Sources and transport of nutrients in the Coorong

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Goyder Institute for Water Research Technical Report Series No. 22/01



www.goyderinstitute.org

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

The Goyder Institute for Water Research is a research alliance between the South Australian Government through the Department for Environment and Water, CSIRO, Flinders University, the University of Adelaide and the University of South Australia. The Institute facilitates governments, industries, and leading researchers to collaboratively identify, develop and adopt innovative solutions for complex water management challenges to ensure a sustainable future.



This program is part of the Department for Environment and Water's Healthy Coorong, Healthy Basin Program, which is jointly funded by the Australian and South Australian Governments.



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Citation

Priestley S, Mosley L, Farkas J, Tyler J, Shao Y, Shanafield M, Banks E, Wong WW, and Leyden E (2022). *Sources and transport of nutrients in the Coorong.* Goyder Institute for Water Research Technical Report Series No. 22/01.

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Respect and reconciliation

Aboriginal people are the First Peoples and Nations of South Australia. The Coorong, connected waters and surrounding lands have sustained unique First Nations cultures since time immemorial.

The Goyder Institute for Water Research acknowledges the range of First Nations' rights, interests and obligations for the Coorong and connected waterways and the cultural connections that exist between Ngarrindjeri Nations and First Nations of the South East peoples across the region and seeks to support their equitable engagement.

Aboriginal peoples' spiritual, social, cultural and economic practices come from their lands and waters, and they continue to maintain their cultural heritage, economies, languages and laws which are of ongoing importance.

Executive summary

The Phase One Trials and Investigations (T&I) Project of the Healthy Coorong, Healthy Basin (HCHB) Program consists of a series of integrated research components that collectively provide knowledge to inform the future management of the Coorong. The work presented in this report investigates nutrient sources and transport in the Coorong as part of T&I *Component 1 - Understanding Coorong nutrient dynamics* via:

- Characterisation and assessment of seasonal variability of bulk nutrients in the water column and sediment
- Tracing of nutrient sources
- Tracing of water sources and mixing
- Investigating groundwater discharge
- Assigning constraints on redox conditions and implications for nutrient sources
- Constructing a nutrient budget.

Key findings were:

- Salinity and key nutrients, such as total dissolved nitrogen and phosphorus, increase systematically from the North Lagoon to the South Lagoon, due to the hydrological restriction of the South Lagoon from the North Lagoon, lack of flushing and evaporative concentration of nutrients and dissolved ions.
- Organic phases dominate the proportion of total dissolved nutrients (~90%) as most of their respective dissolved inorganic nutrients, such as nitrate, ammonium and filterable reactive phosphorus, are at much lower concentrations, often below the detection limit.
- Nitrogen isotopes showed that nitrogen in the sediment is primarily the result of phytoplankton deposition from the overlying water column, with internal cycling and accumulation of nitrogen within the sediment in the South Lagoon due to the oxygen-poor, organic and sulfide-rich sediments.
- Strontium isotopes and stable water isotopes showed that the Coorong water composition is derived from both seawater and continental water sources.
- Strontium isotope mass balance calculations indicate that on average over the March 2019 to February 2021 study period the ocean contributes 40-55% of the strontium and the River Murray and Lower Lakes waters contributed 45-60% of the strontium, and hence water, in the North Lagoon.
- The strontium isotope mass balance calculations also indicate that the South Lagoon was predominantly composed of strontium, and hence water, derived from the North Lagoon; however, Salt Creek also contributes significantly to the water balance of the South Lagoon.
- Groundwater appears to be a relatively minor contributor of nutrients at a lagoonal scale, but groundwater inflows could be locally significant and fresher water lenses were detected under the margins of the South Lagoon.
- The South Lagoon has oxygen depleted or 'less oxic' water column conditions compared to the North Lagoon, but there is no evidence of anoxia occurring.
- The oxygen depleted and more reducing conditions in the South Lagoon sediments have resulted in enrichment of ammonium and possibly total dissolved phosphorus in the South Lagoon.
- Redox processes, in particular sulfate reduction by sulfate reducing bacteria and sulfide oxidation, are also occurring in the South Lagoon, as well as parts of the North Lagoon.
- The South Lagoon sediment has approximately 50 times larger nutrient (nitrogen and phosphorus) stocks compared to the North Lagoon water column.
- There is both seasonal and long-term variability in the nutrient budgets; although there was generally a net export of nutrients at Pelican Point in the North Lagoon, due to the flushing effect of releases

from the River Murray via the barrages, and the ocean. Conversely, there was a net import of nutrients to the South Lagoon at all times between 2009 and 2020, except during the high barrage flows in 2016.

• In the South Lagoon the majority of the nutrients (>50%) are estimated to be coming from the sediments, followed by inputs from the North Lagoon (<50%), with Salt Creek providing only a fraction of the annual nutrient supply (<1%).

A summary of key management questions that were addressed is:

What forms of nutrients are present? The majority of the nutrients in the water column were present as dissolved and particulate organic nutrient species, with concentrations increasing systematically from the estuarine-marine conditions near the barrages and Murray Mouth to the persistently hypersaline waters of the South Lagoon. Dissolved (immediately bioavailable) inorganic nutrients only comprise a very small proportion of the total nutrients.

Where are nutrients residing? Tracing of nutrient signatures in the Coorong indicate that phytoplankton (and other algal) deposition from a highly eutrophic water column is the primary source of carbon and nutrients in surface sediment. This has resulted in sediment nitrogen and phosphorus stocks being the largest and most dominant pool, especially in the South Lagoon. Additionally, estimates of sediment fluxes show that >80% of the nutrient flux into the South Lagoon water column could be from the sediment.

Where are nutrients coming from and what contribution does Salt Creek make to nutrient loads to the South Lagoon? Overall, inputs from the barrages, and thus the River Murray and Lower Lakes system, ocean and local sediments dominate the supply of nutrients, with Salt Creek providing only a fraction of the nutrients (<1%). Nevertheless, local input of nutrients from Salt Creek, as well as from the River Murray and Lower Lakes through the barrages and ocean, are magnified in the South Lagoon by evaporation and lack of flushing. Therefore, dissolved and particulate nutrients are concentrating and accumulating over time to high levels in the South Lagoon leading to hypereutrophic conditions, particularly during summer.

How are nutrients moving within the system? The nutrient budget calculations suggest that there is generally export of nutrients from the North Lagoon out to the Murray Mouth into the ocean. This is driven by improved flushing, with higher River Murray inflow and water levels (driven by both barrage discharge, tides and sea level changes), contributing to a net effect of more water with less nutrients entering the Coorong, and nutrient-rich waters exiting from the Murray Mouth. In contrast the South Lagoon typically gains and retains nutrients from both North Lagoon (ocean and barrages) and Salt Creek sources. Only large barrage inflows over several weeks (e.g. as occurred in late 2016) lead to major flushing and removal of previously retained nutrients from the water column of both the South Lagoon and the North Lagoon. Flushing will also reduce deposition of nutrients to the sediment.

What is the effect of redox (oxidation-reduction) processes on nutrients? Reduction processes are more dominant in the South Lagoon with lower dissolved oxygen levels, higher ammonium, and active microbial redox processes such as bacterial sulfate reduction and ammonification. These in turn point to more anoxic nutrient pathways in this restricted, oxygen-depleted and hypersaline part of the Coorong. Additionally, bacterial sulfate reduction is the driver of monosulfidic black ooze formation which is promoted by high algae and organic nutrient levels and deposition, as well as maintenance of anoxic conditions.

In summary, the work presented in this report has helped to resolve current uncertainties in nutrient sources and transport in the Coorong. The research outcomes link to our other research focused on internal nutrient cycling and fluxes in the Coorong and provides more detail on how biogeochemical processes determine nutrient availability. The research outcomes have also provided key data and information to help parameterise and validate the Coorong Dynamics Model. This will reduce key uncertainties on sources and transport so that the biogeochemical model can be used to more confidently assess scenarios to achieve a "regime shift" back towards an aquatic plant dominated ecosystem, rather than the current algal dominated ecosystem. Another key output will be scientifically defensible advice on how to reduce nutrient availability to algae that will be provided as part of the assessment of nutrient removal options in the Coorong.

Acknowledgments

This project is part of the South Australian Government's Healthy Coorong, Healthy Basin Program, which is jointly funded by the Australian and South Australian governments. The \$77.7 million Healthy Coorong, Healthy Basin Program consists of Australian Government funding contribution of up to \$70 million and South Australian Government funding contribution of up to \$7.7 million.

The Goyder Institute for Water Research is the delivery partner for research components of Healthy Coorong, Healthy Basin, providing independent research to inform future management decisions for the region.

We kindly acknowledge the assistance of Garry Hera-Singh and Glen Hill with boat-based sampling and for sharing their local knowledge. In addition, we acknowledge the assistance of Coorong Rangers Georgina Trevorrow, Tim Hartman, Mathew Hartman and Merv Smith for sharing their local knowledge and with shore groundwater sampling. We would also like to acknowledge Bogumila Tomczak for ICP-OES analysis of water samples at University of Adelaide, and Dr. Sarah Gilbert from Adelaide Microscopy Centre for assistance with ICP MS/MS analysis, as well as support from the Fertiliser Technology Research Centre in Adelaide.

1 Introduction

1.1 Background

The Coorong is culturally, environmentally and economically important at local, national and international scales but has experienced a long-term decline in its ecological condition due to reductions in inflows. Whilst there has been recovery of some elements of the Coorong ecosystem associated with increased inflows since the end of the Millennium Drought in 2010, the South Lagoon has not recovered to the levels expected. There has been a switch of the ecosystem from being dominated by aquatic plants to algae associated with eutrophication (nutrient enrichment), with subsequent impacts on invertebrates, fish and waterbirds. These changes in the ecosystem and the lack of recovery are likely caused by a number of complex, interacting factors, which are not well understood. This is limiting the capacity to forecast the ecological response to future management scenarios and therefore the capacity of water managers to identify management interventions required to improve the health of the Coorong.

The Trials and Investigations (T&I) project of the Healthy Coorong, Healthy Basin (HCHB) program consists of a series of integrated components that will collectively provide knowledge to inform the future management of the Coorong. *Component* 1 - Understanding Coorong nutrient dynamics forms part of the T&I Project. It aims to assess the relative importance of external and internal nutrient sources and processes within the Coorong. The research aims to provide a holistic understanding on how the nutrient load in the Coorong could be lowered to improve the state of the Coorong. T&I Component 1 comprises four main activities as shown in Figure 1.



Figure 1. The main research activities and linkages in the Understanding Coorong nutrient dynamics Component of the Healthy Coorong, Healthy Basin Trials and Investigations project.

1.2 Aims

The research presented in this report investigates nutrient sources and transport in the Coorong as part of *T&I Component 1 - Understanding Coorong nutrient dynamics*. Specifically the aim was to quantify the major external nutrients sources and nutrient transport processes in the Coorong, and to use this to calculate a nutrient budget for the Coorong.

Key management questions (provided by the Department for Environment and Water, DEW) we sought to answer were:

- What forms of nutrients are present?
- Where are nutrients residing? (e.g. water, sediment, algae)
- Where are nutrients coming from?
- How are nutrients moving within the system?
- What contribution does Salt Creek make to nutrient loads to the South Lagoon?
- What is the effect of redox (oxidation-reduction) processes on nutrients?

The answers to these questions will inform optimised operations of the barrages, South East inflows and the Murray Mouth dredging regime to limit nutrient availability to algae in the Coorong and favour the growth and reproduction of *Ruppia*. This will also help inform whether new on-ground works and infrastructure will be able to reduce nutrient availability within the Coorong.

Within this final technical report, results are presented and discussed relevant to sources, transport and biogeochemical cycling of key nutrients (nitrogen, phosphorus and carbon) in the Coorong from investigations during 2020 and 2021. These results are complemented by (i) novel isotope tracing of water source mixing and redox processes, (ii) constraints on groundwater discharge, and (iii) compilation of a nutrient budget within the Coorong, with implications for nutrient sources and their availability. Detailed nutrient cycling and sediment flux investigations will be reported in a separate Goyder Institute for Water Research technical report.

2 Methods

2.1 Sampling locations

In order to better understand temporal variability in the sources, transport and availability of key nutrients in the Coorong, water samples were collected and analysed that represented the following seasons: autumn (March 2019 using legacy samples and March 2020), winter (July 2020), spring (September and November 2020) and summer (February 2021). To answer the key management questions samples aligning with DEW regular monitoring locations that would reflect the spatial extent of the Coorong were collected during July 2020 (winter), September and November 2020 (spring) and February 2021 (summer; Figure 2). Additional sample locations were collected in July 2020 (winter) and February 2021 (summer; Figure 2) in order to obtain more detailed information about lagoon inputs and mixing during the extreme summer and winter seasons. The March 2020 samples were collected at the location of sediment sampling which were used to collect a representative coverage of sediment quality across the Coorong (Figure 2). The water samples were usually collected by boat; however, due to occasional inclement weather and/or boat access issues, some samples were collected by wading from the shoreline.

Surface (0-2 cm and 0-5 cm layer) sediment samples were also collected by boat across the entire Coorong in March 2020. The specific sampling locations and collection seasons for the water and sediment samples are shown in Figure 2.



Figure 2. Map of the Coorong with locations of water and sediment sampling sites color-coded. Noonameena is located at site number 9, Parnka Point is located at site number 14, and Policeman's Point is located at site number 19. Note that water samples collected in March 2019, represent 'legacy samples' from a reconnaissance study performed in the Coorong.

2.2 Sampling methods

2.2.1 Collection of nutrients in water, sediment and algal/organic matter samples

At the time of water and sediment sampling, on-site measurements of physical and chemical water properties were recorded using a calibrated YSI[™] Pro DSS Sonde and handheld meter, including temperature, dissolved oxygen (DO), electrical conductivity (EC), salinity, turbidity and pH.

To obtain samples for nutrient and other water quality parameter (chlorophyll-a, dissolved organic carbon (DOC), total organic carbon (TOC), oxidised nitrogen (NO_x), nitrate (NO₃), ammonium (NH₄⁺), total nitrogen (TN), total phosphorus (TP), filterable reactive phosphorus (FRP) and total Kjehldahl nitrogen (TKN)) analysis, representative water samples were collected from approximately 50 cm below the water surface. The water column throughout the majority of the Coorong is shallow (1.5m) and well mixed. Water samples for oxidised nitrogen (NO_x), nitrate (NO₃), ammonium (NH₄⁺) and filterable reactive phosphorus (FRP) were filtered using 0.45 μ m syringe filters in the field and then all samples were stored in the dark and refrigerated at 4°C.

To obtain samples for concentration and isotopic analysis of total dissolved nitrogen (TDN), total dissolved phosphorus (TDP), ammonium (NH₄⁺) and nitrate (NO₃⁻), water samples were filtered using 0.2 μ m PES syringe filters into acid cleaned HDPE bottles. To obtain samples for concentration and isotopic analysis of particulate organic nitrogen (PON) and particulate carbon (PC), remaining unfiltered water samples were passed separately through PALL Type A/E glass fibre filters with a 1 μ m pore size. All samples including filters containing particulates were stored frozen (at -20°C) until analysis.

Ammonia passive samplers, based on gas-diffusion across a hydrophobic membrane (O'Connor Šraj et al. 2018, O'Connor Šraj et al. 2020), were deployed at two sites in the Coorong for 1 week to determine the time-weighted average concentration of dissolved ammonia (NH_3) by trapping it as ammonium (NH_4^+) in a 0.1M hydrochloric acid (HCl) and 1.8M sodium chloride (NaCl) solution.

Sediment samples were collected using a 'Russian D' auger to a depth of approximately 50 cm. Some shallow shoreline samples were collected with a polycarbonate core tube pushed into the sediment. Sub-samples of the surface (0-2 cm and 0-5 cm layer) were homogenised at the time of sampling for analysis. Samples were immediately placed in sealed vials with no air gap and cooled on ice. Upon return to the laboratory (within 48 hours), samples were frozen at -20°C until analysis. Selected sediment pore water samples were collected in July 2020 at Policeman's Point (Figure 2) using a 70 mm diameter PVC core tube pushed into the sediment. Rhizon[™] pore water samplers were inserted into 2 mm drill holes in the core to collect pore water samples from the sediment.

Additionally, *Ruppia* community, consisting of *Ruppia tuberosa*, *Althenia cylindrocarpa* and *Ruppia megacarpa* (hereafter: *Ruppia*) and cyanobacteria mat samples were collected from Noonamenna, and *Ruppia* and filamentous algae samples were collected from Salt Creek in March 2020.

2.2.2 Collection and preparation of isotope samples

For isotopes, water samples representative of the water column were also collected from approximately 50 cm below the water surface. Groundwater samples were also collected at three selected locations adjacent to the lagoon (a) using a drive point piezometer (Solinst 615) installed at approximately 1 m depth, and (b) from existing groundwater wells near Noonameena and Robs Point (Figure 2). The piezometer outlet was connected to a peristaltic pump and an inline flow cell containing the above water quality meter. Prior to sample collection the piezometer was purged for several minutes until clear water was obtained and water quality readings were stable.

Both the Coorong water and groundwater samples for strontium and sulfur isotopes were filtered through a 1 μ m glass fibre syringe pre-filter (Minisart CA) coupled to a 0.45 μ m cellulose acetate membrane syringe filter (Minisart CA) into acid-cleaned HDPE bottles and refrigerated at 4°C in the dark before elemental concentrations and isotopic analyses were undertaken.

Water samples for stable water (H and O) isotopes were filtered through a 0.45 μ m membrane filter in the field into 2 ml glass vials and refrigerated at 4°C until analysis.

2.3 Analytical procedures

2.3.1 Analytical procedures for nutrient concentrations and isotopes

Chlorophyll-a, dissolved organic carbon (DOC), total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP), filterable reactive phosphorus (FRP) and total Kjehldahl nitrogen (TKN) were measured at the Australian Water Quality Centre (AWQC), South Australia for samples collected in March 2019, March 2020 and July 2020 as well as historical samples described in Mosley et al. (2020). For the samples collected in September and November 2020, and February 2021, these parameters were measured at ALS in Melbourne. Both AWQC and ALS are National Association of Testing Authorities (NATA) accredited laboratories with strict quality control procedures.

