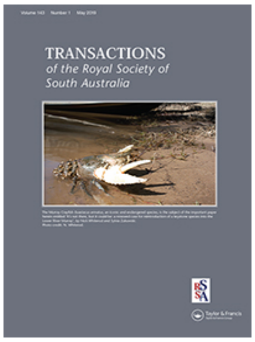

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Biogeochemical response of a secondary-salinised floodplain wetland to experimental freshening

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ABSTRACT
An experimental flooding with freshwater was used to evaluate the biogeochemical impacts of freshening in a semi-arid floodplain wetland that had undergone severe secondary salinisation (Loveday Disposal Basin, Australia). Filling the wetland with freshwater lowered electrical conductivity (EC) from ~60 to 13 dS m^{-1}. This freshening was accompanied by substantial declines in total P (TP), filterable reactive P (FRP), dissolved organic C (DOC), total organic N (TON), dissolved organic N (DON), NH_4^+ and molybdenum-reactive Si (MoR Si) concentrations. Owing to the semiarid climate, the water level receded and EC increased to pre-flooding conditions within seven months. During this drying phase, some chemical species maintained lower concentrations then pre-flooding (TP and FRP), others returned to within their original range (DOC, TON, DON), and others went above their original range (NH_4^+ and MoR Si), the latter reflecting some bank discharge of groundwater. Unexpectedly low turbidity and P concentrations during the drying phase were promoted by the development of an extensive filamentous algal mat following flooding, which limited sediment resuspension as the water level receded. The transient response to freshening highlights that salinity is a key driver of biogeochemical cycles in semi-arid wetlands.

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Salinity; wetlands; River Murray; nutrient cycling

Introduction

In the lower River Murray region (South Australia), a number of floodplain wetlands were converted into disposal basins during the twentieth century to store and evaporate excess irrigation drainage (Hostetler & Radke, 1995; Jolly, 1996; Simmons, Narayan, Woods, & Herczeg, 2002). The aim of these disposal basins was to prevent saline irrigation drainage from discharging into the river, at least outside of major flood events. However, recent management policies aim to remove disposal basins from River Murray floodplains and to return these wetlands to a more natural state when feasible. One proposed strategy to rehabilitate disposal basins and other lower River Murray wetlands is to periodically fill them with freshwater (Beasley et al., 2014). There are three potential limitations to this strategy. First, disposal basins tend to rapidly re-salinise following freshening events (Lamontagne, Hicks, Souter, Walter, & Wen, 2009). Secondly, saline River Murray wetlands (including those used as disposal basins) tend

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to have large sulphide deposits in their sediments (Hall, Baldwin, Rees, & Richardson, 2006; Lamontagne, Hicks, Fitzpatrick, & Rogers, 2006) which may result in wetland acidification and deoxygenation. Thirdly, whilst the potential risks and benefits of flooding and drying cycles in freshwater wetlands have been previously demonstrated in semi-arid rivers (Baldwin & Mitchell, 2000; Boulton & Jenkins, 1992; Nicol & Ganf, 2017; Nielsen et al., 2018; Ning, Petrie, Gawne, Nielsen, & Rees, 2015), whether this also applies to wetlands that have undergone extensive secondary salinisation is unclear.

The biogeochemical response of saline disposal basins to flooding with freshwater was evaluated at the Loveday Disposal Basin site (Figure 1). This site was ideally suited to test the effect of freshening on disposal basins because of the presence of a perennial saline wetland (Loveday – North), an ephemeral saline wetland (Loveday – South) and a perennial freshwater wetland (Mussel Lagoon). Loveday North and South also have large sulphide deposits that had been exposed to the atmosphere for several years prior to flooding (Lamontagne, Hicks, et al., 2006). The water balance, salinity (as total dissolved solids), pH and alkalinity responses to the experimental flooding have been previously reported (Lamontagne, Hicks, Souter, Walter, & Wen, 2008; Lamontagne et al., 2009). These studies concluded the endorheic (i.e. terminal sink) hydrology of disposal basins resulted in only a transient response to freshening because salt is not exported away but also mitigated the acidification risk by conserving alkalinity.

Here, we present the response of nutrient cycles to the freshening event by looking at the trends for suspended inorganic particles (as measured by total Fe concentrations – TFe), nitrogen (N), phosphorus (P), Dissolved Organic Carbon (DOC) and molybdenum-reactive Si (MoR Si). In addition, the biogeochemical response during the flooding and subsequent drying phases in the disposal basins was contrasted with the response of the nearby freshwater Mussel Lagoon, which also underwent a simultaneous wetting and drying cycle. We also evaluated how key drivers of biogeochemical cycles in floodplain wetlands, such as water level (Baldwin, Gigney, Wilson, Watson, & Boulding, 2008; Baldwin & Mitchell, 2000), salinity (Hart et al., 1991; Nielsen, Brock, Rees, & Baldwin, 2003), turbidity (Oliver, 1990), and groundwater – surface water interactions (Crosbie et al., 2009; Jolly, McEwan, & Holland, 2008; Lamontagne, Leaney, & Herczeg, 2005) were involved in changing nutrient concentrations during the freshening event.

Site description

Loveday Disposal Basin is located near the township of Barmera, in the State of South Australia on the lower reaches of the River Murray (Figure 1). The climate is semi-arid, with potential evapotranspiration (~2,000 mm $year^{-1}$) well in excess of precipitation (100–500 mm $year^{-1}$). The primary land-use in the vicinity of Loveday Basin is vineyards irrigated with River Murray water. Prior to the installation of weirs on the River Murray in the 1920s, the area of Loveday Basin would have been a depression supporting an ephemeral lignum swamp (Robinson et al., 2015). Following the installation of Lock 3 and the corresponding rise in River Murray pool level, this area became permanently inundated. However, control structures were built in the 1970s to isolate the wetland from the river. This enabled the use of the wetland as a disposal area for shallow groundwater collected by a drain system under nearby irrigated crops, as these

