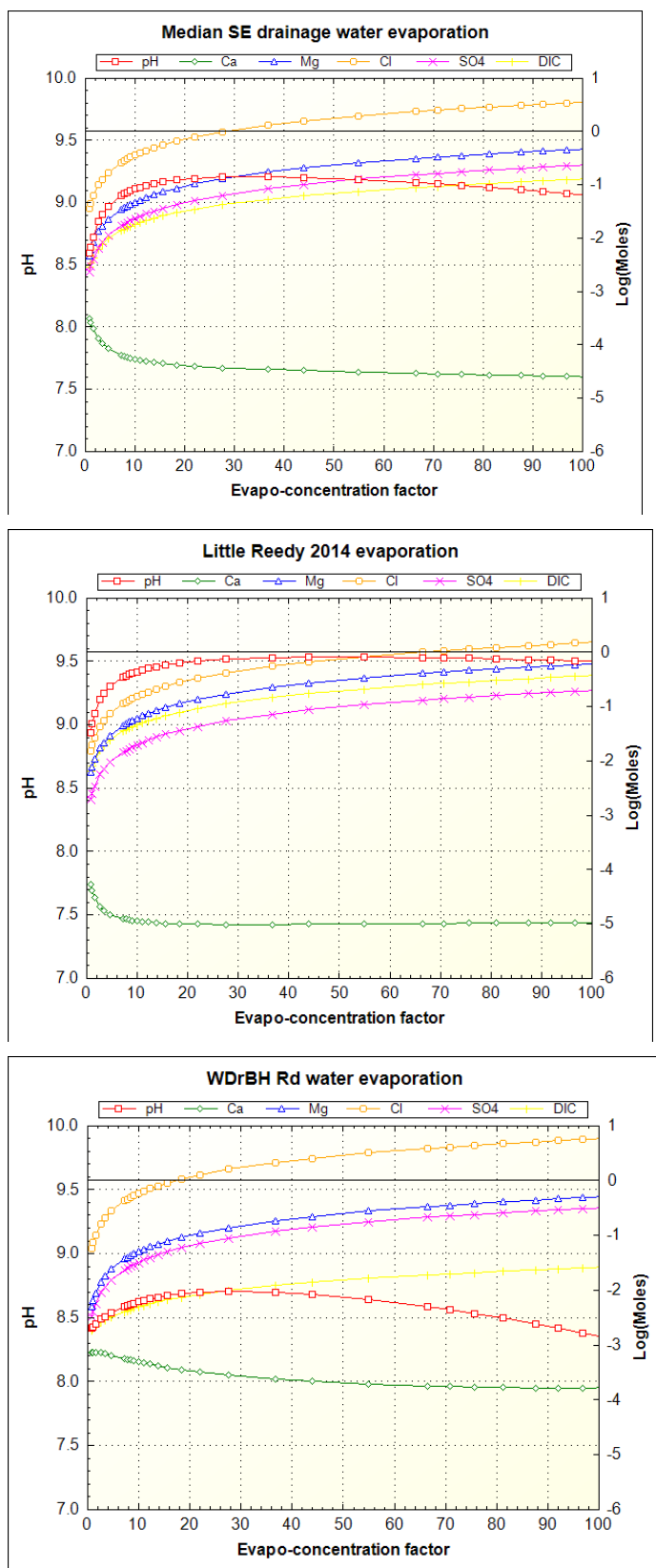
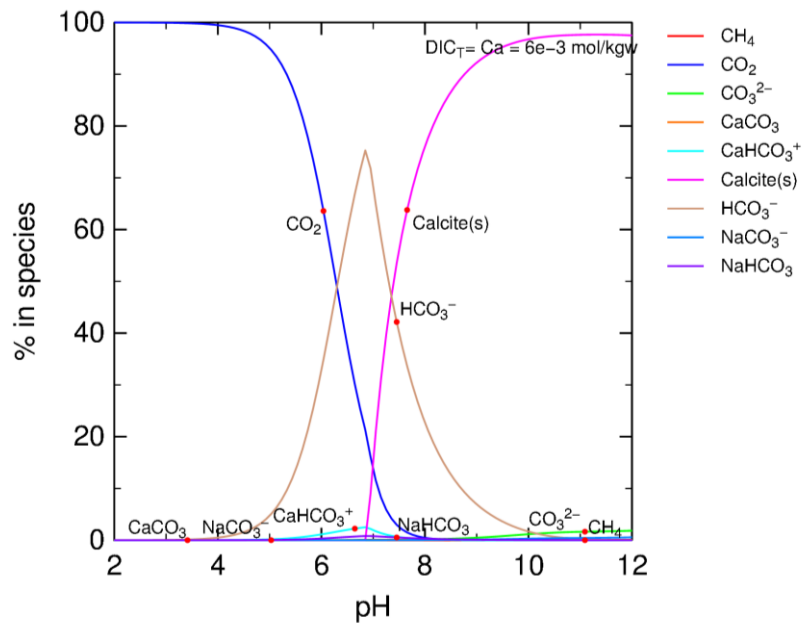