Nitrogen and carbon isotope ratios were also analysed on selected water, sediment, and organic matter samples collected in 2020 and 2021 to help constrain the sources and bio-geochemical pathways of these key nutrients in the Coorong. Nitrogen and carbon both have multiple naturally occurring stable isotopes: ¹⁴N and ¹⁵N and ¹²C and ¹³C, which could be measured and expressed as isotope ratios and/or 'delta values' (see below) which in turn allow tracing of specific sources and local cycling of N and C in the Coorong.

Nitrogen isotope variations in samples were measured as ${}^{15}N/{}^{14}N$ ratios, and expressed as $\delta^{15}N$ values (in per mil, ‰), based on the equation below:

$$\delta^{15}N$$
 (‰) = [(¹⁵N/¹⁴N_{sample}) / (¹⁵N/¹⁴N_{standard}) -1] * 1000

Similarly, the stable carbon isotope variations were analysed as ${}^{13}C/{}^{12}C$ ratios, and expressed as $\delta^{13}C$ values (in per mil, ‰), based on the following relationship:

$$\delta^{13}C$$
 (‰) = [(¹³C/¹²C_{sample}) / (¹³C/¹²C standard) -1] * 1000

Phosphorus (P) is a mono-isotopic element which has only one naturally occurring stable isotope (³¹P). This prevents direct isotope tracing of phosphorus in the environment.

Total particulate nitrogen and particulate carbon concentration, and $\delta^{15}N$ and $\delta^{13}C$ values were analysed from the PALL Type A/E glass fibre filters at Monash University analytical and stable isotopes facility using a continuous flow isotope mass spectrometer (CF-IRMS; Sercon Ltd., UK) (Russell et al. 2018). Dissolved inorganic nitrogen is extremely low, albeit still detectable (Mosley et al. 2020), thus the particulate $\delta^{15}N$ primarily reflects particulate organic nitrogen ($\delta^{15}NPON$). Due to the small sample sizes available and the primary focus of this study being the nitrogen isotope system, particulate carbon samples were not acidified prior to isotope analysis. Therefore the suspended carbon isotope data reported here are strictly 'total particulate carbon' ($\delta^{13}CPc$) and may contain some dissolved inorganic carbon. However, we interpret this signal to primarily reflect the $\delta^{13}C$ of particulate organic carbon as previous comparisons between the concentrations of organic carbon and total carbon suspended in Coorong waters indicated that inorganic carbon accounted for a minor (undetectable) fraction of the suspended load. The C/N molar ratio was estimated based on beam area using internal standards with known amounts of carbon and nitrogen.

Concentration and isotopic analysis of NO_3^- , NH_4^+ , TDN and TDP were undertaken at Monash University analytical and stable isotopes facility, along with dissolved N isotope ratios where detectable. Nutrient concentrations were quantified spectrophotometrically following the procedures in Standard Methods for Water and Wastewater (APHA 2005), using a Lachat QuikChem 8000 Flow Injection Analyzer (FIA). Samples for TDN were digested with alkaline persulfate prior to analysis via FIA. The accuracy of these analyses was estimated to be within ±2% for concentration data, and within ±0.3‰ for C and N isotope data.

The $\delta^{15}N$ values for NO_3^- , NH_4^+ were determined by first converting each species to N_2O (Zhang et al. 2007), before isotope analysis was conducted on a Hydra 20–22 continuous-flow isotope ratio mass spectrometer (CF-IRMS) interfaced to a cryoprep system (Zhang et al. 2007, Wong et al. 2018). The $\delta^{15}N-NH_4^+$ and $\delta^{15}N-NH$

 NO_3^- values were calibrated against internationally recognised standards; USGS 25, USGS 26, USGS-32 and IAEA-N1. The external reproducibility of the isotopic analyses lie within ±0.3‰ for $\delta^{15}N-NH_4^+$.

Selected algal/organic matter (*Ruppia*, cyanobacteria and filamentous algae) samples were dried at 60°C, pulverised and weighed into tin cups before being analysed at Monash University on an ANCA GSL2 elemental analyser interfaced to a Hydra 20-22 continuous-flow isotope ratio mass spectrometer (Sercon Ltd. UK). Quality control was carried out using four internal standards (ammonium sulfate, sucrose, gelatine and bream) which were calibrated against internationally recognised reference materials including USGS 40, USGS 41, IAEA N1, USGS 25, USGS 26 and IAEAC-6. The internal standards were used to correct for any variations as a result of peak size linearity and instrumental drift with typical reproducibility of $\pm 0.2\%$ for both δ^{13} C and δ^{15} N. Based on these internal standards, the accuracy of our data was calculated to fall within $\pm 0.3\%$ for δ^{15} N and $\pm 0.2\%$ for δ^{13} C.

Total carbon and nitrogen in the sediment were measured via high temperature combustion and infra-red detection using a LECO CNS TruMAC Analyser. Total Organic Carbon ($%C_{org}$) was measured using the same analytical method following pre-treatment of the sample with dilute HCl added to remove inorganic carbon. The N and C percentage measurements were also used to calculate the C:N molar ratio. The δ^{15} N and δ^{13} C values of the sedimentary bulk organic matter were analysed by EA-IRMS in the Environmental Analysis Laboratory, Lismore, Australia. The sediment samples for ${}^{13}C/{}^{12}C$ isotope ratio analysis were pre-treated with HCl to remove inorganic carbon. All carbon and nitrogen isotope data are reported using the standard delta notation, relative to the standards air for nitrogen and Pee Dee Belemnite (PDB) for carbon.

2.3.2 Analytical procedures for elemental concentrations

The concentrations of selected dissolved anions (CI^- , SO_4^{2-}) and alkalinity in the filtered water samples were measured at NATA accredited ALS laboratory in Melbourne.

The concentrations of selected dissolved cations (Al, Ba, Ca, Cr, Cu, Fe, K, Mn, Na, S, Mg, P and Sr) in the filtered water samples were measured using a Spectro CIROS Radial Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) at the University of Adelaide, Fertiliser Technology Research Centre in Adelaide. Samples were diluted to <500 mgL⁻¹ concentration with 0.2% v/v ultrapure nitric acid (HNO₃). Cation concentrations were determined against calibration standards with concentrations ranging from 1 ppm up to 500 ppm. The typical uncertainty for all analyses was $\pm 10\%$ (2 standard deviations of the mean; 2SD).

For the legacy samples collected in March 2019, the concentrations of selected dissolved cations (AI, B, Ca, Fe, K, Mg, Mn, Na, P, S, Si and Sr) in the filtered water samples were measured using a Thermo Fisher iCAP 7600 ICP-AES at the Australian Nuclear Science and Technology Organisation (ANSTO). All elemental concentrations were determined against calibration standards with element concentrations ranging from 0.01–10 ppm and up to 500 ppm for Ca, K, Mg and Na. All standards were prepared from certified 1000 ±3 ppm single element National Institute of Standards and Technology (NIST) standards in 3% v/v Merck Suprapure HNO₃. A certified 'cocktail' of multi-element NIST standard was run at the beginning of each analytical session as another independent quality control. A set of standards was added after every 20th sample throughout the analysis session to monitor instrument drift. All samples and standards were spiked with 1 ppm of indium and rhodium for internal standard correction. Samples with concentrations over the instrument calibration range were diluted with 3% v/v HNO₃ and reanalysed and results were corrected to account for this dilution. A separate rinse containing 0.25 ml of 1% v/v Triton X-100 in 5 L of 1% HNO₃ was used for rinsing between standards and samples. The typical uncertainty for all analyses was ±5% (2SD).

2.3.3 Analytical procedures for strontium isotopes by TIMS

Samples of filtered waters were analysed for 87 Sr/ 86 Sr and $\delta^{88/86}$ Sr by thermal ionisation mass spectrometry (TIMS) using a Phoenix Isotopx instrument at the Metal Isotope Group (MIG) facility at the University of Adelaide. The analyses followed the procedures described in Shao et al. (2021). To apply the 87 Sr- 84 Sr double spike method to analyse the $\delta^{88/86}$ Sr in an unknown sample, two aliquots each containing about 500 ng of Sr

were taken from a stock sample solution, where one aliquot was spiked with the ⁸⁷Sr-⁸⁴Sr double spike solution (composition described in Shao et al. 2021), resulting in ⁸⁴Sr_{sp}/⁸⁴Sr_{sa} ratios (i.e., spike to sample ratios) close to 20 (mean = 18.9, 2 standard error of the mean (2SEM) = 0.57, n=60). Prior to TIMS analyses, the Sr fraction from each sample and standard was purified from the sample 'matrix' using a 600 μ L Micro Bio-Spin separation column filled with Sr-specific resin (Eichrom Sr-SPS), then the pure Sr fractions were loaded on single non-zone-refined rhenium filaments (for more detail see Shao et al. (2021)).

The total procedural Sr blanks determined via ⁸⁴Sr isotope dilution were consistently below 150 picograms (pg), on average around 60 pg, corresponding to less than 0.1% of total Sr (~500 ng) sourced from an analysed sample. The long-term average ⁸⁷Sr/⁸⁶Sr and $\delta^{88/86}$ Sr values and uncertainties (±2SEM) of repeat measurements of standards and samples in this study were, respectively, ±0.000003 (n = 46) and ±0.005‰ (n = 51). Typical uncertainty (±2SD) for stable Sr isotope data was in the order of ±0.03‰.

2.3.4 Analytical procedures for oxygen and hydrogen isotopes

The stable water isotope compositions were measured using a Picarro L2130-I Cavity Ring Mass Spectrometer at Flinders University in Adelaide, South Australia.

The ¹⁸O/¹⁶O and ²H/¹H ratios are given as a deviation from Vienna Standard Mean Ocean Water (VSMOW) expressed in per mil (‰) difference using delta (δ) notation, according to the following two equations:

 $\delta^{18}O$ (‰) = [(¹⁸O/¹⁶O)_{sample}/(¹⁸O/¹⁶O)_{VSMOW} -1] × 1000

 δ^{2} H (‰) = [(²H/¹H)_{sample}/(²H/¹H)_{VSMOW} -1] × 1000

The analytical precision for δ^{18} O and δ^{2} H is ±0.025‰ and ±0.1‰ (2SD), respectively.

Additionally, data presented in Chamberlayne et al. (2021) was collated and included in the stable water isotope analyses to trace water sources and mixing.

2.3.5 Analytical procedures for sulfur isotopes

Sulfur (S) isotope variations in samples were measured as ${}^{34}S/{}^{32}S$ ratios, and expressed as $\delta^{34}S$ values (in per mil, ‰), based on the following equation:

 $\delta^{34}S$ (‰) = [(³⁴S/³²S_{sample}) / (³⁴S/³²S_{standard}) -1] * 1000

We used a novel 'collision cell' based ICP-MS/MS approach (Agilent 8900 instrument) to determine the δ^{34} S in selected Coorong water samples (Leyden et al. 2021). Repeated ICP-MS/MS measurement of different S isotope certified reference materials (CRM) resulted in accuracy with certified ranges, with a typical uncertainty on δ^{34} S analysis of around 1.1 to 1.5‰ (±1SD).

2.4 Application of strontium isotopes

Strontium radiogenic and stable isotope compositions or ratios were used to constrain the hydrological mass balance by determining Coorong water sources and quantifying mixing.

The radiogenic strontium ratio (⁸⁷Sr/⁸⁶Sr) is a well-established water source tracer in a number of geological, ecosystem and hydrological studies (Capo et al. 1998, Dickin 2018). The ⁸⁷Sr/⁸⁶Sr ratio of minerals and rocks is dependent on their initial ⁸⁷Rb content and age, controlled through the process of ⁸⁷Rb decay to ⁸⁷Sr over geological time. Weathering and leaching of these geological reservoirs impact the resultant ⁸⁷Sr/⁸⁶Sr of waters and fluids, which can thus be used to trace or 'fingerprint' different water sources and their provenance (e.g., seawater, continental waters, saline brines). For example, modern seawater exposed to weathering of basaltic oceanic crust has a globally homogeneous and relatively low ⁸⁷Sr/⁸⁶Sr ratio of ~0.70917 (Figure 3), while surface waters on continents draining granitic and sedimentary rocks have higher and more radiogenic, although highly variable ⁸⁷Sr/⁸⁶Sr signatures (Kuznetsov et al. 2012).

On the other hand, the stable strontium isotope ratio (88 Sr/ 86 Sr) is a novel tracer that has been recently used to complement the more established radiogenic 87 Sr/ 86 Sr to further refine and constrain the global strontium cycle and its sources and fluxes (Krabbenhöft et al. 2009, de Souza et al. 2010, Krabbenhöft et al. 2010, Vollstaedt et al. 2014, Pearce et al. 2015, Fruchter et al. 2016, Shao et al. 2021). The stable 88 Sr/ 86 Sr is usually reported as a conventional delta notation ($\delta^{88/86}$ Sr) expressed in per mil (‰), where the 88 Sr/ 86 Sr ratio of an unknown sample is normalised relative to the SRM987 standard, according to the following equation:

 $\delta^{88/86}$ Sr (‰) = [(⁸⁸Sr/⁸⁶Sr)_{sample}/(⁸⁸Sr/⁸⁶Sr)_{SRM987} -1] × 1000

The $\delta^{88/86}$ Sr ratio is sensitive to mass-dependent isotope fractionation processes such as precipitation and dissolution of carbonate (e.g. calcite, aragonite) minerals. These processes are often observed in dynamic coastal systems, such as the Coorong, but cannot be quantified properly via the traditional radiogenic 87 Sr/ 86 Sr tracer (Krabbenhöft et al. 2009, Krabbenhöft et al. 2010, Raddatz et al. 2013, Stevenson et al. 2014, Vollstaedt et al. 2014, Pearce et al. 2015, Fruchter et al. 2016, Shalev et al. 2017), as depicted in Figure 3.

A strontium isotope mass balance and theoretical mixing trends can be calculated using the end-member values and the following elemental and isotopes mass balance equations:

 $({}^{87}Sr/{}^{86}Sr)_{MIX} M_{MIX}C_{MIX} = ({}^{87}Sr/{}^{86}Sr)_1 M_1C_1 + ({}^{87}Sr/{}^{86}Sr)_2 M_2C_2$

and

 $C_{MIX} = C_1 X_1 + C_2 (1 - X_1)$

Where 87 Sr/ 86 Sr is the radiogenic strontium isotope ratio, C is the Sr concentration and M is the mass of water, such that M_{MIX} = M₁+ M₂, MIX denotes the theoretical mixture of two water sources denoted by 1 and 2, and X₁ is the mass fraction of water source 1.



Figure 3. Conceptual cross-plots of radiogenic strontium isotope ratio (87 Sr/ 86 Sr) versus stable strontium isotope ratio ($\delta^{88/86}$ Sr) in water samples. The blue dashed line represents a theoretical mixing line between water sources (i.e., a continental water and seawater), and the grey dashed arrows along the mixing line represent the process of pure mixing, resulting in a mixture shown as the red "ideal mixing" circle. The horizontal grey dashed arrows represent the process of carbonate precipitation/dissolution which was reflected in increase/decrease of $\delta^{88/86}$ Sr in the water mixture, where hypersaline waters were typically identified by the increased $\delta^{88/86}$ Sr due to carbonate precipitation.

2.5 Application of sulfur isotopes

Sulfur (S) isotopes are useful to trace sources and redox cycling (i.e., oxidation vs reduction) of S in the environment. For example, seawater has a sulfate-S isotope ratio (${}^{34}S/{}^{32}S$ expressed as $\delta^{34}S$) of +21.45‰, and thus a water sample with a δ^{34} S value close (±1.5‰) to this value is likely to have a dominant seawater influence, whereas freshwater sources typically have lower δ^{34} S values (Leyden et al. 2021). The reduction of sulfate to hydrogen sulfide (H₂S) by sulfate reducing bacteria, fractionates S isotopes (i.e. changes the δ^{34} S). Sulfate reduction leaves residual sulfate (SO4²⁻) in the water enriched in the heavier ³⁴S isotope, while depleting the lighter ³²S isotope which is fractionated to a greater extent into H₂S and iron sulfide minerals such as FeS and FeS₂ (Canfield et al. 2010). As a result the δ^{34} S in water where sulfate reduction is occurring is typically "heavier", >23‰ and the reverse can occur (i.e. lighter δ^{34} S) when sulfide minerals oxidise (Canfield 2001). Sulfate reduction requires anoxic conditions, excess sulfate, and readily available organic matter to be oxidised by sulfate reducing bacteria. Monosulfidic black ooze (MBO) materials found in large areas of the Coorong have high sulfide content due to the sulfate reduction process and this study is the first to assess sulfur isotopes as an indicator of redox processes. Abiotic S mineral (e.g. gypsum, CaSO₄.2H₂O) precipitation may also fractionate S isotopes. Modern sources of gypsum precipitated from seawater usually have δ^{34} S values that are isotopically heavier (+0.62 to +4.3‰) than the parent brine dissolved sulfate (i.e. seawater +21.7%) (Chivas et al. 1991). Gypsum precipitates around a salinity of 80 PSU so this could occur in the South Lagoon in summer.

2.6 Groundwater contributions

2.6.1 Sampling locations

Preliminary field trips to identify suitable study site locations were undertaken on 29 September 2020 and 18 January 2021. Based on a field visit in January 2021, three site locations were selected for further investigation and characterisation of groundwater discharge taking place in the nearshore margins of the South Lagoon of the Coorong (Figure 4). The three sites were named North South Lagoon (NSL), Jack Point (JP) and Ti-Tree (TT). These sites were selected in consultation with Steve Barnett from the Department for Environment and Water (DEW), whose experience in the region suggests that groundwater fluxes to the Coorong would be greatest in areas with sharp topographical contrasts near the shoreline and where groundwater is not intercepted by surface water features (such as the many ephemeral lakes and wetlands) adjacent to the Coorong. Further sites were visited with the Coorong Rangers on 24 February 2021, including the site known as Goodwater (Figure 5).



Figure 4. Location map showing the (a) South Lagoon of the Coorong, and (b) the selected three study sites (North South Lagoon (NSL), Jack Point (JP) and Ti-Tree (TT)). Yellow dots show the locations of all registered bores in the region (waterconnect.sa.gov.au).