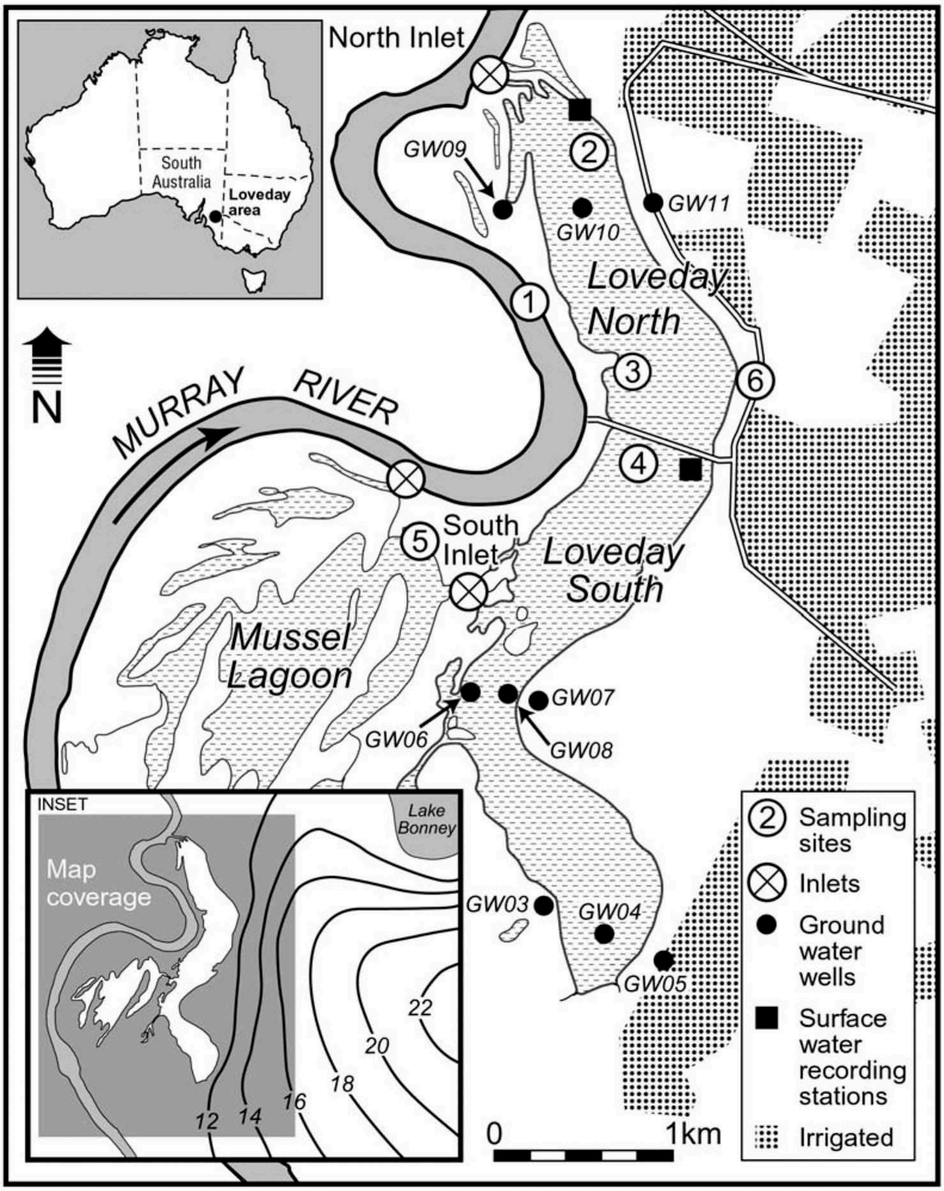

Figure 1. Location of Loveday Disposal Basin, Australia, and of the groundwater mound (inset) discharging saline groundwater to the area (hydraulic head in m Australian Height Datum). Also indicated are the surface water quality monitoring sites. Site 1 – River Murray; Site 2 – North end of Loveday – N; Site 3 – South end of Loveday – N; Site 4 – Loveday – S; Site 5 – Mussel Lagoon; Site 6 – Outlet of the drain system located under nearby irrigated areas.

waters were too saline to be released directly into the river. This drainage system prevents waterlogging in the root zone by rising water tables, a common problem for areas under irrigation in the region. The hydrogeological setting is typical of lower Murray floodplain environments, consisting of a surficial clay cover (or Coonambidgal Clay) of varying thickness (0–2 m) over an alluvial sand aquifer (the Monoman

Formation). Leakage from the Monoman Formation to Loveday Basin occurs either when this formation is exposed to the surface or by water table evaporation (capillary rise) through the Coonambidgal Clay (Doble, Simmons, Jolly, & Walker, 2006; Jolly, Walker, & Narayan, 1994; Wind, 1955). Overall, due to a higher regional water table on the inland side (Figure 1) and a higher river level when the River Murray remains at pool level, the Loveday Disposal Basin became a system from which the main water loss was evaporative (i.e. endorheic; see Lamontagne et al., 2009 for further details). As a result, a large store of salt has accumulated in and around the wetland in the form of Na-Cl brines in surface water, vadose water and groundwater (Herczeg, Dogramaci, & Leaney, 2001; Lamontagne et al., 2009).

Loveday Disposal Basin consists of a North and South basin (hereafter referred to as Loveday – N and Loveday – S) separated by a causeway but connected through several culverts. Following a reduction in drainage disposal in the 1990's, only a part of the North Basin remained permanently inundated. This water originates in part from leakage from the River Murray inlet (Electrical conductivity [EC] = 0.2–0.4 dS m^{-1}), discharge from the groundwater mound under the irrigation district (EC = 7–70 dS m^{-1}), and the drain system (EC = 2–4 dS m^{-1}). The basin sediments have elevated sulphide concentrations and emit noxious odours when exposed (Lamontagne, Hicks, et al., 2006). In order to prevent noxious odours, small releases of River Murray water from the North inlet were made between October 2005 and April 2006 to increase the water cover over the North Basin sediments. In contrast, during the same period, the shallower and slightly more elevated South Basin was ephemeral, maintaining a small pool of water during winter or for a few weeks following larger rain events in summer. Nearby Mussel Lagoon is a freshwater wetland with a regular input of River Murray water. Excess Mussel Lagoon water is discharged to the South Basin by a surface water outlet (Figure 1). Typical for River Murray wetlands, Loveday – N, Loveday – S and Mussel are relatively small (~100–200 ha), shallow (<1.5 m), and small variations in water levels can result in large areas of sediments to be exposed or inundated (see Lamontagne et al., 2009).

Flooding experiment

The monitoring program spanned three periods: 1) Pre-flooding; 2) Active flooding; and, Post-flooding drawdown (Table 1). Prior to the flooding experiment, the culverts between the North and South basins were closed off, thereby isolating the two basins. Flooding of the North Basin was undertaken by opening the Northern inlet control structure, while the South Basin was flooded using the outlet from Mussel Lagoon. Thus, in both cases River Murray water (EC = 0.2–0.4 dS m^{-1}) was used to flood the basins, but it first transited through the Mussel Lagoon in the case of the South Basin.

Table 1. Dates for the different periods of the monitoring program in Loveday North and South Basin. The inlet from the River Murray to Mussel Lagoon was also closed on 1 October 2006, following which Mussel started to dry.

Period	Loveday – North	Loveday – South
Pre-Flooding	31 May 2005–24 May 2006	31 May 2005–8 June 2006
Flooding	25 May 2006–11 August 2006	9 June 2006–1 September 2006
Post-flooding	12 August 2006–7 March 2007	2 September 2006–7 March 2007

Methods

Field sampling

Six sites were sampled on an approximately monthly basis from May 2005 to March 2007. Sites included the River Murray (Site 1 on Figure 1), both ends of the North Basin (Site 2 and Site 3), the South Basin near the causeway (Site 4), Mussel Lagoon (Site 5), and the outlet of the irrigation drainage system (Site 6). Two sites were sampled in Loveday – North because its northern and southern ends are poorly connected at very low water levels and effectively become sub-basins. Surface water was collected by submerging a well-rinsed 1-L Nalgene HDPE bottle below the surface by wading from the shoreline up to ~50 cm water depth, or as far as practical. Drain discharge samples were collected from the weir pool at its outlet. During the flooding period and despite its shallowness (0.4–1.2 m), the North Basin was density-stratified for about a month (6 June – 4 July 2006; Lamontagne et al., 2009) because the incoming freshwater did not readily mix with the resident saline water. During the stratification period, integrated samples of the water column at sites 2 and 3 were collected by inserting a tube vertically up to the sediment surface, capping the top, and rapidly emptying the contents in a well rinsed 1-L bottle. As both the mixolimnion (the surface layer initially containing mostly freshwater) and the chemolimnion (the underlying original saline water) were initially very thin (tens of cm) and difficult to sample individually, the integrated vertical profiles were a pragmatic approach to avoid biasing the sampling. At the deeper Site 2, an inflatable raft was used to collect the integrated water samples and to measure vertical salinity profiles. When no surface water was present at sites 3 (North Basin) or 4 (South Basin) during the pre-flooding period, a pit was dug and a shallow groundwater sample collected instead at the same location as where the water samples would have been collected.

Sample processing and analysis

All water samples were processed in the field shortly following collection. At each site, duplicate 10 mL unfiltered subsamples were pipetted into ultra-clean borosilicate glass tubes for Total P (TP), Total N (TN) and Total Fe (TFe) analyses. Approximately 120 mL was filtered with disposable 0.45 µm Supor membrane filters (Pall) using a syringe (Terumo 50 mL with a Luer lock) and three-way valve system (BD Connecta Plus 3) that minimised sample contact with the atmosphere (to prevent the oxidation of redox-sensitive chemical species if present). One filtered 10 mL subsample was stored in an ultra-clean borosilicate glass tube for DOC analysis. One filtered 60 mL sample was acidified to pH < 2 using high purity HCl and stored in a well-rinsed amber 125-mL PTFE bottle for analysis of major cations, Total Dissolved N (TDN), NH_4^+, NO_3^-, Filterable Reactive P (FRP) and MoR Si. The remaining 60 mL filtered sample remained unacidified and was used for laboratory Electrical Conductivity (EC) and anion concentration measurements. All samples were kept on ice in the field and stored at 4°C in the laboratory. To prevent contamination (especially from high DOC in some of the saline samples), freshwater samples (River Murray and Mussel) were collected first during the sampling trips and filtered using separate equipment. At the end of each sampling trip a field blank was processed in the same manner as the samples, using deionised water.