Figure 20. Simulation of hydro-geochemical evolution of high pH conditions during evaporation of the (top) median South East drainage water composition from Table 1, and (middle) Little Reedy drainage water composition at start of sampling period (10/2/2014, Fig. 4), and (bottom) sample (WDrBH Rd, Jan 2011) with a $\text{Ca}/(\text{HCO}_3 + \text{CO}_3)$ ratio (in meq/L) of 1 . All simulations were equilibrated with a pCO_2 approximating atmospheric values ($10^{-3.5}$ atm).

Carbon speciation – Equal Alkalinity/Ca ratio



Carbon speciation – low Alkalinity/Ca ratio

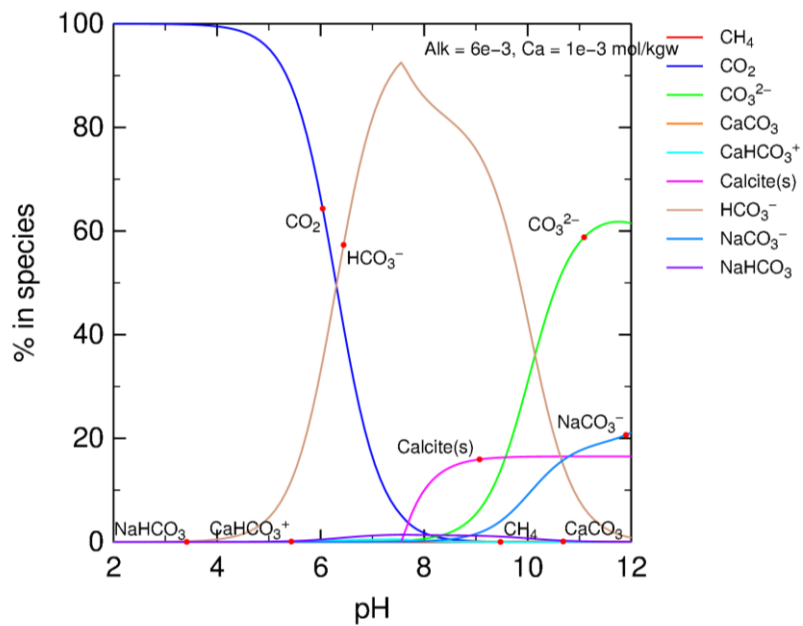


Figure 21. Predominance (zone of stability of major species) diagrams for the Na-Cl-Carbonate system at (top)

Discussion and Conclusions

There is strong evidence in support of our hypothesis that high pH conditions form in the South East wetlands when mineral precipitation and plant uptake remove Ca and Mg carbonates from the water during evaporative concentration. The finding of high pH in low Ca and Mg waters is consistent with the international literature on the development of sodium-carbonate dominated water composition, also known as a “soda” water type (Grant 2004). The South East waters are carbonate-rich, a likely consequence of the calcareous regional geology. When evapoconcentration of this water occurs it results in carbonate ion concentrations increasing, but when Ca and Mg concentrations are proportionally lower in concentration than carbonate these ions decrease to maintain equilibrium (see Appelo and Postma, 2005, for detailed discussion of this divergence effect). As the carbonate ion increases, pH increases (H^+ decreases) to maintain the equilibrium ($CO_3^{2-} + H^+ \leftrightarrow HCO_3^-$). This leads to development of the high pH “soda” systems.

As demonstrated above, when sufficient Ca is present (ie in similar equivalent concentrations to carbonate), pH typically remains buffered to around 8–8.5 as carbonate only increases during evapoconcentration until saturation with carbonate minerals is reached. The buffering to pH average of 8–8.5 was the case during the recent extreme drought in the Lower Lakes where large evapoconcentration effects occurred but alkalinity stabilised and pH did not continue to rise (Mosley et al. 2013).

Large diurnal trends in pH have been observed in many of the high pH wetlands in the South East, indicating a strong influence of primary production and respiration. Typically in many water systems these processes and atmospheric gas exchange would return pH to “normal” levels overnight leading to a diurnal cycle in pH, carbon dioxide and oxygen levels. However, this relies on sufficient exchange with the atmosphere and these wetlands with dense aquatic plant beds may have more restricted exchange.