Figure 5. Groundwater inflows (seeps) into the South Lagoon at a location called "Goodwater", a site towards the northern end of the South Lagoon of the Coorong and suggested by the Indigenous rangers on 24 February 2021. The iron staining in the sediments indicates groundwater inflows.

A range of hydrogeophysical and environmental tracer techniques were trialled and used to characterise and quantify the groundwater discharge along the near-shore of the South Lagoon of the Coorong at the three study sites including the site known as Goodwater. The following sub-sections describe the methodology and approach taken in this study.

The two main fieldtrips were undertaken between 22-26 February and 17 March 2021 (summer field campaign) and between 7-9 September 2021 (late winter field campaign).

2.6.2 Shallow piezometers

Transects of three shallow piezometers were installed perpendicular to the shoreline of the South Lagoon at sites Jack Point (JP) and Ti-Tree (TT) on 23 and 25 February 2021, respectively, to determine the hydraulic gradient and measure the temporal variability of water level and salinity of the shallow groundwater adjacent to the lagoon. At JP, the transect consisted of a location above the high watermark (onshore), a midpoint on the dry tidal mudflats of the lagoon, and within the Coorong which was inundated to a depth of approximately 0.2 mAHD at the time of installation, representing a total transect distance of 171 m. For the onshore site, a hand auger was used to install 25 mm (ID) slotted high density polyethylene pipe to a depth of 0.3-0.5 m below the water table and a Schlumberger Diver water level and electrical conductivity (EC) datalogger was placed near the bottom of the pipe (site name: JP1). Similarly, water level and EC dataloggers were installed approximately 0.15 m below the water table from a slotted poly-vinyl chloride (PVC) pipe at the midpoint location (site name: JP2), and within the surface water (Coorong) at the third location (site name: JP3).

At site TT, all three piezometers were installed onshore due to the sharp gradient from low to high salinity measured within the shallow groundwater adjacent to the wetted shoreline of the lagoon. The distance from TT1 (closest to the Princes Highway) and TT3 (closest to the lagoon) was just over 30 m.

During the winter sampling on 7-9 September 2021, water levels in the South Lagoon were approximately 0.5 m higher than in February; water levels were again measured in the onshore piezometers (TT1 and JP1). A new transect was established at North South Lagoon (NSL) during the September 2021 sampling fieldtrip; similar to the previous two transects, it consisted of a line of three piezometers perpendicular to the shoreline, inserted until a water depth of up to 0.5 m could be measured within the slotted PVC pipe. The distance from NSL1 (closest to the Princes Highway) to the shoreline was 41 m, with NSL3 located approximately 3 m (onshore) from the shoreline.

2.6.3 Seepage meters

Five automatic seepage meters were used to provide seepage measurements for groundwater discharge into the South Lagoon (Solomon et al. 2020). Each seepage meter consists of a control unit (microprocessor) attached to a moving stainless-steel rod driven by a linear actuator. The device is seated on top of a 76 mm (ID) diameter tube (PVC or steel) inserted 0.25-0.3 m into the sediment, with an electric valve mounted to the outside, which controls water in and out of the tube (Figure 6). A stainless-steel rod is attached to the linear actuator, which can be controlled to move up and down over a distance of 50 mm. A second stainless steel rod is attached to an electric ground on the meter and extends into the water within the tube at a fixed depth. To measure the change in water level inside the tube, the linear actuator moves in a vertical direction until the rod touches the water surface, at which point a drop in resistance in the circuit between the two rods is detected by the control unit. At the beginning of a test, the control unit opens the electric valve attached to the side of the tube so that the tube acts as a stilling well to measure the surface water level outside the tube, and 10 measurements are successively collected. Then the valve closes and the water level inside the tube is measured at specified intervals as the water level equilibrates with the pressure experienced at the elevation of the bottom of the tube. For this application, 40 measurements were collected at 30 second intervals. The seepage rate (m/d) was then calculated in a spreadsheet using a combination of the water balance equation and Darcy's law. Further details are described in Solomon et al. (2020).



Figure 6. Automatic seepage meter (left) and Hot Rod (centre) to quantify groundwater fluxes into a surface water pool at the margin of the South Lagoon, February 2021. Note the iron staining at the surface as well as the 'biscuit-like' mineral precipitate in the background as a result of groundwater discharge.

2.6.4 Hot Rod

The Hot Rod is a 56 sensor, 3D temperature array with 3 heat pulse sources developed at Flinders University to measure the flow direction and magnitude up to 200 mm below the water-sediment interface in the streambed (Banks et al. 2018). It consists of a central carbon-fibre rod containing three heating elements along its length, surrounded by eight stainless steel rods each housing seven equally spaced temperature thermistors and attached to a circular baseplate (Figure 6). A terminal program is used to communicate with the data logger, and a sealed 12-volt lead acid battery together with a power supply regulator is used to maintain a constant 12-volt output to the heating elements.

Installation requires gently pushing (or lightly tapping with a shockless impact hammer) the device into the stream or lagoon bed ensuring that there is a sufficient gap between the top of the sediment and the underside of the base plate to prevent streamflow constriction. Once installed and equilibrated with the surrounding sediment, the logger program is executed and the ambient temperature is measured at each thermistor (T0), directly followed by activation of the selected heat element for the chosen duration. The data logger records the temperature differential at the chosen sample frequency to clearly discern the timing and location of the breakthrough curve at each of the thermistors. Field and laboratory tests showed that short, 1-minute heat pulse injections and a 20–30 minute temperature response monitoring period is appropriate for estimating the dominant direction and flux magnitude in sandy streambeds, and this was the procedure used in shallow pools (groundwater seeps) observed at multiple sites along the nearshore mudflats of the Coorong in February 2021. Groundwater flows were expected at these locations based on prior soil salinity measurements and visual observations of iron staining and mineral precipitation. It was not possible to repeat this method in September 2021 due to the higher water levels within the lagoon.

2.6.5 Near-surface geophysical surveys

Near-surface geophysical surveys were performed using two separate, continuous electromagnetic conductivity meters at sites JP, TT, and NSL. These types of geophysical methods are a quick and non-destructive way of mapping shallow subsurface conductivity over an area. These instruments do not make direct contact with the ground as the instrument sets up a time varying electromagnetic field, so received signals are created by electromagnetic induction.

The LoupeEM is a new, portable, time-domain electromagnetic (TEM) system, specifically designed for rapid surveys and near-surface conductivity measurements down to a depth of about 25 m. The receiver and transmitter are each carried by one person on a backpack (Figure 7). Loupe incorporates a 3-component coil sensor with 100 kHz bandwidth, a fast-switching transmitter loop, a simple user-interface integrated with an accurate GPS for position location. The system records full time-series TEM data to memory and processes it in real-time using signal processing methodologies developed for SMARTem receiver systems (Duncan et al, 1988).

The datasets were inverted using the University of Aarhus Aarhusinv 1D inversion code (http://hgg.au.dk/software/aarhusinv/) (Auken et al. 2015). These data were inverted using "smooth model" settings. Each sounding is inverted individually; the result is a vertical "sounding" made up of many layers, each assigned an estimated resistivity, which varies smoothly with depth. Results for a complete line are then presented as a resistivity-depth section or depth slice (providing there are multiple, closely spaced lines) by combining inversion results from each station.



Figure 7. Drs. Eddie Banks and Narges Khajavi conducting a LoupeEM survey at the North South Lagoon field site, 24 February 2021.

2.6.6 Surveying and photogrammetry

High resolution imagery of the three sites was acquired with a DJI Mavic Pro unmanned aerial vehicle (UAV). The UAV flew a grid pattern over the study area at an elevation of 30-50 m above ground level. Georeferencing was undertaken using a Trimble R10 GNSS/GPS Real-Time Kinematic (RTK) survey with ground control points located across the field site. The captured photos were processed using the photogrammetry Pix4D software package (Pix4Dmapper Pro version 3.2, 2017) to generate a high resolution (~1 cm/pixel) digital surface model (DSM). The DSM was treated as a digital elevation model (DEM) as there was very little vegetation present (the exception was the TT site towards the Princes Highway). The generated DEM was re-sampled to a 0.5 m DEM that was used evaluate the subtle features (groundwater seeps) in the nearshore mudflats of the South Lagoon.

2.6.7 Radon

For the measurement of ²²²Rn activity, surface water samples of lagoon water were collected at the DEW regular monitoring locations in the South Lagoon (Salt Creek regulator, 1.8 km west of Salt Creek, Snipe Point, North Jacks Point, Stony Well, Villa de Yumpa, Parnka Point) on 29 September 2020 using a rapid field extraction method developed by Leaney and Herczeg (2006). The PET method involves filling a 1.25 L polyethylene terephthalate bottle with sample water and using a syringe, 50 ml of sample was removed from

the bottle and then 20 ml of mineral oil scintillant was added from a pre-weighed scintillation vial. The bottle was shaken for four minutes so that the radon equilibrates between the water–air–scintillant phases. The bottle was left to stand for one minute, during which time the scintillant settles to the top of the water. The scintillant was returned to the vial using a glass nozzle, sealed and the date and time recorded. The samples were returned to Flinders University within 3 days of sample collection and counted by liquid scintillation using a Perkins Tri-Carb 4910TR Liquid Scintillation Analyzer for two hours. Additional water samples were collected and analysed using the same method on 18 January 2021 at three locations along the shoreline, which were excavated using a spade. For each location, water was gently pumped from a depth of approximately 0.3-0.5 m below the ground into the PET bottle and analysed as described above. Results of the January 2021 sampling round helped to inform the locations of subsequent, more detailed sampling in February 2021.

2.6.8 Water chemistry, stable isotopes and analytical techniques

To initially detect potential areas of groundwater contribution, a Fieldscout soil salinity probe was used (Figure 8). The probe was inserted into the soil to a depth of 0.15, 0.30, or 0.45 m. Electrical conductivity was recorded.

The following field parameters were measured for surface water and groundwater samples: alkalinity, pH, dissolved oxygen (DO), oxidation-reduction potential (ORP), specific electrical conductivity (SEC), and temperature using a YSI 556 multi-meter. In locations where there was no standing surface water, groundwater temperature, pH, SEC, DO, and ORP were measured by inserting a shallow drivepoint piezometer into the sediment and gently pumping the water into a flow-through cell using a peristaltic pump. Other surface water and groundwater samples for major ions, nutrients, alkalinity, δ^{18} O and δ^{2} H of water and dissolved gases were collected using a 12-volt peristaltic pump. Alkalinity (as calcium carbonate (CaCO₃) concentration) was measured in the field using a HACHTM titration kit (www.hach.com).

Major element analyses were conducted on the surface water and groundwater samples that were filtered through a 0.45-micron membrane filter in the field. Major cation and trace element samples were acidified with $1\% \text{ v/v} \text{ HNO}_3$ and analysed by a Spectro CIROS Radial Inductively Coupled Plasma Optical Emission Spectrometer at CSIRO Land and Water Analytical Services, Adelaide, South Australia. Major anions were analysed using a Dionex ICS-2500 Ion Chromatograph. All ion balances were typically better than $\pm 3\%$. Nutrient samples were collected in 500 ml bottles supplied by the University of Adelaide and analysed.

All stable water isotope compositions were measured using a Picarro L2130-I Cavity Ring Mass Spectrometer at Flinders University in Adelaide, South Australia. The results are reported as a deviation from Vienna Standard Mean Ocean Water (vs. VSMOW) in per mil (‰) difference using delta (δ) notation. The analytical precision for δ 180 and δ 2H is ±0.025‰ and ±0.1‰, respectively.



Figure 8. Fieldscout soil salinity probe for measuring salinity to a depth of 0.45 m.

2.6.9 Hydrus modelling

The Hydrus 2-D/3-D software package (Sejna and Simunek, 2007; Simunek et al. 2008) was used to simulate water movement beneath two-dimensional, vertical cross sections that represented the piezometer transect at Jack Point and North South Lagoon. Measured saturated hydraulic conductivities (K) ranged from 0.002 to 10 and are within the range of values for sand, which was the dominant sediment observed along the shoreline. A constant hydraulic conductivity value of 0.35 m/d was applied to the whole model domain in both transects; this value was estimated as the average of multiple samples of sediment measured at NSL during the February 2021 field campaign (samples at NSL were 0.34–0.36 m/d, whereas TT samples were 0.37–0.48 m/d). The model domain was 171 m long for Jack Point, and 82 m long at North South Lagoon, with measured water levels on both sides providing constant head boundaries. Measured water levels at both transects showed no significant level change over several days, therefore constant head was considered reasonable. The model was extended across the 5 m layer of freshwater observed with geophysical surveys, with a no flow boundary beneath. A seepage face was applied to the surface to allow groundwater discharge to the lagoon. The model was run to equilibrium, and velocity vectors across the model domain provided the output of interest.

The results of this modelling are reported along with the shallow piezometer data that was used to parameterise the model.

2.7 Nutrient budget

2.7.1 Nutrient budget construction and nutrient stocks

A nutrient budget was constructed for the Coorong using available data on water source inputs and fluxes, and nutrient concentrations in the water and sediment. A conceptual framework diagram for the nutrient budget is shown in Figure 9. The budget is separated into North and South Lagoons with fluxes of nutrients estimated between the two lagoons. The external surface water and nutrient inputs for the North Lagoon are from the Lower Lakes (via multiple barrages), ocean (via the Murray Mouth), and from Salt Creek for the South Lagoon.



Figure 9. Conceptual framework for the Coorong nutrient budget. The red lines indicate hydrodynamic model flux output points at Parnka Point and Pelican Point that were used in the budget.

The corresponding hydrodynamic model domain used in the seasonal and annual nutrient budget calculations is shown in Figure 10, adapted from the Department for Environment and Water (2022b). Two seasonal periods were selected to calculate a nutrient budget: autumn-winter (April-September); and spring-summer (October-March) for 2019-2020. These periods were selected to represent apparent changes in total flow patterns in or out of the Coorong (Figure 11, based on data from Department for Environment and Water 2022b).

To determine the historical range in nutrient fluxes and budgets two additional periods were selected to represent barrage low-flow and barrage high-flow conditions (Figure 12). The coarse TUFLOW hydrodynamic model historical base case model results used in the barrage high-flow and barrage low-flow conditions nutrient budget calculations are presented in Department for Environment and Water (2022a).

Both measured and modelled data was used to inform the nutrient budget. The modelling results of Department for Environment and Water (2022b), Department for Environment and Water (2022a) included a tracer on the key external surface water sources (ocean, Lower Lakes-barrages, and Salt Creek). This enabled internal tracing of water sources following complex hydrodynamic mixing and transport processes throughout the Coorong. The residual component of a particular water parcel represented the initial water in the Coorong at the start of the simulation. Water quality data from the HCHB program and earlier programs was also utilised to calculate nutrient stocks and fluxes (Mosley and Hipsey 2019, Mosley et al. 2020).



Figure 10. Map of the the Coorong model domain used in the nutrient budget from the Department for Environment and Water (2022b). The red lines indicate hydrodynamic model internal flux output points at Pelican Point and Parnka Point that were used in the nutrient budget.



Figure 11. Water flows across (a) Pelican Point and (b) Parnka Point (model outputs from the Department for Environment and Water (2022b)) from different sources (Lower Lakes barrages, ocean, and residual). Note that in (a) flow into the North Lagoon is indicated by positive flow, and flow towards the Murray Mouth is indicated by negative flow. Also, not that in (b) flow into the South Lagoon is indicated by positive total flow, and flow exiting the South Lagoon (and entering the North Lagoon) by negative total flow. The inflow from Salt Creek is also shown (c) based on Department for Environment and Water gauged data.





Water column nutrient stocks were calculated by multiplying modelled water volume (L, summing up positive and negative flows over period; Department for Environment and Water 2022a and b) and measured nutrient concentration data (mgL⁻¹ average over period).

Surface sediment (0-5 cm) nutrient stocks were estimated using interpolated data (using ArcGIS) for the March 2020 sediment survey as part of T&I Activity 1.3 nutrient cycling and fluxes investigations, also for the HCHB program (Figure 13). Average TN and TP concentrations were estimated for the North and South Lagoon, and sediment stocks calculated using the sediment volume (surface area in m² x 0.05 m sediment depth) and assuming a sediment bulk density of 1000 kg m⁻³ because the black ooze sediments common throughout the Coorong are high in organic matter so have a lower bulk density than regular consolidated lagoon sediments.



Figure 13. Sediment (a) total nitrogen concentrations (%) and (b) total phosphorus concentrations (mg kg⁻¹) (from T&I Activity 1.3 nutrient cycling and fluxes investigations)

2.7.2 Fluxes into or between lagoons

Fluxes into Coorong North Lagoon (at Pelican Point)

Using model output data from the Department for Environment and Water (Figure 11; 2022a and b) the ocean, barrages and Coorong (residual) flux was estimated for each seasonal 6-month period by summing up positive and negative flows at across a cross section at Pelican Point. The nutrient flux for each of these was calculated by multiplying the ocean, barrages and Coorong (residual) flux (Figure 11), by the nutrient concentration representative of that source at that period of time. Note that flow into the Coorong North Lagoon is indicated by positive flow, and flow exiting the North Lagoon (and likely subsequently the Murray Mouth) by negative flow.

Nutrient fluxes between Coorong North and South Lagoons (at Parnka Point)

Using model output data from Department for Environment and Water (Figure 11; 2022a and b) the ocean, barrages and Coorong (residual) flux across the Parnka Point cross section was estimated for the seasonal 6-month periods by summing up positive and negative flows. The nutrient flux for each of these was calculated by multiplying the ocean, barrages and Coorong (residual) flux by the nutrient concentration representative of that source at that period of time. Note that flow into the South Lagoon is indicated by positive total flow, and flow exiting the South Lagoon (and entering the North Lagoon) by negative total flow.

Salt Creek inflow

The Salt Creek gauging station discharge data (A2390568) was obtained from the Department for Environment and Water (water.data.sa.gov.av) for the study period. The nutrient flux into the Coorong from Salt Creek was calculated by multiplying the creek discharge by the nutrient concentration representative of that source at that period of time.