All analyses were performed at the CSIRO Waite Campus Analytical laboratory (Adelaide). TP and TFe samples were first hot-digested with HNO_3 and H_2SO_4 and then brought back to neutral pH. TFe was measured by Inductively Coupled Plasma Optical Spectroscopy (ICPOS; Spectroflame Modula). TN, TDN and DOC concentrations were measured using a high temperature TOC/TN analyser (Skalar Fourmacs). TP, FRP, NH_4^+, NO_3^-, and MoR Si were measured by segmented flow analysis (Alkem). Chloride concentrations were measured by ion chromatography (Dionex ICS – 2500). Laboratory EC was measured in a constant temperature room using daily-calibrated probes (Meterlab CDM230). Total organic N (TON) was estimated as TN – NH_4^+ – NO_3^-, dissolved organic N (DON) as TDN – NH_4^+ – NO_3^-, and total organic P (TOP) as TP – FRP. Total dissolved P was also measured by ICPOS. However, most samples were at the detection limits (3–6 µmol L^{-1} for saline samples and 0.3–1.6 µmol L^{-1} for freshwater samples) and these results are not presented here. A few samples for TN, TP, DOC and TFe were lost in early 2006 (i.e. during the pre-flooding period) following a laboratory mishap.

Results

Changes in Electrical Conductivity

Flooding of Loveday – N and Loveday – S was initiated on 25 May 2006 and on 9 June 2006, respectively (Table 1). The water level in both wetlands increased by about 1 m over a 6-week period (Figure 2(a,b)), following which their respective inlets were closed. While a similar volume of water was added to both basins, the surface area flooded was larger in Loveday S (from 10 to 180 ha) than in Loveday – N (from 70 to 120 ha) owing to different morphometry and antecedent water level conditions (Lamontagne et al., 2009). EC declined in both basins from 40–60 dS m^{-1} prior to flooding (and from >90 dS m^{-1} in residual pools at Site 3) to ~13 dS m^{-1} at the end of the flooding period (Figure 3). Following closure of the inlets, water level in both basins gradually receded and both water level and EC had returned to pre-flooding conditions by March 2007. The inlet from the River Murray to Mussel Lagoon was also closed on 1 October 2006 which resulted in this wetland gradually drying out (about 2/3 loss of volume) and EC increasing (from 0.37 to 0.99 dS m^{-1}) between October 2006 and March 2007. EC in shallow groundwater collected from the pits was variable but higher on average than in Loveday surface water (Table 2).

Total Iron (TFe)

During the pre-flooding period, the River Murray and Mussel Lagoon had relatively high suspended inorganic particle concentrations, with TFe ranging between 14–97 and 2.7–130 µmol L^{-1}, respectively (Table 2). During the same period, TFe in Loveday – N and Loveday – S was generally between <3 to 15 µmol L^{-1} but occasionally peaked to >50 µmol L^{-1}. During and following flooding, TFe concentrations were usually <3 µmol L^{-1} in both Loveday – N and Loveday – S (Figure 4). In contrast, during its drying phase, TFe increased markedly in Mussel Lagoon and

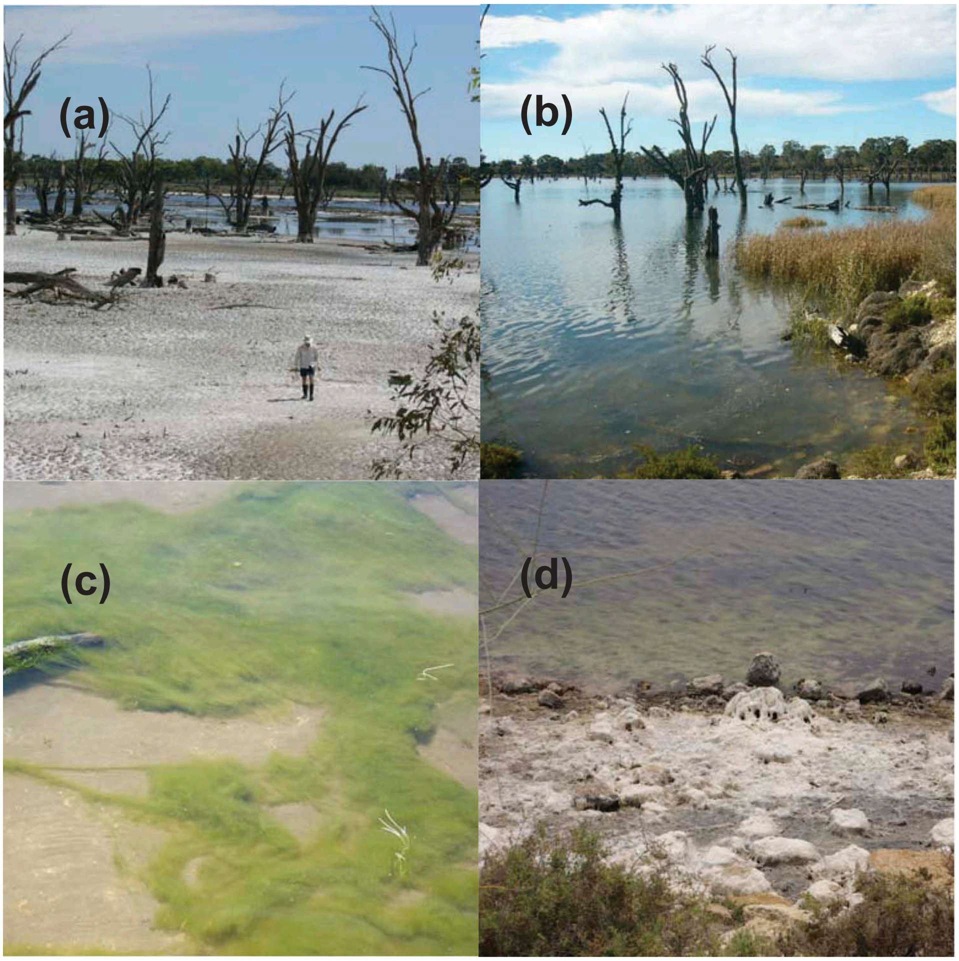

Figure 2. (a) Loveday – N at Site 3 prior to flooding (10 January 2006); (b) Loveday – N at Site 3 during flooding (4 July 2006); (c) Filamentous algal mat (14 November 2006); (d) Desiccated and bleached algal mat along an exposed shoreline during the post-flooding phase (19 December 2006).

ranged between 100–250 µmol L^{-1}. Thus, despite flooding with turbid water, Loveday – N and Loveday – S maintained lower suspended inorganic particle concentrations than prior to flooding, and this tendency persisted in the subsequent drying phase.

Dissolved Organic Carbon (DOC)

While DOC concentration was <1.4 mmol L^{-1} in the River Murray and Mussel Lagoon pre-flooding, elevated DOC concentrations were found in Loveday – N (6.9–12 mmol L^{-1}) and Loveday – S (2.8–4.8 mmol L^{-1}) during this period (Figure 5). DOC concentrations decreased to ~1.6 mmol L^{-1} in both basins during the flooding period but had returned to pre-flooding concentrations by March 2007.