The plants appear to also play a key role in uptake of Ca and Mg. The laboratory experiments in the light showed that Ca and Mg in the water was greatly reduced following photosynthesis of the plants (light treatment). Hence the plants may be critical to development of the low Ca, Mg geochemistry required to maintain a high pH baseline.

As noted above we observed sulfate concentrations declining in Little Reedy wetland during evaporation (Fig. 4) and this has been previously proposed to be driver of high pH conditions in the South East (Baldwin et al. 2012). Supply of additional carbonate from the sediment could occur via sulfate reduction (Kharaka et al. 1994) and this would assist in decreasing the $Ca/(HCO_3 + CO_3)$ ratio. However as sulfate reduction is a near ubiquitous process in coastal and saline landscapes but pH>9 conditions are not, it is considered unlikely to be primary driver in and of itself (Baumgarte 2003). The fact that Baldwin et al. (2012) observed apparent sulfate reduction in many wetland sediments that were not considered high pH systems is consistent with this.

We conclude that while evapoconcentration alone can lead to moderate increases in pH in wetlands, when plants are actively growing, the dominant effect is due to photosynthesis and the sequestration of divalent metals from the water column via plant uptake and mineral precipitation reactions.

Recommendations (for geochemistry/field component)

- Regular and ongoing monitoring of water geochemistry (pH, EC, all major ions, alkalinity) in wetlands susceptible to high pH conditions. Future research should certainly entail high frequency monitoring at a larger number of sites.
- Assessment of the ecological consequences of the high pH conditions. Despite their extreme pH values, soda lakes can have some of the highest productivities of any aquatic environment (Melack and Kilham 1974). Further biological monitoring in high pH systems in the SE is recommended to determine if any ecological impacts may be occurring.
- Direct measurements of dissolved CO₂ in wetlands would be useful to better determine the dynamics of atmospheric-plant-water exchange.
- The sources and pathways of the Ca, Mg and SO₄ ions which limit mineral precipitation in many of the lakes were outside the scope of this study. Chemical analysis of potential sources – such as upstream waters, soils and soil waters, sediments and plant matter – would provide an understanding of the real or potential availability of these ions, and thus the long term stability of pH buffering in these systems. Stable isotope analyses could also provide a valuable means of further constraining the geochemical cycles within these wetlands.
- Coupled groundwater-drain water-wetland hydro-geochemical studies and modelling should be undertaken.