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Sediment fluxes

Flux rates of ammonium, nitrate and phosphorus from the South Lagoon sediment measured during the T&I Activity 1.3 nutrient cycling and fluxes investigations (by Dr Leslie Huang, UniSA) were used to estimate the flux of nitrogen and phosphorus from the South Lagoon sediments. As no flux rates for the North Lagoon were available, the ammonium, nitrate and phosphorus sediment flux rates used in the historical base case model (Department for Environment and Water (2022b) were assumed to be representative of the North Lagoon for the purposes of this nutrient budget.

Rainfall inputs

Rainfall inputs were calculated by multiplying the cumulative rainfall over the period (Bureau of Meteorology 2021) with representative measured nitrogen and phosphorus concentrations (Crosbie et al. 2012).

Volatilisation

The time-weighted average concentration of dissolved ammonia was determined using ammonia passive samplers (O'Connor Šraj et al. 2018, O'Connor Šraj et al. 2020) at Parnka Point and Policeman's Point. The proportion of the dissolved ammonia being lost to the atmosphere was calculated using the gas transfer calculation in Denmead and Freney (1992).

As no measurements for the North Lagoon were available, the rates measured at Parnka Point were assumed to be representative of the North Lagoon for the purposes of this nutrient budget.

Groundwater inflow

The average groundwater flux and nutrient concentration measurements given in section 3.3 were used to determine the localised groundwater flux.

Algal fluxes

Nutrient stocks in macro-algae and *Ruppia* are not included in this budget, however phytoplankton nitrogen and phosphorus is included in the TN and TP measurements. Algal biomass will also be calculated separately as part of HCHB T&I 'Component 2 – Aquatic plants and algae'.
3 Results and discussion

The purpose of this section is to describe and discuss the key findings of the study. Key findings are highlighted at the beginning of each sub-section.

3.1 Variability of nutrients in the Coorong

Key findings

- Salinity and key nutrients, such as total dissolved nitrogen and phosphorus, increase systematically from the North Lagoon to the South Lagoon, due to the hydrological restriction of the South Lagoon from the North Lagoon, lack of flushing and evaporative concentration of nutrients and dissolved ions.
- Organic phases dominate the proportion of total dissolved nutrients (~90%) as most of their respective dissolved inorganic nutrients, such as nitrate, ammonium and filterable reactive phosphorus, are at much lower concentrations, often below the detection limit.
- Nitrogen isotopes showed that nitrogen in the sediment is primarily the result of phytoplankton deposition from the overlying water column, with internal cycling and accumulation of nitrogen within the sediment in the South Lagoon due to the oxygen-poor, organic and sulfide-rich sediments.

3.1.1 Characterisation and seasonal variability of main nutrients in the Coorong

The characteristic salinity gradient along the length of the Coorong, with salinity ranging from brackish, marine to hypersaline conditions (Mosley et al. 2020), was observed during all our sampling seasons. This trend is illustrated for the 'winter' (July 2020) and summer (February 2021) water salinity data plotted in Figure 14.

Similarly, our seasonal studies and monitoring revealed considerable variability in the salinity of lagoon waters throughout the year, which is also characteristic of the Coorong (Figure 14). The highest or most hypersaline conditions (up to 120 practical salinity units (PSU) were documented in the South Lagoon during the summer and autumn seasons (see orange and red circles in Figure 15a), and progressively less saline and more brackish conditions in the North Lagoon during the same summer and autumn seasons. In winter and spring the South Lagoon waters remained more saline than the North Lagoon with hypersaline conditions (up to 80 PSU; see blue and green circles in Figure 15a).



Figure 14. Map showing a spatial distribution of (a) Winter (July 2020) and (b) Summer (February 2021) water salinity measurements and interpolated salinity surface (linear trend in ArcGIS).

Key nutrients in the Coorong; nitrogen and phosphorus, follow the salinity trend where the hypersaline waters of the South Lagoon are also systematically more enriched with the above nutrients compared to more brackish or marine waters in the North Lagoon. These relationships are illustrated below, where the measured concentrations of total dissolved nitrogen (TDN) in the Coorong waters (Figure 15b) and the total dissolved phosphorus (TDP) concentrations across the Coorong (Figure 15c) increase from the North Lagoon to the eutrophic South Lagoon, with concentrations increasing in summer and autumn in the South Lagoon. These relationships are similar for the total nitrogen (TN) and total phosphorus (TP) with concentrations being systematically more enriched in the South Lagoon compared to the North Lagoon (Figure 16). The concentrations of nutrients in both lagoons greatly exceeded the key inflow (barrages and Salt Creek) nutrient concentrations (Figure 15 and Figure 16). The almost linear relationship between increasing TDN and TDP with increasing salinity for most samples (Figure 17) shows that nutrients are accumulating within the Coorong along with salinity, which is a finding consistent with the T&I Activity 1.1 existing data and knowledge collation investigations and previous studies, (see Mosley et al. 2020). The autumn South Lagoon data show TDP and chlorophyll-a increasing with distance south while salinity is more spatially uniform (hence the red vertical clusters of autumn TDP and chlorophyll-a data points in Figure 17). We hypothesise this is due to addition of TDP (from the sediments) to the Coorong causing increased productivity, and hence chlorophyll-a, based on a multiple linear regression interpretation (not shown). Nevertheless, the relationship of increasing salinity and nutrient concentrations highlights that salts and nutrients are not being efficiently removed from the lagoon system into the ocean due to the hydrological restriction of the South Lagoon from the North Lagoon, as well as progressive accumulation due to evapoconcentration of salts and nutrients.



Figure 15. Seasonal and spatial variability of (a) Salinity, (b) Total Dissolved Nitrogen (TDN), and (c) Total Dissolved Phosphorus (TDP) across the Coorong and its main freshwater inputs (River Murray and Lower Lakes (barrages), and Salt Creek regulator). Legend in (a) applies to all figures.



Figure 16. Seasonal and spatial variability of (a) Total Nitrogen (TN), and (b) Total Phosphorus (TP) across the Coorong and its main freshwater inputs (River Murray and Lower Lakes (barrages), and Salt Creek regulator). Legend in (a) applies to all figures



Figure 17. Seasonal and spatial variability of (a) Total Dissolved Nitrogen (TDN), (b) Total Dissolved Phosphorus (TDP), and (c) Chlorophyll-a versus salinity for the Coorong and its main freshwater inputs (River Murray and Lower Lakes (barrages), and Salt Creek regulator). Legend in (a) applies to all figures.

While the total nutrients and total dissolved nutrients are high in the Coorong, especially in the eutrophic South Lagoon, most of the dissolved inorganic nutrients, oxidised nitrogen (NO_x; Figure 18a), ammonium (NH₄⁺; Figure 18b) and filterable reactive phosphorus (FRP; Figure 18c) are generally much lower, often below detection or if detected, close to or below guideline values from ANZECC and ARMCANZ (2000). The apparent phosphorus limitation is consistent with the very low FRP relative to the dissolved nitrogen species, although this could also be due to oversupply of nitrogen (Mosley et al. 2020). There is an increase in FRP concentration in summer and spring from the North Lagoon to the South Lagoon suggesting possible release of FRP from the sediment at those times. Several samples also have high NH_4^+ in summer, which will be discussed further below. Nevertheless, most of the total dissolved nitrogen and phosphorus in the Coorong waters are residing in organic phases.

Another important nutrient in the Coorong is carbon, which can be present in both organic and inorganic forms. To quantify the organic and inorganic forms of carbon in the Coorong waters, concentrations of (i) dissolved organic carbon (DOC), (ii) alkalinity, which reflects dissolved inorganic carbon (DIC) and other proton acceptors (e.g. organic anions), and (iii) chlorophyll-a were measured, with results presented below in Figure 19, plotted as a function of latitude.

The results confirmed that hypersaline waters of the South Lagoon are significantly and systematically enriched in both inorganic and organic carbon species, as well as chlorophyll-a, compared to the marine/brackish waters of the North Lagoon. In addition, there is considerable seasonal variability in all of the above parameters (DOC, alkalinity, chlorophyll-a) which tends to be magnified in the South Lagoon settings. There is an increase in chlorophyll-a and DOC in the summer and autumn seasons (Figure 19a and c). The difference in the chlorophyll-a concentrations during the summer and autumn seasons (Figure 19c) compared to salinity (Figure 15a) highlights there is increased productivity, as well as evapoconcentration, during these seasons. However, the decrease in chlorophyll-a concentrations during summer in the South Lagoon (Figure 19c) indicates a drop in productivity when salinities are high (>100PSU; Figure 15a). This was also identified in the T&I Activity 1.1 existing data and knowledge collation investigations. Alkalinity is consistently higher in winter suggesting addition of DIC in winter, or removal of DIC in other seasons, discussed further below.

Considering the dominance of organic phases in the Coorong, concentrations of particulate organic nitrogen (PON) and particulate carbon (PC) were also examined and for further information see Priestley et al. (2020). These parameters represent the insoluble (i.e. particulate) phase of organic N (PON) and C (PC), which have been sampled and collected from water via filtration. Results indicate the PON and PC follow a very similar trend and pattern to the soluble nutrients (TDN and TDP), with highest concentrations or nutrient availabilities in the hypersaline and highly eutrophic South Lagoon (Figure 20). This trend (i.e., more nutrients in more saline settings) seems to be further magnified during the warmer and drier summer and autumn seasons. The strong correlation between particulate nitrogen and carbon (PON and PC) throughout the seasons in the Coorong (Figure 21a), and correlation of both with chlorophyll-a concentration (Figure 21b), suggests that PON and PC variability across the lagoon likely primarily reflects living or dead phytoplankton biomass.

The increase in salinity, nutrient concentrations and productivity (i.e. chlorophyll-a) from north to south in the Coorong, and above the source water input concentrations, appears to primarily be controlled by the lack of flushing due to the hydrological restriction of the South Lagoon from the North Lagoon meaning the South Lagoon is effectively an endorheic 'closed basin' system with no major outflows. This lack of flushing means that salts and nutrients are not efficiently removed from the lagoon system into the ocean, and are then evapo-concentrated, further exacerbating their progressive accumulation in the South Lagoon. This is consistent with findings from previous studies (e.g. Ford (2007) and Stone et al. (2016)). It is also important to note that the end of the Millennium Drought and the increase in flows since (Figure 12a) has not been sufficient to change this endorheic state.



Figure 18. Seasonal and spatial variability of (a) nitrate and nitrite (oxidised nitrogen NO_x), (b) ammonium and (c) filterable reactive phosphorus (FRP) versus salinity for the Coorong and its main freshwater inputs (River Murray and Lower Lakes (barrages), and Salt Creek regulator). Legend in (a) applies to all figures. Horizontal blue lines/zones show default guideline values from ANZECC and ARMCANZ (2000).



Figure 19. Seasonal and spatial variability of (a) dissolved organic carbon (DOC), (b) alkalinity, and (c) chlorophyll-a, across the Coorong and its main freshwater inputs (River Murray and Lower Lakes (barrages), and Salt Creek regulator). Legend in (a) applies to all figures.



Figure 20. Seasonal and spatial variability of (a) Particulate Organic Nitrogen (PON), and (b) Particulate Carbon (PC), in the Coorong and its main freshwater inputs (River Murray and Lower Lakes (barrages), and Salt Creek regulator). Legend in (a) applies to all figures.

(a)



Figure 21. A cross-plot of (a) Particulate Organic Nitrogen (PON) and Particulate Carbon (PC) data and (b) PON and Chlorophyll-a data in the Coorong and its main freshwater inputs (River Murray and Lower Lakes (barrages), and Salt Creek regulator). Legend in (a) applies to all figures.

(a)

3.1.2 Nitrogen and Carbon: Isotope tracing of nutrient sources and cycling

To better understand the sources and local biogeochemical cycling of key nutrients in the Coorong we also present here a compilation of N and C isotope data ($\delta^{15}N$ and $\delta^{13}C$ values) from the Coorong. As the $\delta^{15}N$ values of dissolved inorganic nitrogen species nitrate (NO₃) and ammonium (NH₄⁺) were mostly below detection limit and phosphorus is a monoisotopic element, we focus on the $\delta^{15}N_{PON}$ and $\delta^{13}C_{PC}$ values in the Coorong.

The $\delta^{15}N_{PON}$ and $\delta^{13}C_{PC}$ values in the Coorong show opposite trends with $\delta^{15}N_{PON}$ increasing from the North Lagoon to South Lagoon and $\delta^{13}C_{PC}$ values decreasing across the same latitudinal gradient (Figure 22a and b). Specifically, there is a subtle increase in average $\delta^{15}N_{PON}$ from the North Lagoon (+3.8 ±2‰) to the South Lagoon (+4.5 ±1‰; Figure 22a). Likewise, there is a subtle increase in average $\delta^{15}N_{PON}$ from north to south with increasing salinity (Figure 22c). There is also a 2‰ increase in $\delta^{13}C_{PC}$ values from the South Lagoon (-27.4 ±1.5‰) to the North Lagoon (-25.2 ±1.8‰; Figure 22b) and a general decrease in $\delta^{13}C_{PC}$ with increasing salinity (Figure 22d).

To further elucidate the N and C isotope variability in the main nutrient pools in the Coorong, we have also analysed the N and C content, and the δ^{15} N and δ^{13} C values in 'bulk' sediments (see 'black squares' in Figure 22a and b).

Nitrogen isotopes

Firstly, it is important to note that the South Lagoon sediments have a greater proportion (approximately double) of total nitrogen and total organic carbon than those in the North Lagoon, reflecting higher net deposition of organic matter in the South Lagoon (Haynes et al. 2020). Moreover, comparison of $\delta^{15}N_{PON}$ and sediment δ^{15} N values (Figure 22a) shows that generally sediment δ^{15} N overlaps with the 'long-term' average $\delta^{15}N_{PON}$. This would suggest that phytoplankton derived nitrogen represents the primary source of N to the lagoon sediment. This is consistent with algal deposition from a highly eutrophic water column (Pérez-Ruzafa et al. 2019) and previous research using nitrogen and carbon isotopic biomarkers in the Coorong (Krull et al. 2009, McKirdy et al. 2010). Hence, the input and accumulation of nutrients, and resultant phytoplankton productivity, which is primarily controlled by the lack of flushing, seems to explain the similarity of the $\delta^{15}N_{PON}$ and sediment $\delta^{15}N$. The overlap of $\delta^{15}N_{PON}$ and sediment $\delta^{15}N$ values in the northern section of the North Lagoon with River Murray $\delta^{15}N_{PON}$ suggests that the River Murray is potentially a major source of nitrogen to the Coorong. However, the increase in $\delta^{15}N_{PON}$ and sediment $\delta^{15}N$ values in the South Lagoon cannot be explained by mixing of North Lagoon waters with Salt Creek inputs as Salt Creek has lower $\delta^{15}N_{PON}$ values. Instead, we hypothesise that the increase in sediment $\delta^{15}N$ and $\delta^{15}N_{PON}$ values in the South Lagoon is due to internal or local nutrient cycling and associated isotope effects. Specifically, we suggest that the anoxic, reduced, organic matter-rich sediments of the South Lagoon would favour biogeochemical pathways that lead to higher δ^{15} N values in sediment and PON in the South Lagoon.

Firstly, nitrification of ammonium is likely to be severely limited in the oxygen-poor, organic matter and sulfide-rich sediments, as nitrifying bacteria have a higher affinity for oxygen than aerobic heterotrophs and other chemoautotrophs and are out competed by these under oxygen limited conditions (Kemp et al. 1990, Nizzoli et al. 2006, Molnar et al. 2013). Instead the sediment type present in the South Lagoon would favour dissimilatory nitrate reduction to ammonium (DNRA) over denitrification as a nitrate reduction process (An and Gardner 2002, Nizzoli et al. 2006, Molnar et al. 2013). This limits nitrogen loss as N₂ by recycling the nitrate produced from ammonium by nitrification back to ammonium leading to enhanced retention of nitrogen in the system (Burgin and Hamilton 2007, Giblin et al. 2013, Hardison et al. 2015, Magri et al. 2020). The T&I Activity 1.3 nutrient cycling and fluxes investigations found no N₂ production during incubations of Coorong sediment cores and reduced abundance of denitrifiers in the South Lagoon, confirming our hypothesis that denitrification in these sediments was severely limited. Thus, overall benthic N-cycling dominated processes favour the retention, accumulation and recycling of N, thereby supporting ongoing eutrophication of the South Lagoon. This hypothesis is supported by the higher nitrogen content in sediments in the South Lagoon. Further, high NH₄⁺ concentrations (up to 10 mg/L) measured in sediment pore waters in the South Lagoon would support high diffusive fluxes of ammonium to the overlying water to fuel phytoplankton production and further PON loads to the sediment. This suggests a self-reinforcing feedback loop that is causing further retention of N in the South Lagoon. Additionally, this implies that that even if external sources of nitrogen were to be reduce, e.g. River Murray, the internal nutrient load would remain high in South Lagoon. Hence it is probable that multiple seasons, and even years of high water flows would be required to remove the retained N in the absence of other processes (e.g. denitrification) changing.

Secondly, in the absence of other quantitatively significant N-loss processes (i.e. flushing and denitrification) volatilisation of ammonia (NH₃) to the atmosphere could be a quantitatively important N-loss process and result in isotopic fractionation due to preferential volatilisation of light ¹⁴NH₃ compared to ¹⁵NH₃ (Li et al, 2012). This is supported by NH₃ being measured in the Coorong waters during summer 2021. Specifically, ammonia passive samplers (O'Connor Šraj et al. 2018, O'Connor Šraj et al. 2020) deployed for seven days in March 2021 recorded a time-weighted average concentration of ammonia between 1.6 and 3.1 µg/L (NH₄⁺ = 17 to 32 µg/L), with cumulative ammonia concentrations between 0.2 and 0.5 mg/L (NH₄⁺ = 1.5 to 4.5 mg/L). Published data also indicate that such volatilised NH₃ gas is typically enriched in light N isotopes, and thus a process of ammonia volatilisation can also partly explain the observed high δ^{15} N signatures of the dissolved NH₄⁺ of reservoirs in the South Lagoon. However, further work is required to determine the flux and N isotope composition of such local ammonia flux to the atmosphere.