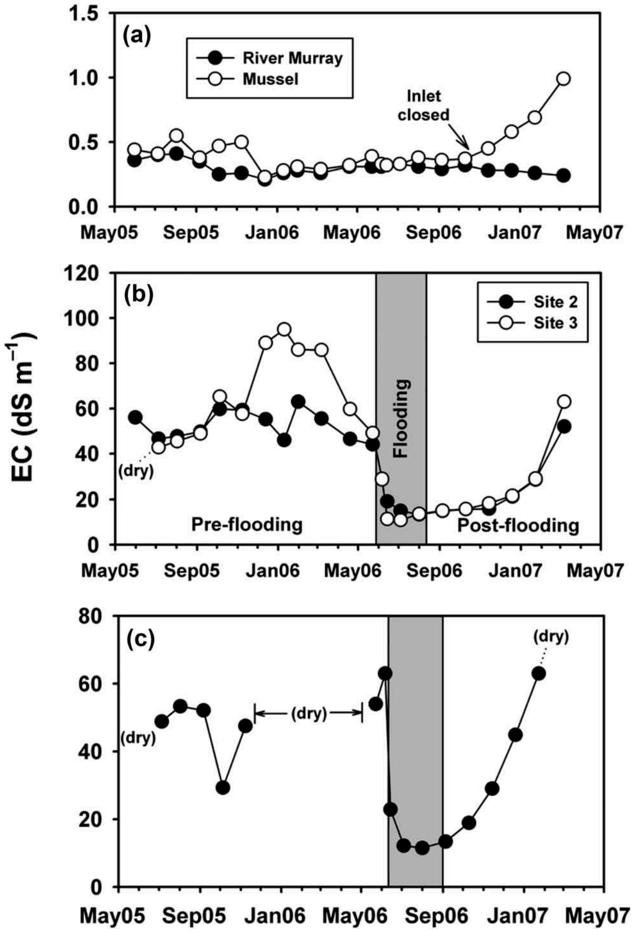

Figure 3. Change in electrical conductivity in (a) River Murray and Mussel Lagoon; (b) Loveday – N; (c) Loveday – S. Note that Site 3 in Loveday – N is nearly completely dry and partially disconnected from the rest of Loveday – N at low water levels, resulting in higher salinities than the rest of the basin during summer months. Also indicated are the pre-flooding, flooding and post-flooding periods in each basin. Note that Loveday – N was flooded earlier than Loveday – S (see also Table 1). Also note that the inlet from Mussel Lagoon to the River Murray was closed in October 2007, at which point this wetland also started to dry.

Phosphorus

TP and FRP concentrations in the River Murray were lower relative to Mussel Lagoon and the Loveday basins, averaging 1.2 and 0.098 μmol L^{-1}, respectively, during the pre-flooding period. Both TP and FRP tended to be slightly higher in Mussel Lagoon than in the River Murray (Figure 6). However, TP and possibly FRP concentrations pre-flooding were notably higher in Loveday – N and Loveday – S than in either freshwater body. For example, in Loveday – N, pre-flooding TP concentrations ranged between 5–19 μmol L^{-1} and FRP between <0.1–2.1 μmol L^{-1}. However, there was a distinct pattern in TP in Loveday – N pre-flooding, with concentrations gradually decreasing over time (Figure 6). TP concentrations in Loveday – N and Loveday – S declined to <5 μmol L^{-1}

Table 2. Mean and range in EC and chemical species concentration in various sources of water during the pre-flooding period at Loveday Disposal Basin. All concentrations in μmol L^{-1} unless otherwise shown.

	River Murray		Loveday – N		Mussel Lagoon		Drain		Pits	
Lab EC (dS m^{-1})	0.31	(0.21–0.41)	52	(44–63)	0.38	(0.23–0.55)	3.4	(2.4–4.4)	60	(14–100)
TFe	45	(14–97)	11	(2.7–48)	36	(2.7–130)	3.6	(2.7–7.2)	–	–
TP	1.0	(<0.5–2.8)	12	(5–19)	1.9	(<0.5–5.5)	1.2	(0.30–3.2)	–	–
FRP	0.098	(<0.08–0.22)	0.63	(<0.1–2.1)	0.30	(<0.08–1.5)	0.56	(<0.08–2)	14	(0.97–42)
TOP	0.97	(<0.5–2.6)	11	(4.6–19)	1.7	(<0.5–5.1)	–	–	–	–
DOC (mmol L^{-1})	0.54	(0.19–0.72)	8.6	(6.9–12)	0.73	(0.057–1.4)	1.7	(0.17–3.2)	5.1	(0.24–15)
TON	110	(77–180)	740	(480–990)	130	(64–240)	–	–	–	–
DON	39	(<15–85)	530	(290–880)	37	(<15–76)	–	–	150	(36–310)
NH_4^+	1.1	(<0.3–3.7)	73	(38–130)	1.2	(<0.3–4)	5.5	(<0.3–23)	170	(110–240)
NO_3^-	0.29	(<0.3–0.8)	2.1	(<0.3–21)	1.2	(<0.3–6.4)	1300	(720–2500)	16	(1.3–66)
MoR Si	9.5	(2.5–23)	34	(8.1–110)	31	(7.3–91)	330	(220–500)	571	(160–1250)
DOC:DON	23	(8–39)	17	(12–24)	30	(16–56)	–	–	35	(10–75)
TON:TOP	82	(35–120)	62	(51–85)	82	(17–207)	–	–	–	–

during flooding and only started to increase late in the post-flooding period. FRP was also generally lower in both basins during the flooding and post-flooding periods (Figure 6). In contrast to the disposal basins, TP in Mussel Lagoon increased from <1 μmol L^{-1} to >12 μmol L^{-1} during its drying phase.

Nitrogen

Pre-flooding TON (64–240 μmol L^{-1}) and DON concentrations (<5–88 μmol L^{-1}) were similar in the River Murray and Mussel Lagoon (Table 2). However, pre-flooding TON and DON concentrations were higher in the disposal basins. For example, in Loveday – N, TON and DON concentrations ranged between 480–990 μmol L^{-1} and 290–880 μmol L^{-1}, respectively. TON and DON concentrations decreased in the two basins following flooding, especially for TON (Figure 7), but were back within the pre-flooding range by the end of the post-flooding period. TON and DON concentrations also increased well above pre-flooding levels in Mussel Lagoon as it was drying (Figure 7). Shallow groundwater from pits had elevated DON concentrations (36–310 μmol L^{-1}; Table 2).

NH_4^+ and NO_3^- concentrations were low in the River Murray and in Mussel Lagoon throughout the monitoring program (usually between <0.3–4 μmol L^{-1}). However, NH_4^+ was high in Loveday – N and Loveday – S during the pre-flooding period, ranging from 38–130 μmol L^{-1} (Table 2). NH_4^+ concentrations decreased to <20 μmol L^{-1} during the flooding period in both basins, but the highest NH_4^+ concentrations (>160 μmol L^{-1}) were observed at the end of the post-flooding period (Figure 8). In contrast, NO_3^- usually remained near or at the detection limit in the disposal basins during and following flooding. Shallow groundwater from the pits generally had high NH_4^+ (110–240 μmol L^{-1}) and NO_3^- concentrations (13–66 μmol L^{-1}). Drain discharge to Loveday – N had very high NO_3^- concentrations (720–2500 μmol L^{-1}).

Molybdenum-Reactive Si (MoR Si)

Pre-flooding MoR Si concentrations were lowest in the River Murray (2.5–23 μmol L^{-1}) when compared to Mussel Lagoon (7.3–91 μmol L^{-1}) or the disposal basins (8.1–200 μmol L^{-1}; Table

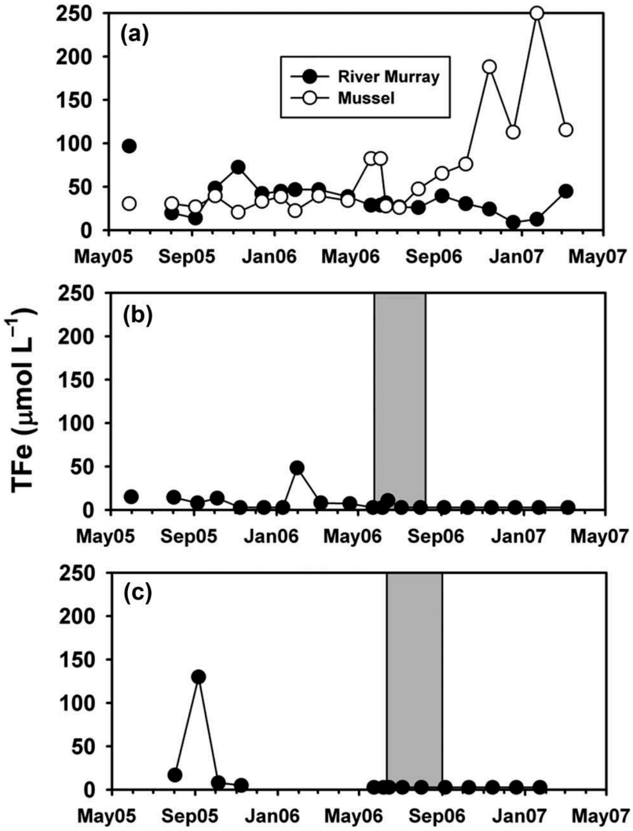

Figure 4. Total Fe concentration (a measure of suspended inorganic particle concentration) in (a) River Murray and Mussel Lagoon, (b) Loveday – N (Site 3) and (c) Loveday – S. Shaded areas represent the flooding period in Loveday – N and Loveday – S.