General Conclusions

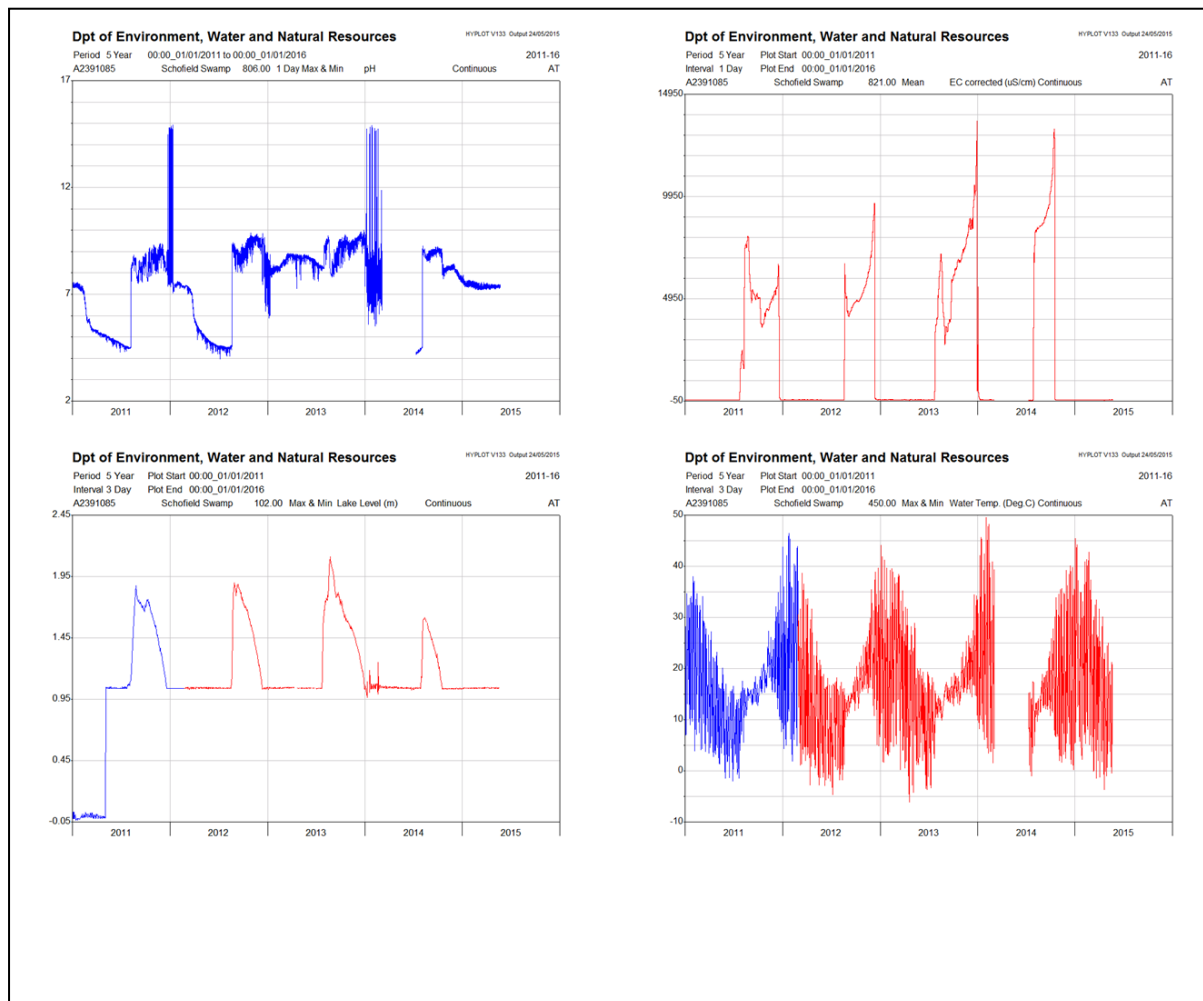
On the basis of environmental sampling, mesocosm studies and geochemical modelling, we propose that the high pH is a natural phenomenon driven by productive plant growth in the wetlands. It supports a diversity of plant life and a quick look under a microscope will show that the alkaline water is teeming with small biota. The high pH SE wetlands appear to be unable to maintain sufficient Ca and Mg carbonate precipitation, the main pH buffer preventing high pH (>9) developing in most water systems. However, because of the low buffering, organisms may be able to create microcosms of more moderate pH by excretion of small amounts of acid, a common phenomenon in plants.

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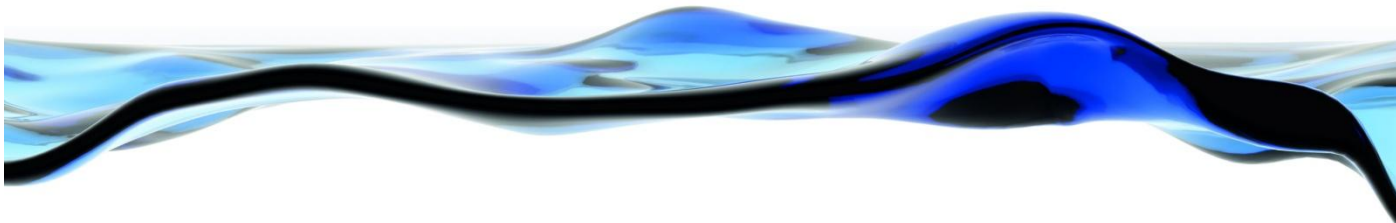
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Appendix A1. Five year telemetry data for Schofield Swamp



Appendix A2. Analytical data from water samples collected from wetlands in spring 2014