The above nitrogen cycling processes likely result in the residual dissolved ammonium available for phytoplankton being ¹⁵N-enriched and the ammonium regenerated during remineralisation of this phytoplankton biomass also being ¹⁵N-enriched. Thus, progressively over time repeated cycles of ammonium assimilation and remineralisation, and isotopic fractionation during ammonia volatilisation may have contributed to the heavier $\delta^{15}N$ values in sediment and PON in the South Lagoon, and the overlap in the sediment and PON $\delta^{15}N$ values (Figure 22a; Priestley et al. (2020)).

In summary, the sediment $\delta^{15}N$ values represent a composite of phytoplankton deposition and subsequent bacterial degradation, with release of nitrogen as ammonia from the sediment in the South Lagoon due to the oxygen-poor, organic matter and sulfide-rich sediments.

Carbon isotopes

Similarly to nitrogen, the higher net deposition of organic matter in the South Lagoon has led to the South Lagoon sediments having a greater proportion of total organic carbon (approximately three times as high) than those in the North Lagoon. However, the deposition of carbon to the sediment appears to be more complex than nitrogen as the sediment δ^{13} C signatures (-21 ±1‰) are consistently higher (5 to 7‰) and less geographically variable compared to $\delta^{13}C_{PC}$ (Figure 22b).

It is unlikely that the sediment δ^{13} C values represent a mixture between algae and aquatic plant, or terrestrial detritus, since aquatic plants are absent, in particular deeper (>1 m) basins, or in poor health in large areas of the South Lagoon due to hypersalinity and turbidity-driven light limitations (Dick et al. 2011, Kim et al. 2013, Aldridge et al. 2020). Also, δ^{13} C values vary between -25 to -30‰ for local terrestrial plants (Krull et al. 2009), and it is likely <10% of terrestrial organic matter is preserved in the Coorong sediments (Herczeg et al. 2001). Therefore, a mixture of algae and aquatic plant, or terrestrial detritus cannot entirely explain the observed sediment δ^{13} C values.

Instead, there are three potential sources of the sediment δ^{13} C signatures. Firstly, it is possible that methanogenesis or preferential microbial mineralisation of ¹²C leads to isotopically light carbon being lost from the sediment. Secondly, if isotopically heavy carbon is delivered to the lagoon sediment as carbonate, whereupon it dissolves in the low pH environment, the isotopically heavy CO₂ produced could be assimilated by phytoplankton and bacteria. Thirdly, is possible that the $\delta^{13}C_{PC}$ measured in this study is influenced by DIC and the sediment organic $\delta^{13}C$ carbon is a result of algal deposition similar to the sediment $\delta^{15}N$ values. This is supported by Krull et al. (2009) who found that the organic matter $\delta^{13}C$ from the top 0-5 cm of sediment fluctuates around -22 ±1.2‰ and is predominantly degraded phytoplankton. This is identical within error to our analyses of -21 ±1.3‰. In addition, the sediment C:N atomic ratios of 9 ±2 are consistent with a phytoplankton source (Krull et al. 2009, McKirdy et al. 2010).

The above interpretations can all explain the observed δ^{13} C variability in sedimentary carbon archives across the Coorong (Priestley et al. (2020)) and further process-based investigations are needed to corroborate the validity of these different hypotheses and scenarios.



Figure 22. A cross-plot of (a) Particulate Organic Nitrogen (PON) and bulk sediment $\delta^{15}N$ results and (b) Particulate Carbon (PC) and bulk sediment $\delta^{13}C$ results against sample latitude. Legend in 4 (b) applies to 4(a) as well. In both (a) and (b) the grey regression line represents all Coorong PON or PC isotope values and black regression line represents the bulk sediment isotope values. (c) $\delta^{15}N_{PON}$ results and (d) $\delta^{13}C_{PC}$ results against salinity. Legend in 4 (d) applies to 4(c) as well.

3.2 Tracing of water sources in the Coorong

Key findings

- Strontium isotopes and stable water isotopes showed that the Coorong water composition is derived from both seawater and continental water sources.
- Strontium isotope mass balance calculations indicate that on average over the March 2019 to February 2021 study period the ocean contributes 40-55% of the strontium and the River Murray and Lower Lakes waters contributes 45-60% of the strontium, and hence water, in the North Lagoon.

• The strontium isotope mass balance calculations also indicate that the South Lagoon was predominantly composed of strontium, and hence water, derived from the North Lagoon; however, Salt Creek also contributes significantly to the water balance of the South Lagoon.

3.2.1 Tracing of water sources and mixing via strontium isotopes

Data presented in Shao et al. (2018, 2021) and Shao (2021) was collated and included with the strontium isotope results of this study to trace water sources and mixing.

The Coorong radiogenic ⁸⁷Sr/⁸⁶Sr ratios are all higher than the ocean (0.70917; Figure 23b). There is a distinctive spatial trend along the Coorong salinity gradient (Figure 23a and b), where most of the samples from sites south of Mark's Point along the Coorong yielded homogeneous and higher ⁸⁷Sr/⁸⁶Sr ratios of ~0.70925 \pm 0.00002 (Figure 23b). Among all water samples, the River Murray and Lower Lakes are the most radiogenic with the highest ⁸⁷Sr/⁸⁶Sr ratios of 0.711553 \pm 0.0006, which is consistent with the weathering of 'old' and generally felsic (e.g. igneous rocks such as granite) and thus more radiogenic bedrocks of the surrounding catchment areas (Rippon et al. 2020). Salt Creek water samples had ⁸⁷Sr/⁸⁶Sr ratios of 0.70927 \pm 0.00002, slightly higher than the southern Coorong samples. Finally, the local groundwater samples yielded rather variable ⁸⁷Sr/⁸⁶Sr signatures (see Figure 23b). Groundwater sampled along the North Lagoon showed comparable values to Salt Creek (⁸⁷Sr/⁸⁶Sr ratios = 0.70929 \pm 0.00002), whereas the groundwater samples collected along the South Lagoon had slightly higher and more radiogenic values reaching up to 0.70938 (0.70934 \pm 0.00003; Figure 23b).

The $\delta^{88/86}$ Sr values of the North Lagoon water samples yielded values of 0.40 ±0.05‰, close to the typical seawater value of 0.395‰ (Figure 23c). The $\delta^{88/86}$ Sr value of waters from Parnka Point and the South Lagoon of 0.43 ±0.03‰ were systematically higher than that of North Lagoon and seawater, whereas all of the continental waters samples yielded $\delta^{88/86}$ Sr values below that of seawater. River Murray and Lower Lakes water samples gave $\delta^{88/86}$ Sr values of 0.30 ±0.04‰, groundwater samples along the North Lagoon had $\delta^{88/86}$ Sr values of 0.27 ±0.02‰ and groundwater samples along the South Lagoon had $\delta^{88/86}$ Sr values of 0.37 ±0.06‰, which was the highest of continental water samples.

In order to (i) identify the different water sources and (ii) quantify their relative mixing in the Coorong via elemental and isotope mass balance calculations, we need to plot a conservative element, or element ratio, that is not sensitive to evaporation and/or mineral formation, such as carbonate or gypsum precipitation, against the ⁸⁷Sr/⁸⁶Sr ratio. As the elemental Sr/Na ratio may be affected by Sr loss due to carbonate precipitation at high salinities (Shao et al. 2018) we focus on the elemental Mg/Na ratio which is considered to be conservative (i.e., concentrations increase linearly with increasing water salinity; Shao et al. 2021).

Considering the lack of seasonal variation in 87 Sr/ 86 Sr ratios and $\delta^{88/86}$ Sr values (Figure 23b and c) in the Coorong, the average values of potential inputs (River Murray and Lower Lakes, Salt Creek, Groundwater from along North Lagoon and South Lagoon, and ocean) were used to calculate the continental-ocean water mixing lines shown in Figure 24.

Overall, the data in Figure 24 indicates that continental (i.e. River Murray, Salt Creek, groundwater) water sources played an important part in the Coorong water composition, as almost all lagoon waters showed 'non-marine' characters with higher and more radiogenic ⁸⁷Sr/⁸⁶Sr signatures compared to the ocean. Several of the North Lagoon samples plotted closer to seawater values indicating that these waters were predominantly sourced from the ocean during the time of sampling. These samples are generally winter and autumn samples from downstream of Tauwitchere barrage and at Mark Point, Long Point and Noonameena (Figure 2), emphasising that ocean water can push into the North Lagoon at this time of year (Mosley 2016). Additionally, three summer and spring downstream (DS) Tauwitchere barrage samples sit along the River Murray and Lower Lakes-Ocean water mixing line outside of the figure axis (see purple line in Figure 24) as there is a large component of River Murray and Lower Lakes water due to barrage discharge at this location (Figure 2).

The remaining North Lagoon and South Lagoon samples ⁸⁷Sr/⁸⁶Sr ratios cluster higher along the River Murray and Lower Lakes-Ocean water mixing line (see purple line in Figure 24). However, several of the South Lagoon

samples plot towards the Groundwater-Ocean water mixing line (see grey line in Figure 24) and Salt Creek-Ocean water mixing lines (see red line in in Figure 24). This highlights that South Lagoon waters are potentially sourced from other continental waters, such as Salt Creek and local groundwater (examined further in Section 3.3) in addition to the Ocean and River Murray and Lower Lakes waters.

Consequently, the radiogenic ⁸⁷Sr/⁸⁶Sr signatures indicate possible water inputs to the Coorong being River Murray and Lower Lakes, ocean and possibly Salt Creek and/or South Lagoon groundwater as is further discussed below (Section 3.2.3).

The three-isotope plot or ⁸⁷Sr/⁸⁶Sr ratios versus. $\delta^{88/86}$ Sr values cross-plot (Figure 25) shows that hypersaline waters at Parnka Point and within the South Lagoon, and several samples from northern North Lagoon, all plotted to the right of the continental water-seawater mixing lines with elevated $\delta^{88/86}$ Sr (0.43-0.44‰). This further corroborates the difference in water chemistry and isotope composition between the North Lagoon and South Lagoon, where the latter has been significantly impacted by hypersaline conditions and evaporation, which led to local carbonate oversaturation and carbonate precipitation (Shao et al. 2021). Secondly, this documents the potential for the northern North Lagoon to be impacted by the same processes during periods of low 'fresh' water flushing (Shao et al. 2021), which could occur during extended periods of low barrage releases and reduced Murray Mouth openness. Therefore, the $\delta^{88/86}$ Sr values highlight the occurrence of carbonate deposition, especially in the South Lagoon; meaning they cannot be used to further distinguish between the water sources.



Figure 23. Seasonal and spatial variability of (a) Salinity, (b) radiogenic strontium isotope ratio (87 Sr/ 86 Sr) and (c) stable strontium isotope ratio (${}^{88/86}$ Sr) plotted against latitude. The blue horizontal line illustrates ocean values. Also, note that in (b) all seasons water samples from River Murray and Lower Lakes 87 Sr/ 86 Sr = 0.711553 ±0.0006 (n = 19), as well as DS Tauwitchere barrage samples in spring and summer 87 Sr/ 86 Sr = 0.711076 ±0.0004 (n = 2) and 0.709766, respectively, so plot out of scale and thus are not shown.



Figure 24. Cross-plots of radiogenic strontium isotope ratio (⁸⁷Sr/⁸⁶Sr) versus the magnesium/sodium elemental ratio (Mg/Na) of water samples and mixing lines between ocean and average values from the River Murray and Lower Lakes, Salt Creek and groundwater from along the North Lagoon and South Lagoon. The range of the respective mixing lines are shown by faint lines of same colour. Also, note that most River Murray and Lower lakes, as well as DS Tauwitchere barrage samples in spring and summer plot out of scale and thus are not shown.



Figure 25. Cross-plots of radiogenic strontium isotope ratio (87 Sr/ 86 Sr) versus stable strontium isotope ratio (88 / 86 Sr) of water samples and mixing lines between ocean and average values from the River Murray and Lower Lakes, Salt Creek and groundwater from along the North Lagoon and South Lagoon. The range of the respective mixing lines are shown by faint lines of same colour. Also, note that most River Murray and Lower Lakes, as well as DS Tauwitchere barrage samples in spring and summer plot out of scale and thus are not shown.

3.2.2 Tracing of water sources and evaporation via stable water isotopes

The stable water (H and O) isotopes were also used to verify the water sources in the Coorong (Figure 26). Stable water isotopes of both the North Lagoon and South Lagoon, as well as all water sources, displayed a strong ($r^2 > 0.97$) linear relationship (Figure 26a) with the slope of their respective lines consistent with a Local Evaporation Line (LEL) representative of highly seasonal evaporation (Gibson et al. 2016, Chamberlayne et al. 2021). This highlights that both the North Lagoon and South Lagoon, and even some of the water sources, such as Salt Creek are highly evaporated water bodies. Considering the majority of samples sit along the LEL, it is not possible to use the stable water isotopes cross-plot to verify the water source. Instead we need to use the cross-plots of salinity and δ^{18} O (Figure 26b) to try and distinguish the various water sources.

The salinity and δ^{18} O cross-plot (Figure 26b) shows that the low salinity (<20 PSU) North Lagoon samples overlap with the range of δ^{18} O values of the River Murray and Lower Lakes samples. In fact, most of the samples sit between the ocean and River Murray and Lower Lakes samples. Thus, it is clear that as expected the River Murray and Lower Lakes and ocean are significant sources of water to the North Lagoon. The low

salinity South Lagoon samples (salinity ≈ 20 -40PSU and $\delta^{18}O \approx 2\%$) overlap with a portion of the North Lagoon water samples (salinity ≈ 20 -40PSU and $\delta^{18}O \approx 2\%$) rather than the Salt Creek water samples (salinity ≈ 10 PSU and $\delta^{18}O \approx 1-2\%$; Figure 26b). While this does not rule out Salt Creek being a source of water to the South Lagoon, it likely only represents a small proportion. Whereas the North Lagoon water likely represents a large proportion of the water entering the South Lagoon, which is consistent with DEW modelling (Department for Environment and Water 2022b, Department for Environment and Water 2022a). Finally, it is clear that the groundwater samples plot away from the North Lagoon and South Lagoon samples, indicating that groundwater is not a major source of water to the Coorong either. However, groundwater is possibly still important in localised areas, as examined further in section 3.3. Overall, the analysis of stable water isotopes confirms that water inputs to the Coorong are predominantly from the River Murray and Lower Lakes and ocean, with lesser inputs from Salt Creek, and with possible but minor localised contributions from groundwater.



Figure 26. Cross-plots of (a) δ^{2} H versus δ^{18} O of water samples and lines of best fit of the Coorong and the main potential water sources. The local meteoric water line (LMWL) for Adelaide rainfall is sourced from the Global Network for Isotopes in Precipitation (Hollins et al. 2018) and the local evaporation line (LEL) is shown as the line of best fit through all Coorong water samples. (b) Salinity versus δ^{18} O and lines of best fit of the Coorong and the main potential water sources.

3.2.3 Proportion of the Coorong water from water sources using strontium isotope mass balance calculations

It is clear from Figure 26b, as well as Figure 24, that North Lagoon waters are predominantly sourced from ocean and River Murray and Lower Lakes waters, and the South Lagoon waters are predominantly sourced from the North Lagoon waters, with a small proportion from Salt Creek and groundwater.

The strontium isotope mass balance calculations can be used as proxy to determine the source and potentially proportion of various water sources, although such calculations need to account for water evaporation effects as Sr isotopes are not sensitive or responsive to water evaporation. The proportion of strontium, and by inference water sources in the Coorong derived from the ocean and River Murray and Lower Lakes are presented in Table 1. Generally, the ocean contributes 40-55% of the strontium and the River Murray and Lower Lakes waters contributes 45-60% of the strontium to the overall Sr budget in the Coorong.

Looking at the seasonal breakdown of the Coorong samples (Figure 27), there is a significant increase in the proportion of ocean water-derived strontium entering the North Lagoon in autumn, up to 100% (Table 1). Likewise, ocean water contributes up to 60% of the strontium at DS Tauwitchere barrage in winter. This is due to low atmospheric pressure, increased wind/storm action, and high sea level driving seawater into the Coorong and raising water levels in winter (Mosley 2016), with the lagoons then tending to drain out in spring-summer. With reduced seawater input in spring and summer, the source of strontium, and by inference water, at DS Tauwitchere barrage is predominantly from the River Murray and Lower Lakes with ocean water only contributing around 5% of the strontium (Table 1). This site is immediately downstream, in the mixing zone of the barrage, and hence the water composition is dominated by river-lakes water. In summer, water samples from Mark Point and Long Point had distinctive Sr isotope signatures (i.e., low $^{87}Sr/^{86}Sr$ (Figure 27c) and $\delta^{88/86}Sr$ (Figure 25) compared to other Coorong sites at that time, implying some local events or processes brought external or additional Sr from continental waters, such as local groundwater discharge.

Finally, in all seasons several of the South Lagoon samples plot towards the Salt Creek-Ocean water mixing lines in the Sr isotope vs elemental ratio plots (see Figure 24, Figure 25 and Figure 27). Considering the North Lagoon and several South Lagoon samples were shown to be a mix of River Murray and Lower Lakes with ocean water, rather than just ocean water, a representative North Lagoon sample has been used to determine a mixing line with Salt Creek water (Figure 27). The proportion of the South Lagoon-derived strontium (estimated to be sourced from Salt Creek or the North Lagoon based on a theoretical mixing line; Figure 27) is presented in Table 2. Based on these estimates, Salt Creek can contribute up to 50% of the strontium into the South Lagoon, with one outlier sample showing up to 85%, although the South Lagoon strontium is often predominantly sourced from North Lagoon water. The North Lagoon water composed of River Murray and Lower Lakes water sources mixed with ocean water, which together result in a mixture that has a similar Sr isotope signature as Salt Creek water. However, the evapoconcentration and retention of nutrients and dissolved ions in the South Lagoon (Department for Environment and Water 2022b) leads to the strontium mass balance for the South Lagoon being rather complex to quantify and link to the water balance, but further work based on water isotopes could constrain the local evaporation effects, thus providing a more accurate water source apportionment in the South Lagoon. Additionally, the monitored period (2020-early 2021) represented a low Salt Creek flow year even in winter-autumn (Figure 12b), therefore it is unlikely that this (i.e., the above mentioned 85% contribution) accurately reflects the water balance and the more typical contribution of Salt Creek is likely to be <50%. The extent of evapoconcentration would need to be determined for the South Lagoon to better quantify the actual water balance for the South Lagoon. Nevertheless, our data and observations demonstrate that the North Lagoon and Salt Creek both contribute to waters in the South Lagoon.