2). Unlike most other chemical species, MoR Si concentrations in Loveday – N during the flooding period remained within the range observed pre-flooding (Figure 9). However, MoR Si concentrations increased to well above the pre-flooding range in Loveday – N (>200 μmol L^{-1}) during the post-flooding period. The patterns in MoR Si were more complex in Loveday – S. MoR Si first peaked late in the pre-flooding period (but after flooding had been initiated in Loveday – N), decreased to <10 μmol L^{-1} during flooding, and then increased to >200 μmol L^{-1} post-flooding. Both drain discharge (220–500 μmol L^{-1}) and shallow groundwater (160–1250 μmol L^{-1}) had greater MoR Si concentrations than nearby surface waters (Table 2).

In summary, flooding a saline disposal basin with freshwater temporarily lowered salinity, DOC concentration, and the concentration of most nutrients. However, suspended inorganic particle concentrations (as TFe) did not increase despite flooding the basins with turbid water. During the subsequent drying phase, salinity, DOC, TON and DON gradually returned to pre-flooding concentrations. However, TP and suspended inorganic particle concentrations remained lower, while NH_4^+ and MoR Si increased to above pre-flooding concentrations. Drying also impacted on water quality in the freshwater Mussel Lagoon, with large increases in TFe, TON, TP and MoR Si concentrations. In addition, the increase in NH_4^+ and MoR Si late in the post-flooding period in the

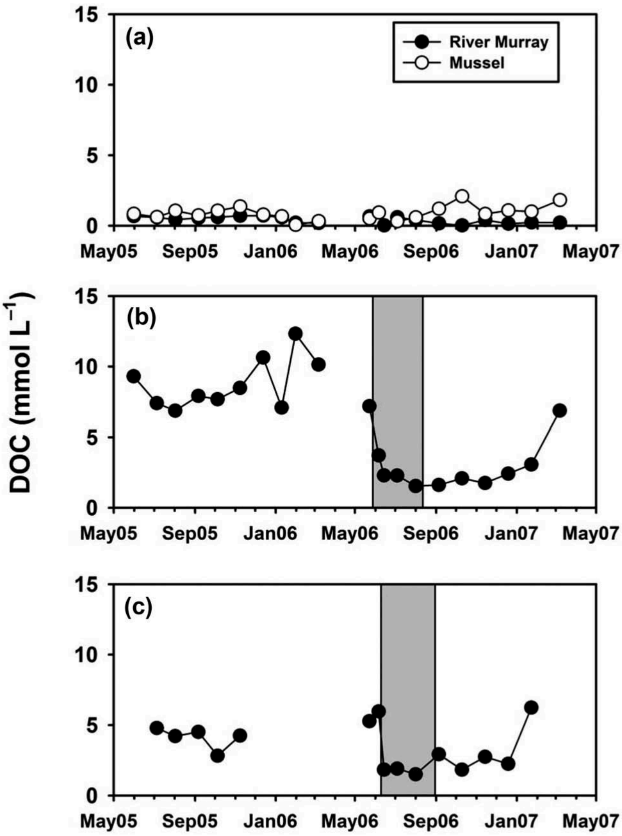

Figure 5. DOC concentration in the (a) River Murray and Mussel Lagoon; (b) Loveday – N (site 3); (c) Loveday – S.

disposal basins (when water levels were dropping most rapidly) suggests that an input of shallow groundwater may have occurred at that time because groundwater tends to be enriched in these chemical species in the vicinity of the wetlands (as inferred from the pit samples; Table 2).

Discussion

The response of Loveday Disposal Basin to experimental freshening and drying was complex, in part because several of the environmental drivers of small floodplain wetlands, such as water level, salinity, turbidity and groundwater – surface water interactions, were simultaneously impacted. Early during the flooding period, the principal factor changing chemical concentrations was dilution with River Murray water. The largest input of water to the disposal basins during the experiment was surface water from the River Murray and the main loss was by evaporation (Lamontagne et al., 2009). Thus, conservative chemical species in Loveday should have roughly followed the trends in salinity during the experiment. Salinity itself would have been largely conservative because the brine was mostly Na–Cl and concentrations always remained below halite saturation (Lamontagne et al., 2009). While most

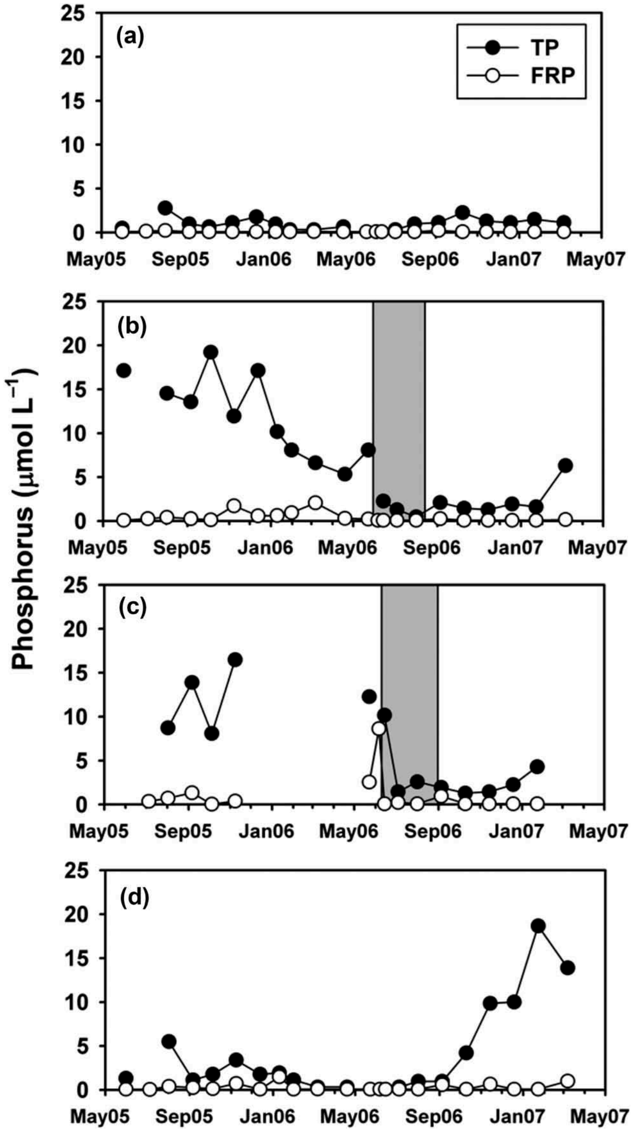

Figure 6. Phosphorus concentrations in (a) River Murray; (b) Loveday – N (Site 3); (c) Loveday – S; (d) Mussel Lagoon.

chemical species considered did have a dilution effect upon flooding (Figure 10), other factors were also involved in determining their concentrations before or after flooding. The relative role of geochemical, biological and hydrological processes in determining nutrient concentrations post-flooding is discussed in the following.