				Sampling date				
				29-Sep	7-Oct	13-Oct	22-Oct	27-Oct
Sample Description	Test Name	Result Name	Units					
Englands Wetland A2391101	Bromide	Bromide	mg/L	5.7	6.2	6.88	8.11	9.71
Englands Wetland A2391101	Calcium	Calcium	mg/L	43.2	44.9	49.1	59.6	67.4
Englands Wetland A2391101	Chloride	Chloride	mg/L	2440	2610	2870	3300	3860
Englands Wetland A2391101	Fluoride	Fluoride	mg/L	1.1	1.2	1.2	1.3	1.4
Englands Wetland A2391101	Potassium	Potassium	mg/L	32.4	34	37.4	47.6	52.5
Englands Wetland A2391101	Magnesium	Magnesium	mg/L	161	166	176	206	221
Englands Wetland A2391101	Sulphur	Sulphate	mg/L	318	330	363	402	423
Englands Wetland A2391101	Silica - Reactive	Silica - Reactive	mg/L	24	24	23	27	22
Englands Wetland A2391101	Alkalinity Carbonate	Alkalinity as Calcium Carbonate	mg/L	329	354	391	449	507
Englands Wetland A2391101	Alkalinity Carbonate	Bicarbonate	mg/L	132	172	170	205	312
Englands Wetland A2391101	Alkalinity Carbonate	Carbonate	mg/L	132	128	151	169	151
Englands Wetland A2391101	Alkalinity Carbonate	Hydroxide	mg/L	0	0	0	0	0
Englands Wetland A2391101	pH	pH	pH units	9.8	9.6	9.7	9.7	9.5
Englands Wetland A2391101	Ammonia as N	Ammonia as N	mg/L		0.12	0.03	0.008	0.008
Englands Wetland A2391101	Sodium	Sodium	mg/L		1480	1920	2010	2370
Schofields Swamp A2391085	Bromide	Bromide	mg/L	8.07	9.02	4.82		
Schofields Swamp A2391085	Calcium	Calcium	mg/L	111	108	31.2		
Schofields Swamp A2391085	Chloride	Chloride	mg/L	2930	3420	882		
Schofields Swamp A2391085	Fluoride	Fluoride	mg/L	1.6	1.8	1		
Schofields Swamp A2391085	Potassium	Potassium	mg/L	38.2	39.7	28.6		
Schofields Swamp A2391085	Magnesium	Magnesium	mg/L	213	223	83		
Schofields Swamp A2391085	Sulphur	Sulphate	mg/L	594	621	27		
Schofields Swamp A2391085	Silica - Reactive	Silica - Reactive	mg/L	<1	<1	5		
Schofields Swamp A2391085	Alkalinity Carbonate	Alkalinity as Calcium Carbonate	mg/L	450	476	595		
Schofields Swamp A2391085	Alkalinity Carbonate	Bicarbonate	mg/L	499	581	535		
Schofields Swamp A2391085	Alkalinity Carbonate	Carbonate	mg/L	24	0	94		
Schofields Swamp A2391085	Alkalinity Carbonate	Hydroxide	mg/L	0	0	0		
Schofields Swamp A2391085	pH	pH	pH units	8.5	8.2	9.1		
Schofields Swamp A2391085	Ammonia as N	Ammonia as N	mg/L	0.007	0.037	0.028		
Schofields Swamp A2391085	Sodium	Sodium	mg/L	1700	2010	719		
Little Reedy Swamp A2391086	Bromide	Bromide	mg/L	3.86	4.27	10.3	5.53	6.57
Little Reedy Swamp A2391086	Calcium	Calcium	mg/L	28.1	32.2	104	35.9	36.1
Little Reedy Swamp A2391086	Chloride	Chloride	mg/L	710	805	4130	918	1030
Little Reedy Swamp A2391086	Fluoride	Fluoride	mg/L	0.83	0.91	2	1	1.1
Little Reedy Swamp A2391086	Potassium	Potassium	mg/L	27.9	28.1	47.5	35	38.4
Little Reedy Swamp A2391086	Magnesium	Magnesium	mg/L	73.4	78.1	245	98.9	111
Little Reedy Swamp A2391086	Sulphur	Sulphate	mg/L	20.4	22.5	729	33.3	45.6
Little Reedy Swamp A2391086	Silica - Reactive	Silica - Reactive	mg/L	3	6	<1	8	9
Little Reedy Swamp A2391086	Alkalinity Carbonate	Alkalinity as Calcium Carbonate	mg/L	498	558	475	644	754
Little Reedy Swamp A2391086	Alkalinity Carbonate	Bicarbonate	mg/L	506	586	514	595	785
Little Reedy Swamp A2391086	Alkalinity Carbonate	Carbonate	mg/L	50	47	32	94	66
Little Reedy Swamp A2391086	Alkalinity Carbonate	Hydroxide	mg/L	0	0	0	0	0
Little Reedy Swamp A2391086	pH	pH	pH units	9.8	8.8	8.5	9.1	8.8
Little Reedy Swamp A2391086	Ammonia as N	Ammonia as N	mg/L	0.007	0.007	0.1	0.028	0.181
Little Reedy Swamp A2391086	Sodium	Sodium	mg/L	1340	528	2700	752	930



The Goyder Institute for Water Research is a partnership between the South Australian Government through the Department of Environment, Water and Natural Resources, CSIRO, Flinders University, the University of Adelaide and the University of South Australia.