SEASON	LOCATION	OCEAN	RIVER MURRAY AND LOWER LAKES
All seasons	North and South Lagoon	40-55%	45-60%
Autumn	North Lagoon	60-100%	0-40%
Summer/spring	DS Tauwitchere barrage	0-5%	95-100%
Winter	DS Tauwitchere barrage	60%	35%

Table 1. Strontium isotope mass balance calculations for mixing of River Murray and Lower Lakes with ocean water.

Table 2 Strontium isotope mass balance calculations for mixing of Salt Creek with representative North Lagoon water.

SEASON	LOCATION	SALT CREEK	NORTH LAGOON
All seasons	South Lagoon	0-50%	50-100%



Figure 27. Cross-plots of radiogenic strontium isotope ratio (⁸⁷Sr/⁸⁶Sr) versus the magnesium/sodium elemental ratio (Mg/Na) of water samples and mixing lines between ocean and average values from the River Murray and Lower Lakes, Salt Creek and groundwater from along the North Lagoon and South Lagoon for (a) winter, (b) spring, (c) summer and (d) autumn. The range of the Salt Creek mixing lines are shown by faint lines of same colour. Also, note that most River Murray and Lower lakes, as well as DS Tauwitchere barrage samples in spring and summer plot out of scale and thus are not shown.

3.3 Quantifying groundwater contribution to the Coorong

Key findings

• Groundwater appears to be a relatively minor contributor of nutrients at a lagoonal scale, but groundwater inflows could be locally significant and fresher water lenses were detected under the margins of the South Lagoon.

3.3.1 Shallow piezometers and Hydrus model

Drivepoint piezometer water levels showed a distinct gradient towards the Coorong and a transition from groundwater to Coorong water (apparent in measured specific conductivity values) during both summer and winter (Figure 28 and Figure 29). The water levels in both the groundwater and the Coorong were higher in winter than in summer.

Water levels measured in the piezometers were approximately constant over the three-week summer period of measurement at Jack Point, validating the decision to use constant water levels in the model. Correspondingly, estimates of groundwater fluxes for Jack Point modelled in Hydrus were approximately 0.2 m/d, with the location of modelled discharge at the surface roughly corresponding to the pools of fresher water observed between the shoreline and approximately 30 m offshore during summer. The winter model estimated similar magnitude fluxes along that shoreline in the winter, with some fluxes up to 1 m/d at the shoreline break in slope in winter. It should be noted that this model does not consider the difference in salinity between the groundwater and the Coorong; this will impact the location of discharge more in winter, since the area of groundwater discharge along the shoreline is under the more saline Coorong water in winter.

Similarly, water levels measured in the three shallow piezometers were constant over three days of winter at North South Lagoon (NSL). The water table at NSL1 was only ~0.2 m higher than the surface water level, with a gradient of 0.008 between the two piezometers, and a steady state Hydrus model of the transect yielded inconclusive results (Figure 29).



Figure 28. Summer and winter water levels across the Jack Point (JP) transect measured in the field (top). Fluxes (cm/day) modelled for the summer conditions (bottom left) and winter conditions (bottom right) in Hydrus. The left-hand boundary of the model is JP1 and the right-hand boundary is JP2.



Figure 29. Winter water levels across the North South Lagoon (NSL) transect measured in the field (top) and modelled groundwater fluxes in Hydrus (bottom). The left-hand side of the boundary is NSL1, while the right-hand side is approximately 40 m from the shoreline into the Coorong.

The datalogger at Ti-Tree site location TT1 failed during the sampling period; therefore, time series water levels are only available at TT3 for that transect, and no model was constructed for TT. In contrast to the drivepoints at the other transects, the data at TT3 shows strong diurnal variation in the water level and EC, while temperature remains constant, showing the effects of plant water use (Figure 30). Estimates of evapotranspiration, using these water levels in the White Method (1932) as in Shanafield et al. (2017), suggested daily values of 1-2 mm/d. These are relatively low, given the high density of melaleuca in the area; however, this may be an underestimate given that the piezometer was located ~20 m from the melaleuca grove. It is apparent from the strong diurnal variation in the water table that evapotranspiration plays a dominant role in groundwater fluxes in this region.



Figure 30. Measured water elevation (m above sea level) (top) and estimated evapotranspiration rates (daily ET) at Ti-Tree site location TT1 in Summer.

3.3.2 Seepage meters, Hot Rod and shallow soil EC

Seepage meters successfully measured groundwater fluxes of –0.09 (weakly infiltrating) to 1.42 m/d (strongly upwelling) into the South Lagoon at the study sites: JP, NSL and Goodwater (Figure 31, Figure 32 and Table 3). It was not possible to use the seepage meters at the TT site due to the much lower lagoon water level and distance from the shoreline.

Analysis of nine Hot Rod datasets at the JP (n=3), NSL (n=3), TT (n=1) and Goodwater (n=2) sites indicated oblique upward groundwater fluxes that ranged from 0.34 to 10.52 m/d (average = 4.2 m/d), which was a factor of approximately 3x the 20 individual seepage meter measurements.

The location of the groundwater discharge into the lagoon was extremely localised (Figure 32). Visual indicators of the location of groundwater discharge included: small sand boils at the near surface, evidence of mineral precipitation and staining amongst the lagoon tidal flats, measured lower salinity water (<50 mS/cm) compared to the lagoon water (>100 mS/cm), and low soil EC (<20 mS/cm). The spatial heterogeneity and variability meant that it was very difficult to position the seepage meters within the lagoon to be able to measure the flux. This was more of a challenge in September 2021 when the lagoon water level was higher, and it was not as obvious as to where the localised discharge was occurring in the nearshore.





Seepage (m/d)	All data	Jacks Point	North South Lagoon	Goodwater	North South Lagoon	North South Lagoon
	(n=37)	summer (n=16)	summer (n=9)	summer (n=1)	winter (n=11)	summer/winter (n=20)
median	0.006	0.004	0.114	0.209	0.000	0.011
mean	0.111	0.006	0.302	0.209	0.098	0.190
First quartile	-0.001	-0.001	0.006	0.209	-0.001	0.000
Third quartile	0.056	0.011	0.471	0.209	0.070	0.184
IQR	0.057	0.012	0.464	0.000	0.071	0.185
Lower bound	-0.087	-0.019	-0.690	0.209	-0.107	-0.277
Upper bound	0.142	0.028	1.167	0.209	0.177	0.462

Figure 31. Whisker-box plot showing the range of seepage flux (m/d) measurements from the study sites in February/March (summer) and September 2021 (late winter). Photo shows installation of seepage meter at North South Lagoon (NSL) in summer where there was observable groundwater discharge to the lagoon.

Table 3. Groundwater flux estimates into the South Lagoon based on seepage meter measurements inFebruary/March (summer) and September 2021 (late winter) at Jack Point, Goodwater and North South Lagoon (NSL).Positive values equal groundwater discharge.

Site name	Start Time	Eastings	Northings	Elevation (mAHD)	Seepage(m/d)	± md	Seepage (mm/d)
Jack Point	2/23/21 18:35	371055	6012412	0.133	0.003	0.02	2.9
Jack Point	2/23/21 17:35	371057	6012432	0.186	0.001	0.05	1.4
Jack Point	2/23/21 15:55	371050	6012418	0.095	-0.001	0.01	-0.8
Jack Point	2/23/21 17:20	371046	6012461	0.126	0.002	0.01	2.2
Jack Point	2/26/21 12:35	371076	6012648	0	-0.015	0.01	-15.3
Jack Point	2/26/21 13:39	371135	6012519	0	-0.002	0.04	-2.3
Jack Point	2/26/21 13:27	371123	6012595	0	0.012	0.02	12.4
Jack Point	3/17/21 10:42	371119	6012308	0	0.010	0.01	9.9
Jack Point	3/17/21 10:30	371140	6012427	0	0.014	0.07	13.8
Jack Point	3/17/21 10:19	371187	6012371	0	-0.008	0.01	-7.9
Jack Point	3/17/21 11:14	371003	6012381	0	-0.020	0.02	-20.3
Jack Point	3/17/21 10:56	371150	6012213	0	0.022	0.03	21.9
Jack Point	3/17/21 12:34	371088	6012262	0	0.007	0.03	6.6
Jack Point	3/17/21 11:55	371187	6012284	0	0.005	0.03	4.9
Jack Point	3/17/21 12:25	371106	6012137	0	0.007	0.02	7.2
Jack Point	3/17/21 12:30	371241	6012168	0	0.056	0.04	56.5
Goodwater	2/24/21 13:28	366935	6018423	0.018	0.209	0.03	208.6
NSL	2/24/21 17:57	361386	6024488	0	0.251	0.03	251.2
NSL	2/24/21 17:04	361324	6024506	0	1.166	0.60	1165.9
NSL	3/17/21 14:15	361384	6024483	0	0.114	0.14	114.2
NSL	3/17/21 14:26	361389	6024485	0	0.016	0.05	16.1
NSL	3/17/21 14:32	361386	6024489	0	0.787	0.25	787.0
NSL	3/17/21 14:41	361382	6024486	0	-0.004	0.04	-3.5
NSL	3/17/21 14:50	361388	6024482	0	0.471	0.04	470.9
NSL	3/17/21 15:09	361386	6024481	0	0.006	0.25	6.5
NSL	3/17/21 15:14	361383	6024482	0	-0.087	0.03	-87.0
NSL	7/09/2021	361368	6024518	0.29	-0.026	0.0	-25.9
NSL	7/09/2021	361366	6024516	0.225	0.000		0.0
NSL	7/09/2021	361365	6024513	0.158	-0.001	0.1	-1.4
NSL	7/09/2021	361364	6024510	0.144	0.000		0.0
NSL	7/09/2021	361362	6024507	0.111	0.050	0.1	50.2
NSL	9/09/2021	361403	6024471	-0.047	0.000		0.0
NSL	9/09/2021	361404	6024470	-0.046	0.091	0.2	90.7
NSL	9/09/2021	361407	6024467	-0.025	-0.055	0.1	-55.3
NSL	9/09/2021	361396	6024471	-0.047	0.000		0.0
NSL	9/09/2021	361398	6024470	-0.046	0.395	0.4	395.1
NSL	9/09/2021	361399	6024467	-0.025	0.620	0.1	619.8



Figure 32. Seepage measurement locations and measured fluxes (mm/d) and shallow soil electrical conductivity (EC) measurements at the North South Lagoon site.

3.3.3 Near-surface geophysics

Results from the near-surface geophysical LoupeEM data showed that there was very low subsurface resistivity (Ohm-m) (i.e. high conductivity) in the nearshore environment, as expected given the very saline conditions of the Coorong. Preliminary inversion results from the JP and NSL sites show some interesting spatial heterogeneity in the resistivity measurements in the near surface, which indicates changes in the geological material and/or changes in the water quality (Figure 33 and Figure 38). Note that the resistivity scale that is shown in the figures for the JP site is two orders of magnitude larger than for the NSL site. This was done to show greater contrast in the measurements. At JP the resistivity values were higher for the sandy material on the eastern side of the Princes Highway. The depth sections or slices represent depth below ground level.

At the JP site there was a distinct change from more resistive (100 ohm-m) material in the near surface to a layer of material with values of 20 ohm-m at an elevation of about -2 to -3 mAHD (Figure 35 and Figure 36). This relatively thin layer transitioned to less resistive material (5 ohm-m) at about -5 mAHD before decreasing further with depth to very low resistivity values (high conductivity), indicative of saturated saline sediments. A similar trend was also noted at the NSL site, however, the thin layer overlying the lower resistive material appeared at a shallower depth (-1 mAHD) (Figure 37 and Figure 38).

This thin layer as well as the very low resistivity deeper sediments appear to extend quite far eastwards (away from the Coorong) beneath the dunes and beyond the nearshore environment of the Coorong.

The resistivity depth sections orientated in a West-East direction across the Coorong mudflats show that the low-lying vegetated dunes have higher resistivity values and are above the regional watertable.



Figure 33. Depth slices (top left: 0-2 m, top right: 2-4 m, bottom left: 4-6 m, bottom right: 6-8 m) showing resistivity (Ohm-metre) from selected inverted LoupeEM data at Jack Point (JP), February 2021.



Figure 34. Depth slices (top left: 8-10 m, top right: 10-12 m, bottom left: 12-14 m, bottom right: 14-16 m) showing resistivity (Ohm-metre) from selected inverted LoupeEM data at Jack Point (JP), February 2021.



Figure 35. Profile sections of inverted LoupeEM data showing resistivity (Ohm-metre) of selected North-South survey lines. Top: Line 1 (farthest east), middle: Line 2 (mudflats) and bottom: Line 3 (west, closest to the Coorong) at Jack Point (JP). Selected profile locations are shown in Figure 33.



Figure 36. Profile sections of inverted LoupeEM data data showing resistivity (Ohm-metre) of selected West-East survey lines. Top: Line 1 (farthest north), middle: Line 2 (middle) and bottom: Line 3 (south) at Jack Point (JP). Selected profile locations are shown in Figure 33.



Figure 37. Resistivity depth sections of inverted LoupeEM data at the North South Lagoon (NSL) site. Top left: 0-2m (top left), top right: 2-4m (top right), bottom left: 4-6m (bottom left) and bottom right: 6-8m (bottom right). Survey line numbers (1 through to 10 with every second survey line labelled) are shown in top left figure.



Figure 38. Profile sections 1, 3, 5 and 7 (top to bottom) of inverted LoupeEM data showing resistivity (Ohm-metre) of selected Northwest-Southeast survey lines at the North South Lagoon (NSL) site. Survey line numbers (1 through to 10 with every second survey line labelled) are shown in Figure 37.

3.3.4 Radon

Radon is an inert noble gas that is naturally present in soils and rocks; it is therefore also naturally present in aquifers, where water interacts with rocks over long periods of time. Because it is a gas, radon is not typically present in surface water, which is open to the atmosphere, allowing the gas to escape (off-gas) from the water. However, where groundwater is discharging to the surface, the radon carried by the groundwater provides a good tracer of such fluxes. Radon was not detectable in the nine samples of radon collected in surface waters (Table 4). However, this result does not necessarily indicate the absence of groundwater, as
windy conditions and shallow waters would allow rapid off-gassing. Radon was present in two out of three subsurface samples measured in January/February 2021, indicating the presence of groundwater, however, the radon concentration was relatively low (<0.28 Bq/L) at the shoreline, and even in the sample from Wedge 1 (<0.36 Bq/L), which represents the regional groundwater (Figure 39). Given these low concentrations and our success with the seepage meter and Hot Rod; radon measurements were not collected in the September 2021 (late winter) sampling campaign.

Site	Sample type	Collection method	²²² Rn (Bq/L)
Outlet at Salt Creek	Surface	PET	0
1.8 KM	Surface	PET	0
Snipe Point	Surface	PET	0
Seagull Point	Surface	PET	0
N Jack Point	Surface	PET	0
Stony Well	Surface	PET	0
Villa de Yumpa	Surface	PET	0
Long Point	Surface	PET	0
Parnka Point	Surface	PET	0
Jack Point	Groundwater	PET	0
Ti Tree	Groundwater	PET	0.28
Wedge 1	Groundwater	Rad7	0.36

Table 4. Results of radon analyses in September 2020, January 2021 and February 2021. As described above, the Rad7and PET methods of sample collection were used.

3.3.5 Water chemistry and stable isotopes

Water chemistry indicated areas of regional groundwater inflow and mixing between groundwater and Coorong water (Table 5). The samples that were collected from the wedges had measured EC values between 15 and 20 mS/cm. These values are representative of regional groundwater in this region and are consistent with the range of reported values described in Barnett (2019). At the shoreline and across the tidal mudflats, measured EC values in the shallow drivepoints were >15 and <50 mS/cm. In comparison, measured EC of the Coorong water from the lagoon was >84 mS/cm and up to 150 mS/cm in the summer field campaign; close to three times seawater.

The stable isotope composition of the regional groundwater samples from the Wedges have $\delta 180$ of -3.9 to 0‰ and $\delta 2H$ values between -25.1 and -4.7% (Figure 40). The regional groundwater samples plot closely to the local meteoric water line (MWL) (except for Wedge 2 that shows signs of evaporative enrichment), whilst the samples of the Coorong water show clear trends of isotopic enrichment, along an evaporation line (to the right of the MWL). The water samples from the drivepoints plot close to the regional groundwater and also along the evaporation line in between the samples from the Coorong. This is more apparent in Figure 41, which shows that the water samples from the shallow drivepoints are predominantly regional groundwater and some of them are a mix with the more saline and isotopically enriched water from the Coorong.



Figure 39. There are few suitable regional aquifer boreholes in the vicinity of the Coorong; however, the chemistry of the regional groundwater can be assessed by sampling local "wedges" on pastoral land adjacent the South Lagoon.