DOC

DOC was the only chemical species evaluated that was apparently conservative during the Loveday flooding and drying cycle (Figure 10(a)). DOC concentrations

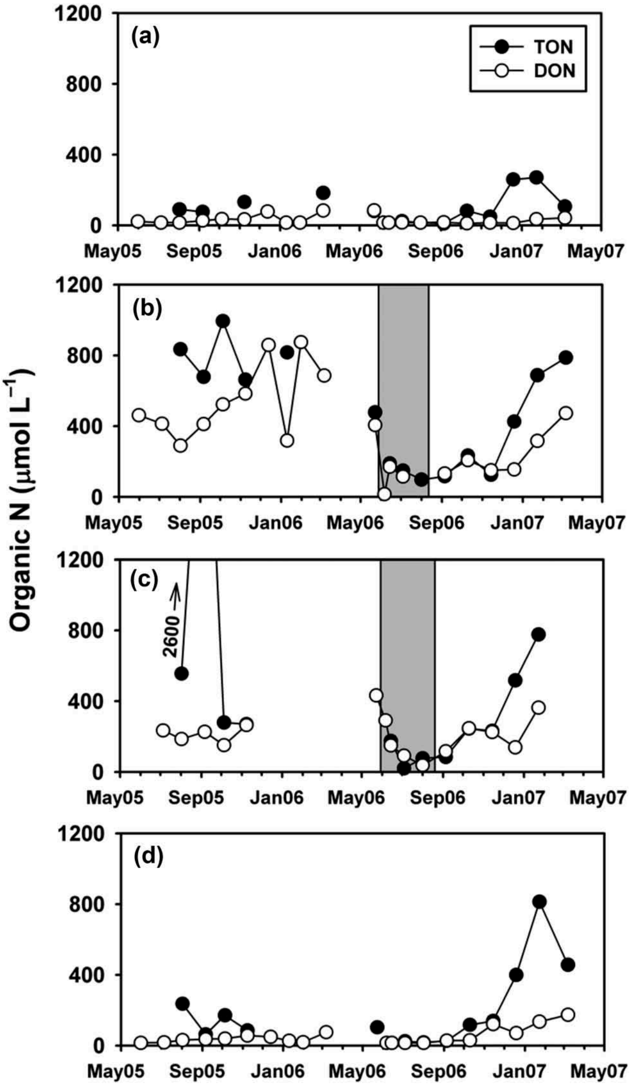

Figure 7. Organic N concentrations in (a) River Murray; (b) Loveday – N (Site 3); (c) Loveday – S; (d) Mussel Lagoon.

were elevated in the disposal basins, but were not outside of the range found in other endorheic environments (Curtis & Adams, 1995; Ford, 2007). For example, in the Coorong (an inverse estuary at the end of the Murray-Darling Basin), DOC concentrations increased from ~300 to ~3,000 μmol L^{-1} along an estuarine (EC < 50 dS m^{-1}) to hypersaline (EC > 150 dS m^{-1}) salinity gradient (Ford, 2007). Curtis and Adams (1995) proposed that the dissolved organic matter (DOM) pool in semi-arid saline Alberta lakes is mostly allochthonous (i.e. terrestrially derived) in origin and refractory because of long-term exposure to biological and geochemical degradation. However, the DOC:DON ratios in the Loveday basins (~17), the River Murray (~23) or Mussel Lagoon (~30) were generally lower than in

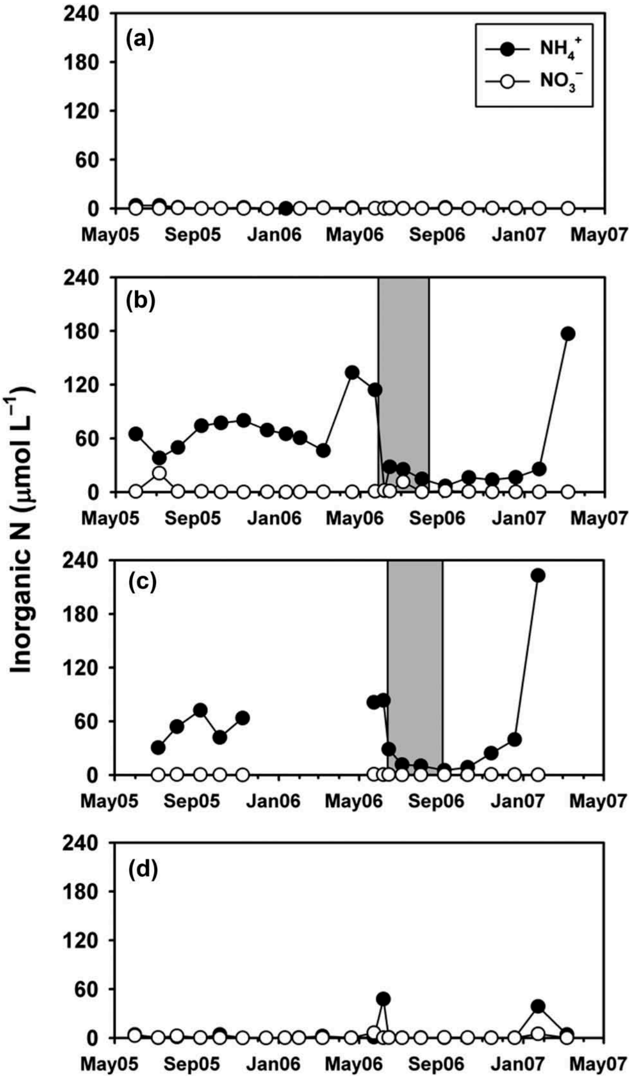

Figure 8. Inorganic N concentrations in (a) River Murray; (b) Loveday – N (Site 3); (c) Loveday – S; (d) Mussel Lagoon.

saline Alberta lakes (25–75). This indicates that Loveday DOM may be primarily autochthonous (that is, river or wetland derived) because aquatic DOM sources are thought to have lower C:N ratios than terrestrial sources (McKnight, Andrews, Spaulding, & Aiken, 1994; Schindler et al., 1992). This is consistent with the current understanding for organic C cycling in the lower River Murray, where extensive river regulation has disconnected the river channel from surrounding floodplains (Gawne et al., 2007; Oliver & Merrick, 2006; Robertson, Bunn, Boon, & Walker, 1999). Conditions at the time of the study (Millenium Drought) would not have been conducive to a large input of floodplain DOC to the River Murray as overbank flooding had not occurred locally for over a decade (Lamontagne et al., 2009).

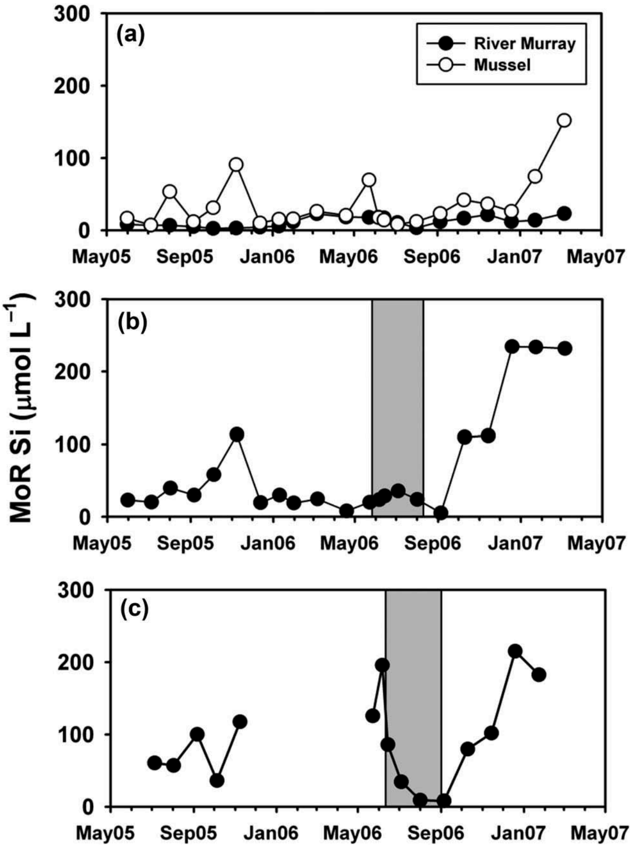

Figure 9. MoR Si concentrations in (a) River Murray and Mussel Lagoon; (b) Loveday – N (Site 3); (c) Loveday – S.