SampleID	Description	Date	Eastings	Northings	Elevation	Temp	SEC	DO	рН	Redox	Field to alkalinity	otal	δ ¹⁸ 0	δ²Η	TDN	TDP	NO2+NO3
			GDA94 z	one 54	mAHD	٥C	mS/cm	mg/L		mV	mg/L		‰ re VSMOW	l ‰ rel VSMOW			
JP1	drivepoint	23/02/21	371079	6012427	1.55	23.7	22.5	8.7	7.9	-65	N/S		-4.2	-26.5	0.122	-	0.014
JP2	Lagoon JP	23/02/21	371018	6012418	0.036	22.9	117.8	1.86	7.0	-422	N/S		4.1	18.9			
Coorong JP	Lagoon JP	17/03/21	370909	6012420	-0.181	15.2	123.7	N/A	7.2	-31	N/S		6.5	31.8			
GoodWater	Goodwater	24/02/21	366938	6018424	0.054	21.3	25.7	8.74	7.9	-72	369		-5.1	-31.4			
NSL2	drivepoint	24/02/21	361391	6024501	0.524	22.4	41.9	12	7.7	-72	N/S		-4.2	-27.0	0.874	-	0.008
TT3	drivepoint	25/02/21	377499	6001988	0.592	19.2	26.0	10.6	7.3	-62	620		-0.3	-3.5	1.36	0.021	0.012
TT1	drivepoint	25/02/21	377560	6001996	1.354	19.2	26.6	12.72	7.2	-28	940		-1.8	-12.2	1.43	0.042	0.028
TT2	drivepoint	25/02/21	377533	6001994	0.74	18.7	17.8	9.8	7.2		720		N/S				
TTC	Lagoon TT	17/03/21	377349	6001853	0	23.4	152.8	13.6	7.9	24	N/S		6.4	30.2			
JPA	drivepoint	26/02/21	371065	6012419	0.659	24.5	23.8	56.56	8.3	-93	N/S		-1.5	-13.7			
JPB	drivepoint	26/02/21	371073	6012413	1.331	24.0	24.2	12.21	8.3	-95	N/S		-2.8	-18.6			
JPC	drivepoint	26/02/21	371078	6012409	1.547	24.7	23.3	15.69	8.5	-101	N/S		-2.1	-15.5			
Wedge 1	Regional groundwater	26/02/21	373155	6016433	7	21.9	15.4	9.9	7.6	-52	N/S		-3.9	-25.1	0.329	-	0.002
Coorong JP	Lagoon JP	7/09/21	371064	6012426	0.463	14.2	93.4	6.91	8.2	74	N/S		N/S				
JP1	drivepoint	7/09/21	371080	6012428	1.4	16.5	16.5	2.32	7.4	68	377		-4.3	-26.4			
NSL1	drivepoint	7/09/21	361392	6024556	2.575	15.4	28.7	3.8	7.2	7	525		-4.6	-28.6	0.88	0.05	0.44
NSL2	drivepoint	7/09/21	361375	6024529	0.704	16.6	45.2	2.36	6.8	24	500		-3.7	-24.6	0.95	0.03	0.14

Table 5. Results of physical water quality and stable isotope measurements for groundwater samples from the February and September 2021 field surveys.

Coorong NSL	Lagoon NSL	7/09/2021	361368	6024518	0.461	17.4	92.5	6.55	7.8	57	177	1.7	10.3	1.88	0.03	<0.001
TT1	drivepoint	8/09/21	377560	6001996	1.354	14.9	19.4	3.73	6.7	-134	735	-1.3	-8.7	1.09	0.05	<0.001
Coorong TT	Lagoon TT	8/09/21	377533	6001994	0.74	15.9	84.6	7.8	7.9	41	215	1.0	5.3	1.47	0.02	<0.001
Wedge 2	Regional groundwater	8/09/21	371497	6016486	2.556	17.7	15.1	4.4	7.2	-284	290	0.0	-4.7	1.83	0.03	<0.001
Wedge 3*	Regional groundwater	8/09/21	368632	6016721	0.964	17.5	23.8	0.9	6.6	-310	1300	-3.8	-24.3	16.2	5.2	0.01
Stony well	Regional groundwater	9/09/21	366642	6019292		14.4	22.7	13	7.2	40	390	-3.9	-23.8			

*Note that Wedge 3 water was stagnant; this water source is not pumped regularly, and measured water quality may not reflect aquifer values. N/S indicates no sample.



Figure 40. Bivariate plot of δ^{18} O and δ^{2} H with the local meteoric water line (MWL) and weighted average rainfall for Adelaide (Hollins et al. 2018). Water samples collected during the summer and winter field campaigns.



Figure 41. Bivariate plot for δ^{18} O versus electrical conductivity (mS/cm) for samples collected during the summer and winter field campaigns.

3.4 Constraints on redox conditions in the Coorong

Key findings

- The South Lagoon has oxygen depleted or 'less oxic' water column conditions compared to the North Lagoon, but there is no evidence of anoxia occurring.
- The oxygen depleted and more reducing conditions in the South Lagoon sediments have resulted in enrichment of ammonium and possibly total dissolved phosphorus in the South Lagoon.
- Redox processes, in particular sulfate reduction by sulfate reducing bacteria and sulfide oxidation, are also occurring in the South Lagoon, as well as parts of the North Lagoon.

3.4.1 Insight from dissolved oxygen data and implications for nutrient sources

Oxidation-reduction (redox) reactions of chemical species (nutrients, organic matter, metals etc.) in the Coorong and other natural waterways are primarily controlled by the availability of oxygen (O₂) and organic matter in the system. The redox conditions control the chemical/redox speciation and availability of nutrients in the water column or at the sediment-water interface. For example, dissolved nitrogen in waters can be present either as 'oxidised' or 'reduced' species, where the former oxidised nitrite (NO₂⁻) and nitrate (NO₃⁻) ions are more dominant in O₂-rich (oxic) settings, while the latter reduced species ammonium (NH₄⁺) ions are more abundant in O₂-depleted (anoxic) conditions. Similarly, carbon can be present either as the oxidised carbon species (i.e., dissolved inorganic carbon: HCO_3^{-} or $CO_3^{2^{-}}$ ions, or CO_2 gas) or as the reduced carbon species in the form of methane (CH₄) and organic matter (i.e., $C_xH_xO_x$).

An understanding of the spatial and temporal changes in dissolved oxygen (DO) availability and the redox conditions in the Coorong is required to understand the chemical speciation of the main nutrients in the system. Firstly, during our sampling campaigns DO levels were measured in Coorong waters (Figure 42a) to better quantify these local redox conditions. As the levels of DO in coastal waters can vary throughout the day due to a daily photosynthesis/respiration cycle, the sampling strategy was designed to minimise these effects. Specifically, two different sampling teams simultaneously (i.e., from morning to noon) measured DO levels in waters in both the North Lagoon and South Lagoon. This sampling approach limited the possibility that the measured DO patterns across the Coorong were an artefact of daily DO cycling. Instead, the results (Figure 42a) showed that the DO levels were systematically higher (between 6 and 12 mg/L) and thus 'more oxic' in the North Lagoon, compared to the South Lagoon, which is relatively more depleted in oxygen (with DO measurements ranging from 4 to 8 mg/L). This DO gradient along the Coorong suggests reducing processes are more influential in the South Lagoon, which could have implications for nutrient speciation and availability as discussed below.

Under the HCHB program's Water Resource Optimisation project new water quality instruments have been installed that enable, for the first time, continuous measurements of DO and other parameters at certain locations. Preliminary data from these *in situ* instruments also confirm there is no evidence of anoxia in the South Lagoon (Figure 43, see NW Snipe Island and Parnka Point sites), consistent with the field monitoring results at time of water sampling.

Importantly, the nutrient data suggest that the oxygen depleted and more reducing conditions in the South Lagoon have resulted in enrichment of ammonium (NH₄⁺) in the South Lagoon (Figure 42b). Interestingly, total dissolved phosphorus (TDP) concentrations also show systematic enrichments in the South Lagoon waters (Figure 42c). This enrichment could be partly due to a redox effect on local phosphorus cycling, which is known to be tightly linked to redox cycling of iron (Fe) (Azzoni et al. 2001, Pagès et al. 2012). Specifically, in more oxic waters where there is predominantly formation of iron-oxy-hydroxides the dissolved phosphorus ions in waters (i.e., phosphate anion, PO_4^{3-}) can be readily adsorbed to these Fe-oxide minerals, removing phosphorus from the ambient waters. In contrast, more reducing waters will facilitate release of phosphorus from iron-oxy-hydroxides in the sediment into the Coorong waters. Total organic carbon (TOC) is much higher in the South Lagoon water (Figure 42d) and mineralisation of this by heterotrophic bacteria could exert a higher oxygen demand in the water compared with the North Lagoon.



Figure 42. Cross plot of (a) dissolved oxygen (DO), (b) ammonium (NH4⁺), (c) total dissolved phosphorus (TDP), and (d) total organic carbon (TOC) against salinity for the Coorong and its main freshwater inputs (River Murray and Lower Lakes, and Salt Creek regulator). Note several South Lagoon samples plot out of scale and thus are not shown (see Figure 18).



Figure 43. Snapshot of dissolved oxygen (DO) concentrations in the Coorong from continuous monitoring stations installed as part of the HCHB program's Water Resource Optimisation project. Locations include Long Point (blue), Parnka Point (green) and NW Snipe Island (orange). Data obtained from: www.water.data.sa.gov.au

3.4.1 Sulfur isotope variability in the Coorong and implications for local redox conditions

To further constrain the spatial and temporal variability in local redox conditions across the Coorong we also applied a redox-sensitive isotope tracer, specifically stable sulfur (S) isotopes. Like dissolved nitrogen or carbon species, which can be present in waters in both oxidised and reduced forms (see section 3.4.1), sulfur is also a redox-sensitive element and can be available in waters either as oxidised sulphate (SO_4^{2-}) anion, or as highly reduced hydrogen sulphide (HS^-) species that are common in anoxic/euxinic waters.

Sulfur isotope data from the key sources of water to the Coorong indicate (i) the River Murray has an average δ^{34} S signature of 18‰, (ii) ocean water has a typical seawater δ^{34} S of 21‰, and (iii) Salt Creek water has a δ^{34} S that is typically slightly lower than seawater (Figure 44). A two-component (seawater, River Murray) water mixing scenario was created for these different dissolved S sources to explore whether mixing in and of itself could explain the δ^{34} S patterns in the Coorong water. If this was the case δ^{34} S values would plot on the typical two-component 'hyperbolic mixing' trends seen in Figure 44a-c, or with a logarithmic horizontal axis, where the two-component mixing trend would be displayed as a straight line (Figure 44d-f). However, the δ^{34} S composition of most of the North Lagoon and South Lagoon water samples is generally higher than the ocean and therefore does not fit along an obvious 'River Murray-seawater mixing trend line' (Figure 44d-f). Neither do the samples fit on a Salt Creek-ocean or Salt Creek- River Murray mixing line.

Instead, we hypothesise that the 'heavier' and variable (>10‰) δ^{34} S values in the North and South Lagoons are a result of local redox processes, in particular sulfate reduction and sulfide oxidation. The North and South Lagoons have abundant carbon available for sulfate reduction via sulfate reducing bacteria, as confirmed by Total Organic Carbon (TOC) data in Figure 42d, but also DOC and PC data in Figure 19a and Figure 20b, respectively. In aqueous sediments where sulfate reduction to sulfide is occurring in conjunction with iron reduction (Fe^{III} to Fe²⁺), iron monosulfide minerals can form (also known as monosulfidic black oozes, MBOs). Indeed, MBOs are widespread in the anoxic sediments of much of the South Lagoon and southern regions of the North Lagoon, as evidenced by Acid Volatile Sulfide (AVS) concentrations >0.01% in the sediment (from T&I Activity 1.3 nutrient cycling and fluxes investigations).

There was variability in the δ^{34} S values in the South Lagoon and interestingly the δ^{34} S sometimes shifted to well below that of seawater (δ^{34} S < 21‰). It was considered whether the periodic lower δ^{34} S values could be due to input of isotopically lighter SO₄²⁻ into the South Lagoon from Salt Creek (δ^{34} S ~+19‰) or the River Murray (δ^{34} S ~+15‰), but input from these sources was low throughout 2020 and early 2021 and the δ^{34} S was often lower than Salt Creek in the South Lagoon. An alternative potential driver may be when MBOs are periodically resuspended into the water column with wind and wave action on the shallow Coorong lagoons. This could result in their oxidation and dissolution as MBOs are very reactive when in contact with dissolved oxygen (Bush et al. 2004). This resuspension and oxidation process could result in release of more 'light' ³²S isotopes that had previously fractionated into the reduced inorganic sulfur MBO phases, similar to when pyrite (FeS₂) oxidation occurs (Leyden et al. 2021). Another environmental factor that could contribute to lower δ^{34} S values, is localised groundwater input, which is expected to be more consistent over time. Further research is required to unravel all the complexities on S cycling in the Coorong but the data are consistent with redox processes, in particular sulfate reduction, influencing the water body.



Figure 44. Spatial variability in sulfur isotope composition (δ^{34} S) of the Coorong and main freshwater inputs, plotted as the function of (a) salinity, (b) concentration of dissolved Calcium (Ca), and (c) sulphate ions (SO₄²⁺). The δ^{34} S values are again plotted as the function of (d) salinity, (e) concentration of dissolved Ca, and (f) sulphate ions with logarithmic horizontal axis. The blue horizontal line illustrates ocean seawater values.

3.5 Nutrient budget

Key findings

- The South Lagoon sediment has approximately 50 times larger nutrient (nitrogen and phosphorus) stocks compared to the North Lagoon water column.
- There is both seasonal and long-term variability in the nutrient budgets; although there was generally a net export of nutrients at Pelican Point in the North Lagoon, due to the flushing effect of releases from the River Murray via the barrages, and the ocean. Conversely, there was a net import of nutrients to the South Lagoon at all times, except during the high barrage flows in 2016.
- In the South Lagoon the majority of the nutrients (>50%) are estimated to be coming from the sediments, followed by inputs from the North Lagoon (<50%), with Salt Creek providing only a fraction of the annual nutrient supply (<1%).

3.5.1 Water nutrient stocks

For the 2019-2020 period, there is nitrogen stock between 559 and 671t and phosphorus stock between 22 and 33t in the South Lagoon (Table 6). In comparison nutrient stocks in the North Lagoon are about 40-50% lower. Nutrient stocks are slightly higher in the Coorong in autumn-winter, likely reflecting higher water levels at this time. Long term nitrogen and phosphorus stocks (Mosley and Hipsey 2019) are similar to those calculated for the 2019-2020 period for the South Lagoon, and phosphorus for the 2019-2020 period in the North Lagoon (Table 6) However, current nitrogen stocks seem to be higher (approximately double) for the North Lagoon compared to the long-term average.

The uncertainties calculated for the water nutrient stocks (Table 6), as well as sediment nutrient stocks (Table 7) and nutrient fluxes (Table 8Table 13), reflect monitoring data measurement uncertainties. The uncertainties do not include estimates of uncertainties in model assumptions, nor model sensitivity to parameters, although this has been done for the annual time series biogeochemical modelling and nutrient budgets for TN, TP and other nutrients in Grigg et al. (2009). Nevertheless, the nutrient budget estimates presented below include more recent measurements, more detail modelling of volume fluxes, disaggregation of budgets into two seasons, and the inclusion of inputs from Salt Creek, as well as exchanges with sediment and groundwater.

	SOL	JTH LAGOON	NOF	RTH LAGOON
	NITROGEN	PHOSPHORUS	NITROGEN	PHOSPHORUS
	(tonnes)	(tonnes)	(tonnes)	(tonnes)
Long term average stock (1997-2019)	640	30	160	13
	April–Sept	ember		
Average	671	33	311	18
± SE	18	1	2	0.1
	October–I	March		
Average	559	22	274	11
± SE	15	1	2	0.1

Table 6. Coorong water nutrient stocks for the approximate long term (1997-2019) average calculated in this study from DEW monitoring data (Mosley et al. 2020) and 2019-2020 calculated from modelled water volume and total Nitrogen (TN) and total Phosphorus (TP) concentration data measured in this study.

3.5.2 Sediment nutrient stocks

The Coorong surface (0-5 cm) sediment has a very large stock of nitrogen and phosphorus (Table 7); there is 50-70 times more phosphorus and 30-40 times more nitrogen in this upper sediment layer compared to the whole water column. The South Lagoon sediment has much higher (>2 times) nitrogen and phosphorus stocks compared to the North Lagoon sediment.

	SOL	JTH LAGOON	NOF	TH LAGOON
	NITROGEN	PHOSPHORUS	NITROGEN	PHOSPHORUS
	(tonnes)	(tonnes)	(tonnes)	(tonnes)
Average	25506	2204	9377	924
± SE	8982	751	5929	441

 Table 7. Sediment nutrient stocks and standard deviation of interpolated data. Assumed to represent 'long-term' stocks.

3.5.3 Nutrient fluxes and budget

Nutrient fluxes in seasonal 6 month periods is shown for the Pelican Point cross section in Table 8, Parnka Point cross section in Table 9, Salt Creek inflow in Table 10, and rainfall inputs in Table 11. It should be noted that the nutrient fluxes at Pelican Point represent barrages, as well as the ocean and residual Coorong flux from the Department for Environment and Water (2022b) modelling results (Table 8). These nutrient fluxes were integrated into an April–September (Figure 45) and October–March seasonal (Figure 46) and annual (Figure 47) nutrient budget to assess how nutrient stocks change in the two lagoons over these time periods due to nutrient fluxes.

The two seasonal nutrient budgets highlight the high seasonal variability across the system. In autumn-winter (April–September) there is a net export of nutrients from the North Lagoon out to the Murray Mouth (see Figure 45 and Table 8). The total water exported is dominated by water and nutrients that have previously entered the Coorong from the River Murray and Lower Lakes through the barrages (Figure 11a). The apparent flushing of nutrients in winter, despite increased nutrient inputs from the Murray-Darling Basin is likely due to better mixing with higher water levels (driven by both inflow and higher sea levels). The net effect is water with less nutrients entering the Coorong, and more nutrient-rich water leaving the system. In contrast, there is a net transport of nutrients into the North Lagoon in spring-summer (October–March) that is also dominated by water and nutrient load originating from the River Murray and Lower Lakes through the barrages (Figure 46 and Table 8).

Overall nutrient fluxes are lower at Parnka Point, and during both seasonal periods nutrients enter the South Lagoon from the North Lagoon (Figure 45, Figure 46 and Table 9). This supports previous findings that the North Lagoon is still being flushed but that the South Lagoon is gaining and retaining nutrients, i.e. is a nutrient sink, in the current flushing regime (Mosley et al. 2020). There are fluxes of water back and forth through Parnka Point, particularly in summer (Figure 11b), but this appears to be mainly "residual water", i.e. water that was already in the Coorong at the start of the model simulation.