The source of DOC to the Loveday Basins was probably not the key factor determining its conservative behaviour during the experiment. Regardless of the origin of the DOC, the long water residence times in the basins (essentially infinite due to their endorheic nature) would result in only the most refractory DOC compounds not being photo- or biologically-degraded over time. However, the composition and cycling of DOM in River Murray wetlands remains largely unknown (Baldwin, 1999; Howitt, Baldwin, Rees, & Hart, 2008; McDonald, Pringle, Prenzler, Bishop, & Robards, 2007).

Turbidity

The River Murray is turbid in part because of high suspended inorganic particle concentrations, which accounts for more than half of the light absorption through the water column (Oliver, 1990). Suspended particles are maintained in the water column by turbulence and removed by coagulation and sedimentation, the latter processes are facilitated by higher cation concentrations (Grace, Hislop, Hart, & Beckett, 1997). Suspended particle concentrations can be lower in floodplain wetlands, especially when they become disconnected from the river outside of flood events. However, water level draw downs tend to increase suspended sediment concentrations

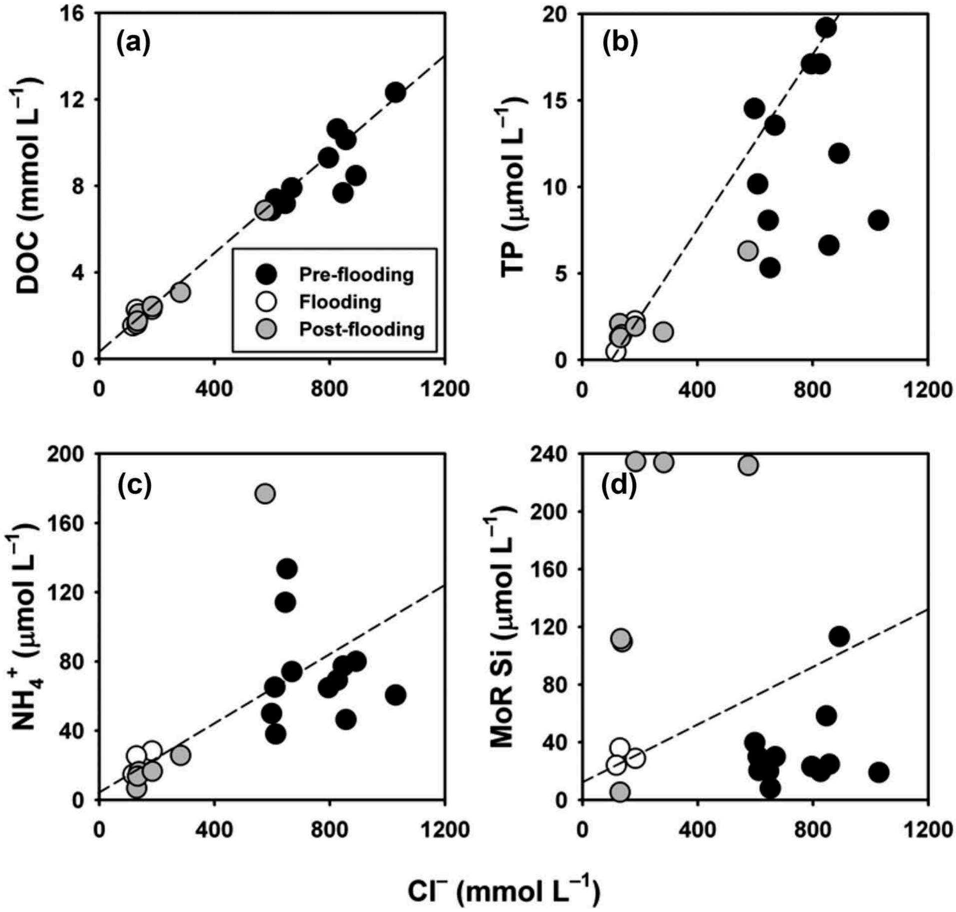

Figure 10. Comparison of Cl^- concentrations (a conservative chemical species) relative to (a) DOC; (b) TP; (c) NH_4^+; (d) MoRSi. Si concentrations in the disposal basin are partially controlled by equilibrium with a mineral phase (Lamontagne et al., 2009). The dashed lines represent the expected evapoconcentration trends during the post-flooding phase.

by exposing deeper, finer-grained sediments to wave-mixing (Aldridge, Lamontagne, Deegan, & Brookes, 2011; Bloesch, 1995).

Despite adding turbid water to Loveday – N and Loveday – S, the basins maintained lower suspended sediment concentrations during than before flooding. EC in both basins remained well within the range (EC > 13 dS m^{-1}) where cation concentrations should have been sufficient to favour enhanced rates of sedimentation from the water column. For example, Grace et al. (1997) found that turbidity was lowered six-fold following an increase in EC from 0.21 to 1.4 dS m^{-1} along a 9 km stretch of the Darling River where mixing with saline groundwater discharge takes place. Raising the water level by about one metre in the Loveday basins during flooding may also have been sufficient to diminish wave-driven sediment resuspension. However, unlike in nearby Mussel Lagoon, suspended inorganic sediment concentrations remained low in both Loveday basins when they subsequently dried. We hypothesise that sediment resuspension was prevented during the drying phase by the presence of extensive filamentous algal mats. These mats had developed in both basins during and following flooding (Figure 2(c)). The mats were several mm thick, covered most of the shallow areas in the basins, and persisted for several months in the form of desiccated, bleached mats once exposed (Figure 2(d)). In addition to low suspended particle concentrations, the growth of the biofilm may have been facilitated by higher light penetration through the water column because of lower phytoplankton biomass (see *Phosphorus* below) and DOC concentrations following flooding. These are also two important contributors to light attenuation in River Murray wetlands (Oliver, 1990). In contrast to the Loveday basins, no filamentous algal mat was present in the turbid Mussel Lagoon during its drying phase.

Phosphorus

Wetting-drying cycles play an important role in P cycling in River Murray wetlands (Baldwin & Mitchell, 2000; Scholz, Gawne, Ebner, & Ellis, 2002). The partial drying of sediments can decrease the availability of P by generating sorption sites, while complete desiccation or flooding may increase P availability through mineralisation and sediment anoxia, respectively (Baldwin & Mitchell, 2000). However, the flooding of Loveday – N and Loveday – S did not result in an increase in TP concentration, as would have been expected in freshwater wetlands. TP concentrations decreased in the basins following flooding because TP concentrations in the River Murray were lower than in Loveday – N and Loveday – S. The higher TP concentrations in the basins prior to flooding were probably caused by a greater algal biomass in the basins than in the River Murray (Dillon & Rigler, 1974; Oliver, 1993).

Several processes could have favoured a greater algal biomass in the disposal basins than in the River Murray or nearby freshwater wetlands. Lower suspended sediment concentration may have improved the light regime (Oliver, 1990; Schallenberg & Burns, 2004) or diminished the competition for bioavailable P between algae and suspended sediments (Hansen, Phlips, & Aldridge, 1997; Oliver, Hart, Douglas, & Beckett, 1993). Greater rates of sulfate reduction in saline wetland sediments could result in greater P availability, for example by converting Fe oxides, which tend to sorb P, into iron sulphides (FeS) which do not (Caraco, Cole, & Likens, 1989; Roden & Edmonds, 1997). This is consistent with the tendency to find higher reduced S concentrations in disposal basins sediments than in nearby freshwater wetlands (Lamontagne, Hicks, et al., 2006).

The PON:TOP ratios in the River Murray (82), Mussel Lagoon (82) and the Loveday basins (62) were all well above Redfield (16), suggesting that primary production was more likely P than N-limited (Table 2; Hecky, Campbell, & Hendzel, 1993). The River Murray system was experiencing a regional drought at the time of the study (CSIRO, 2008). Historically, there is a tendency for lower nutrient concentrations and higher N:P ratios during extended low flow periods in the lower River Murray (Cook, Aldridge, Lamontagne, & Brooks, 2010; Mackay, Hillman, & Rolls, 1988). This can be attributed to lower inputs of P-rich floodplain sediments in the absence of overbank flow events and the increased likelihood of N-fixing cyanobacterial blooms under low flow conditions (Baker, Brookes, Burch, Maier, & Ganf, 2000; Baldwin & Mitchell, 2000).

TP concentrations remained relatively low in the disposal basins for most of the post-flooding period, while TP concentrations increased markedly in Mussel Lagoon as it was simultaneously drying. The recovery of phytoplankton biomass in the disposal basins following flooding may have been slowed by competition for nutrients with the developing filamentous algal mats. In addition, grazing by large filter feeding zooplankton (Ostracoda, Daphniidae and *Bosmina* spp.) which were either not present or had a lower biomass pre-flooding (D. Nielsen, CSIRO Land and Water, *unpublished data*), may have slowed the re-establishment of a large phytoplankton biomass. Decay of exposed filamentous algal mats and the disappearance of several large zooplankton taxa as the basins dried and re-salinised may have favoured the return of a higher phytoplankton biomass during the later stages of the post-flooding period. Increased rates of sediment and meroplankton re-suspension may have favoured greater TP concentrations in Mussel Lagoon during its drying phase (Schallenberg & Burns, 2004).

Nitrogen

The effects of salinity (Ehlrich, 2002; Rysgaard, Thastum, Dalsgaard, Christensen, & Sloth, 1999) and wetting and drying cycles (Baldwin & Mitchell, 2000; Scholz et al., 2002; Woodward, Fellows, Mitrovic, & Sheldon, 2015) on the inorganic N cycle have been reviewed in detail elsewhere and will only be briefly be discussed here. In general, inorganic N concentrations were low in the River Murray and in Mussel Lagoon, but NH_4^+ concentrations were elevated in the two disposal basins. The unusually low inorganic N concentrations in the River Murray during the study (Cook et al., 2010; Mackay et al., 1988) can be attributed to the low flow conditions generated by the drought. Lack of overbank flows during the study would have reduced the input of mineralised NH_4^+ and NO_3^- from floodplains to the river (Baldwin & Mitchell, 2000; Lamontagne, Leaney, & Herczeg, 2006) and the low flow velocities would have increased the potential for consumption of inorganic nutrients by algal biomass (Baker et al., 2000; Sherman, Webster, Jones, & Oliver, 1998). The high NH_4^+ relative to NO_3^- concentrations in the saline wetlands is consistent with the tendency for lower nitrification rates, the potential for dissimilatory NO_3^- reduction to NH_4^+ and greater potential for desorption of NH_4^+ from the particulate phase in saline environments (Gardener et al., 2006; Rysgaard et al., 1999).

The low NO_3^- concentrations measured in surface waters do not necessarily mean nitrification does not occur in this environment. Shallow saline groundwater in pits occasionally contained high concentrations of both NH_4^+ and NO_3^-. In a similar floodplain environment, Lamontagne, Herczeg, Dighton, Jiwan, & Pritchard (2005) found that a thin oxygenated layer at the water table promoted nitrification on the top of otherwise anoxic groundwater. In addition, nitrification rates can also be substantial in River Murray floodplain soils (Lamontagne, Leaney, et al., 2006). Thus, the mixture of NH_4^+ (which is favoured under anoxic conditions) and NO_3^- (which is favoured under oxic conditions) in freshly dug pits indicate the water table at Loveday is also a redox interface.

Like in the case of TP, NH_4^+ remained relatively low in the disposal basins (especially Loveday – N) for most of the post-flooding period. It can be hypothesised that the filamentous algal mats effectively consumed NH_4^+ from the water column or physically prevented the exchange of NH_4^+-rich porewater from the sediments. There was a distinct spike in NH_4^+ concentrations at the end of the post-flooding period in both basins, when water level was decreasing and salinity was increasing rapidly.

Decomposition of exposed algal mats or of organisms vulnerable to rising salinity (cladocerans, etc.), cation exchange (Rysgaard et al., 1999), or groundwater discharge (see below) could all have been involved.

Groundwater – surface water interactions

While the role of surface water hydrology in controlling biogeochemical cycles in Murray wetlands has been investigated in some detail (Baldwin & Mitchell, 2000), the role of groundwater – surface water interactions has received limited attention. Secondary salinisation and associated changes in biogeochemical cycles (Lamontagne, Hicks, et al., 2006) in River Murray floodplains are the result of raised water tables (Jolly, 1996; Jolly et al., 2008). In general, permanently raised saline water tables will tend to favour anaerobic over aerobic nutrient cycling because of waterlogging (Baldwin & Mitchell, 2000; Nielsen et al., 2003).

Groundwater – surface water interactions were also involved in a significant mass transfer of elements in the Loveday wetlands during the experiment. When no river water is added, the surface water levels in the Loveday basins essentially reflect the local water table. This water table rises across the floodplain during winter because of decreased evapotranspiration rates and drops by 30–75 cm during summer when the evaporation rates are higher (Doble et al., 2006). Because the South Basin is slightly more elevated (~9.0 m AHD) than the North Basin (~8.5 m AHD), this seasonal rise and fall of the water table results in the ephemeral nature of the South Basin because the water table there can drop below the soil surface (Lamontagne et al., 2009).

Flooding started 2 weeks earlier in Loveday – N than Loveday – S (Table 1) but a spike in NH_4^+, MoR Si and FRP concentrations was observed in Loveday – S during this period. As these chemical species are enriched in groundwater at the site, this increase in concentration was probably groundwater-related. The likely mechanism was that the underlying Monoman Formation was pressurised by raising the surface water level in Loveday – N (Lamontagne et al., 2009). In other words, by adding surface water in Loveday – N the water table and its dissolved solutes rose above the surface in the adjacent Loveday – S.

A different groundwater – surface water process may have contributed to the spike in NH_4^+ and MoR Si concentrations late in the post-flooding phase in both basins. Water and salt balances in the basins during the experiment, especially for Loveday – S, indicated additional sources of water and salt to the basins post-flooding (Lamontagne et al., 2009). The most likely source would be drainage of porewater or shallow groundwater from the Coonambidgal Clay as the surface water levels receded in the basins. This process was greater in Loveday – S because of a greater expansion and subsequent contraction of its surface area. While shallow groundwater in the Coonambidgal Clay was not sampled post-flooding, it is reasonable to expect that it would have been enriched in chemical species such as NH_4^+ and MoR Si (Lamontagne, Leaney, et al., 2006; Table 2). At the scale of River Murray floodplains, the bulk of the salinity and dissolved nutrient pool is stored in porewater and shallow groundwater rather than in the relatively thin (<1.5 m) water column of wetlands (Lamontagne et al., 2009).

Conclusion

Lamontagne et al. (2009) had previously demonstrated that the benefits of freshening are likely to be short-lived in disposal basins from a salinity point of view because of the occurrence of strong re-salinisation mechanisms, including evapoconcentration, saline groundwater discharge and mixing with the large salt pool surrounding the wetlands. The overall effects of freshening were also short-lived for nutrients, with concentrations generally returning to pre-flooding conditions within seven months of the cessation of flooding. This highlighted the overall strong control of salinity in the biogeochemical cycles of semi-arid wetlands. Whilst effects were short-lived, a more permanent improvement in salinity may be achievable by combining flooding with other management interventions (Lamontagne & Herczeg, 2009). As increasing salinity is becoming a worldwide environmental issue in semi-arid climates (Rengasamy, 2006; Scanlon, Jolly, Sophocleous, & Zhang, 2007), nutrient cycling in semi-arid wetlands may gradually shift towards processes more common in saline environments.

Whilst an emphasis here was given to physical and chemical processes, freshening also triggered a significant unanticipated biological response via the development of an extensive filamentous algal mat. The apparent effect of this mat on sediment resuspension persisted well after the water level had receded and the mats had desiccated. A similar filamentous algal bloom has recently been observed following release of fresh to brackish water into the hypersaline Southern Lagoon of the Coorong, compromising its use as a habitat for waterbirds (Brookes et al., in press; Paton, Paton, & Bailey, 2015). Whether filamentous algal blooms in saline River Murray wetlands are the result of a changed light, water level, nutrient or salinity environment (or some combination thereof) is unclear and warrants further investigation.

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Disclosure statement

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