Nutrient fluxes from Salt Creek are higher in the October-March period (Table 8 and Figure 46), likely reflecting the late 2019 Salt Creek water release (Figure 11c). Nevertheless, total nutrient loads entering the South Lagoon from Salt Creek are relatively small compared with loads through Parnka Point. It is noted however that on average, 2019-2020 had relatively low Salt Creek inflows.

A portion of the total water nutrients (incorporated in algae/organic matter) are being deposited and stored in the sediment, hence the high sediment nutrient stock in the South Lagoon (Table 7). Estimates of sediment fluxes (Table 12) show an overall flux of nutrients from the sediment into the water column (Figure 45, Figure 46 and Figure 47), which appears to be >80% of the nutrient flux into the South Lagoon. However, this does not account for nitrogen fixation (to be determined in HCHB T&I 'Component 2 – Aquatic plants and algae'

activities) and other nutrient fluxes to the sediment, so is likely to be an overestimation (i.e. the overall flux is not entirely attributable to sediment depositions). Therefore, further work to constrain the flux of nutrients to and from the sediment is needed. Nevertheless, these estimates highlight the potential for the nutrient rich sediments to be a source of nutrients to the Coorong.

Table 8. Nutrient fluxes at Pelican Point as derived from modelling results (Department for Environment and Water2022b) and measured nutrient concentrations.

	00	CEAN	BARRAGES-	LOWER LAKES	COORONG	G (RESIDUAL)	TOTAL TO N	ORTH LAGOON
	NITROGEN	PHOSPHORUS	NITROGEN	PHOSPHORUS	NITROGEN	PHOSPHORUS	NITROGEN	PHOSPHORUS
	(t/6months)	(t/6months)	(t/6months)	(t/6months)	(t/6months)	(t/6months)	(t/6months)	(t/6months)
			A	pril–Septembe	r			
Average	-84	-8	-1052	-130	-363	-19	-1499	-157
± SE	0.3	0.02	0.6	0.1	0.3	0.02		
			(October–March	I			
Average	126	22	448	38	-42	-2	532	58
± SE	0.2	0.03	0.8	0.1	0.1	0.003		

Table 9. Nutrient fluxes at Parnka Point as derived from modelling results (Department for Environment and Water2022b) and measured nutrient concentrations.

	00	CEAN	BARRAGES-	LOWER LAKES	COORONO	(RESIDUAL)	TOTAL TO SO	OUTH LAGOON
	NITROGEN	PHOSPHORUS	NITROGEN	PHOSPHORUS	NITROGEN	PHOSPHORUS	NITROGEN	PHOSPHORUS
	(t/6months)	(t/6months)	(t/6months)	(t/6months)	(t/6months)	(t/6months)	(t/6months)	(t/6months)
			A	pril–Septembe	r			
Average	16	2	76	9	-58	-3	34	7
± SE	0.04	0.003	0.2	0.02	0.8	0.1		
			(October–March	1			
Average	1	0.2	70	6	200	8	271	14
± SE	0.002	0.0003	0.1	0.01	0.6	0.02		

 Table 10. Nutrient fluxes from Salt Creek into the South Lagoon as derived from Salt Creek gauging station discharge data (A2390568) (water.data.sa.gov.av) and measured nutrient concentrations.

	SALT CREEK	GAUGED DATA
	NITROGEN	PHOSPHORUS
	(t/6months)	(t/6months)
	April–Septembe	er
Average	4	0.4
± SE	0.001	0.0002
	October–Marcl	h
Average	6	0.7
± SE	0.002	0.0002

 Table 11. Nutrient fluxes from rainfall into the Coorong as derived from cumulative rainfall (Bureau of Meteorology 2021) and representative measured nitrogen and phosphorus concentrations (Crosbie et al. 2012).

	RAI	NFALL
	NITROGEN	PHOSPHORUS
	(t/6months)	(t/6months)
	April–Septembe	er
Average	12	8
± SE	5	5
	October–Marc	h
Average	4	3
± SE	2	2

Table 12. Nutrient fluxes from the sediment and standard deviation of measured flux data (from T&I Activity 1.3 nutrient cycling and fluxes investigations). Standard deviations are relatively large because of flux measurement variability between locations, as well as light and dark conditions. Nutrient fluxes to the sediment are estimated based on deposition rates (Haynes et al. 2020) and nutrient concentrations, but do not account for nitrogen fixation rates. Assumed to represent 'long-term' sediment nutrient fluxes.

	SOL	JTH LAGOON	NOF	TH LAGOON
	NITROGEN	PHOSPHORUS	NITROGEN	PHOSPHORUS
	(t/6months)	(t/6months)	(t/6months)	(t/6months)
Average flux from the sediment	1948	103	1794	193
± SD	3163	268	1258	183
Average flux to the sediment	-255	-22	-150	-15
± SD	90	8	94	7

 Table 13. Nutrient fluxes from measured localised groundwater fluxes into the South Lagoon and groundwater nutrient concentrations. Assumed to represent 'long-term' groundwater nutrient fluxes.

	SOL	JTH LAGOON
	NITROGEN	PHOSPHORUS
	(t/6months)	(t/6months)
Average	5	0.2
± SD	13	0.4



Figure 45. April–September seasonal nutrient budget. Water and sediment stocks units = tonnes. Fluxes units = tonnes over 6 month period. The size and direction of the arrows provides a relative indication of the magnitude and direction of nutrient fluxes. The dashed red vertical lines correspond to model flux output points (see Figure 9; Department for Environment and Water 2022b).



Figure 46. October–March seasonal nutrient budget. Water and sediment stocks units = tonnes. Fluxes units = tonnes over 6 month period. The size and direction of the arrows provides a relative indication of the magnitude and direction of nutrient fluxes. The dashed red vertical lines correspond to model flux output points (see Figure 9; Department for Environment and Water 2022b).



Figure 47. Annual (1 July 2019 to 30 June 2020) nutrient budget water and sediment stocks. Water and sediment stocks units = tonnes. Fluxes units = tonnes over 12 month period. The size and direction of the arrows provides a relative indication of the magnitude and direction of nutrient fluxes. The dashed red vertical lines correspond to model flux output points (see Figure 9; Department for Environment and Water 2022b).

Historical range in nutrient fluxes and budgets

Nutrient budgets for barrage low-flow conditions (October 2009 to March 2010; Figure 48) versus barrage high-flow (April 2016 to September 2016; Figure 49) were also constructed using long term (1990-2019) coarse TUFLOW historical base case model results (Department for Environment and Water (2022b) in order to determine the measured historical range in water (Figure 12) and nutrient fluxes. There are marked differences in the nutrient delivery to the Coorong during April 2016 to September 2016 barrage high-flow versus October 2009 to March 2010 barrage low-flow conditions. Large variability in TN and TP, as well as other nutrients such as FRP, have also been demonstrated by annual time series biogeochemical modelling and their 'flow years' (before January 2002) and 'no flow years' (after January 2002) nutrient budgets in Grigg et al. (2009).

During the Millennium Drought October 2009 to March 2010 low-flow conditions there was only a relatively small outflow of nutrients from the North Lagoon due to minimal barrage flows and hence flushing (Figure 48). Despite this there was still a relatively large transfer of nutrients from the North Lagoon to the South Lagoon. This has been found in previous nutrient budget estimates for the Coorong as well (Grigg et al. 2009). We hypothesise that this is driven by evaporation in the South Lagoon 'pulling in' water from the North Lagoon due to the relative water level difference between the North and South Lagoons. Even though nutrient concentrations in the lagoons were relatively high (TN = 5.5mg/L and TP = 0.3) the water nutrient

stocks are not as high as expected. This is due to low water levels throughout the Coorong during this time (Department for Environment and Water 2022b). Similar to the nutrient budgets above, Salt Creek inflows only account for a small fraction of nutrients at this time.



Figure 48. Low-flow (1 October 2009 to 31 March 2010) nutrient budget water and sediment stocks. Water and sediment stocks units = tonnes. Fluxes units = tonnes over 6 month period. The size and direction of the arrows provides a relative indication of the magnitude and direction of nutrient fluxes. The dashed red vertical lines correspond to model flux output points (see Figure 9).

During the selected April 2016 to September 2016 high-flow conditions, there was an extremely large outflow of nutrients (approximately 10 times the amount of nutrients compared to other time periods e.g. Figure 45) from the North Lagoon (Figure 49). Additionally, a large proportion of nutrients was also flushed into the North Lagoon from the South Lagoon (Figure 49), which has acted as a nutrient sink in all other scenarios except this one (e.g. Figure 48). This is despite there being minimal Salt Creek flows during this period. Finally, water nutrient stock levels were very low even though the water levels were high. This highlights the importance of barrage flows for diluting and flushing excess salt and nutrients out of the Coorong.

In summary, the nutrient budget calculations for the Coorong suggest the majority of nutrients are coming from the River Murray and Lower Lakes through the barrages followed by inputs from the ocean. Likewise, Grigg et al. (2009) identified that higher River Murray flows deliver much larger quantities of nutrients to the Coorong than low flow conditions, which is when the ocean provides nutrients to the Coorong. There was evidence of an export of nutrients from the North Lagoon out to the Murray Mouth and into the ocean, which was correspondingly identified by Grigg et al. (2009) with the majority of the water and nutrients representing what entered the Coorong from the barrages previously. While River Murray-barrage flows are

a primary source of nutrients to the system, they are also the primary nutrient-removal process, with nutrients accumulating in the system except in flood years.

Similarly to Grigg et al. (2009), we also determined that the South lagoon is generally a sink for nutrients, although the South Lagoon is a source of ammonium. This also supports previous findings that the South Lagoon is gaining and retaining nutrients, i.e. is a nutrient sink due to the limited flushing out through Parnka Point, while the North Lagoon is still being flushed in the current flow regime (Mosley et al. 2020). Thus rather than nutrients being exported out of the South Lagoon they are being retained in the water, with a portion deposited and stored in the sediment, which thus has a high nutrient stock.



Figure 49. High-flow (1 April 2016 to 30 September 2016) nutrient budget water and sediment stocks. Water and sediment stocks units = tonnes. Fluxes units = tonnes over 6 month period. The size and direction of the arrows provides a relative indication of the magnitude and direction of nutrient fluxes. The dashed red vertical lines correspond to model flux output points (see Figure 9).

3.5.4 Comparison with strontium isotope mixing calculations

The strontium isotope mass balance calculations (Figure 27), suggested relatively equal contributions of strontium, and hence water from the River Murray and Lower Lakes through the barrages and ocean over the long-term. Higher nutrient concentrations in the water entering from the River Murray and Lower Lakes through the barrages causes the waters flowing through the barrages from the River Murray and Lower Lakes to deliver the largest proportion of nutrients to the Coorong. Thus, the strontium isotope mass balance calculations, as well as Department for Environment and Water (2022a) modelling, support the finding that

the water balance, and by inference also the nutrient budget, are dominated by relatively equal contributions of water from the River Murray and Lower Lakes through the barrages and ocean over the long-term.

The strontium isotope mass balance calculations (Figure 27), as well as carbon and nitrogen isotope data in the water column and sediment (Figure 22), also suggest that Salt Creek is not the primary source of nutrients in the Coorong.

4 Management implications

The purpose of this section is to discuss the broader implications of the study findings for the Coorong and its management. Detailed assessment of options to remove nutrients from the Coorong will occur in T&I Activity 1.4 nutrient removal options of this Component that will utilise the findings of this study.

4.1 What forms of nutrients are present?

Within the water column, approximately 90% of the nutrients are residing in organic phases in the form of dissolved and particulate organic nutrient species. This is similar to previous findings that the total nutrients (i.e. not just dissolved phases) are dominated by organic nutrients (Mosley et al. 2020). This could comprise nutrients contained within both living phytoplankton and bacteria, and particulate and dissolved organic matter. The dissolved and particulate organic nutrient species also increase systematically where the hypersaline waters of the South Lagoon are more enriched with the above nutrients compared to more brackish or marine waters in the North Lagoon. In contrast, the dissolved inorganic nutrients, such as nitrate, ammonium and filterable reactive phosphorus are generally much lower and only comprise a small proportion of the total nutrients. Overall these results highlighted that organic matter is being retained in the system, with high levels of organic nutrients being deposited in the sediment.

4.2 Where are nutrients residing? (e.g. water, sediment, algae)

Based on our nutrient budget calculations (see Figure 45 to Figure 49) the surface sediment has the largest reservoir stocks of nitrogen and phosphorus, especially in the South Lagoon. In fact, there are approximately 50 times more nutrients in the top 5 cm of sediment compared to the entire water column in the Coorong.

Most of the nutrients in the water and sediment are residing in algal-organic phases as noted above, including both dissolved and particulate organic nutrient species. Stocks of nutrients in macro-algae and <u>Ruppia</u> biomass are being assessed through HCHB T&I Component 2 – Aquatic Plants and Algae, and are also likely to be important in some areas of the lagoon.

The links between sediment-water-algal fluxes are being studied in detail in other T&I Component 1 Activities (e.g. T&I Activity 1.3 nutrient cycling and fluxes investigations). The implication of large sediment nutrient stocks is that they could provide an ongoing supply of nutrients to the water (i.e. an internal nutrient loading), even if for example flushing of the lagoon is improved. However, large flows leading to improved flushing and lower salinities were demonstrated in this study to greatly lower total nutrient levels in the Coorong. Hence nutrient-enrichment in the South Lagoon can be reduced by flushing, which could also promote improved sediment and water column oxygenation. For example, via less sediment organic matter deposition and breakdown, recolonisation of burrowing macro-invertebrates due to lowering salinity, improving *Ruppia* health and distribution due to improved water quality) that could reduce nutrient flux from the sediment or promote nitrogen loss pathways (nitrification-denitrification). This will be considered in more detail in T&I Activity 1.4 nutrient removal options.

4.3 Where are nutrients coming from?

Surface water sources

The nutrient budget calculations for the Coorong suggest the majority of nutrients, especially in the North Lagoon, are coming from the River Murray and Lower Lakes through the barrages followed by inputs from the ocean. Compared to these sources Salt Creek brings in only a fraction (<1%) of the nutrients as the Salt Creek discharge is approximately one order of magnitude lower compared to inputs from the barrages, with roughly similar nutrient concentrations (see TDP and TDN data in Figure 15). While River Murray-barrage flows are a primary source of nutrients to the system, and they are also the primary nutrient-removal process, with nutrients accumulating in the system except in flood years.

Likewise, the strontium isotope mixing calculations, as well as Department for Environment and Water (2022b) modelling, support the finding that the Coorong water balance is dominated by relatively equal contributions from the River Murray and Lower Lakes through the barrages and ocean over the long-term. However, higher nutrient loads in the water entering the Coorong from the River Murray and Lower Lakes are a product of higher barrage releases. Nevertheless, when barrage inputs are large enough (such as in 2016, Figure 49) the large barrage inflows lead to flushing and removal of previously retained nutrients. This suggests environmental flow targets should include floods that are large enough in magnitude to induce nutrient flushing from the system. Strong relationships of total nutrient, organic carbon, and chlorophyll levels with salinity suggest that salinity can in general function as an appropriate proxy for nutrient and organic matter flushing. Any future sustained reductions in River Murray flows (e.g. due to climate change, Basin Plan changes) could have large implications for the Coorong, creating water and sediment quality risks.

The strontium isotope mixing calculations, as well as carbon and nitrogen isotope data in the water column and sediment (see Figure 22 and Figure 27) also suggest that Salt Creek is not the dominant input or primary source of nutrients in the Coorong. However, the sampling was undertaken during a period of low flows from Salt Creek, thus Salt Creek may contribute more nutrients during high flow periods.

Nevertheless, the local input of nutrients from Salt Creek, as well as from the River Murray and Lower Lakes through the barrages, and the ocean, are magnified in the South Lagoon by evaporation and lack of flushing. This is because the South Lagoon represents a highly restricted and evaporative depositional system that acts as an 'endorheic basin' with very limited or no water outflow, particularly during periods of low River Murray flows. Thus, dissolved and particulate nutrients are concentrating and accumulating over time to high levels in the South Lagoon, leading to local hypereutrophic conditions that are amplified by the lack of effective flushing and outflow. Overall, the data suggests that the evaporation of water and progressive concentration of nutrients caused by the lack of flushing of the lagoon is the main driver of nutrient enrichment in the South Lagoon, particularly during summer.

Sediment sources

More direct tracing of local nutrient sources in the Coorong via stable nitrogen isotopes ($\delta^{15}N$) indicate a consistency between the $\delta^{15}N$ signatures of lagoon sediment and a water organic nitrogen (PON) source. This is consistent with phytoplankton deposition from a highly eutrophic water column being the primary constituent of nitrogen in a top-sediment reservoir across the whole of the Coorong. These conclusions derived from our isotope tracing studies are consistent with previous findings of a predominantly algal derived organic matter composition in the Coorong surface sediment, with a larger contribution of nutrients from seagrasses before Murray-Darling Basin water regulations and extractions were implemented causing a decline in barrage releases (Krull et al. 2009; McKirdy et al. 2010). Based on visual observations, filamentous algal deposition is also likely to be an important contributor to sediment nutrient loads at particular times and locations. Altered internal nutrient cycling processes in the South Lagoon (limited nitrification-denitrification) also promotes nitrogen retention and higher ammonia flux and shifts in $\delta^{15}N_{PON}$ signature.

Given the high total concentrations of nutrients in the lagoon surface sediment, this likely promotes high sediment-to-water fluxes of dissolved nutrients (i.e. mineralised by bacteria from organic and particulate forms and returned to dissolved forms), especially for the South Lagoon. Inclusion of preliminary local nutrient flux rates from T&I Activity 1.3 nutrient cycling and fluxes investigations in the nutrient budget calculations show that >80% of the nutrient flux into the South Lagoon could be arising from the sediment. However, the nutrient flux calculations provided from T&I Activity 1.3 nutrient cycling and fluxes investigations have been based on core incubation experiments at a limited number of sites and hence have a large degree of uncertainty when translated to a lagoonal scale. Measurement of nutrient deposition rates and potential for nitrogen fixation from the atmosphere would also be beneficial to constrain the nutrient budget.

Groundwater sources

Overall, groundwater appears to be a relatively minor contributor of nutrients at a lagoonal scale. Nevertheless, fresher water lenses were detected under the margins of the South Lagoon thus groundwater inflows could be locally significant. The results have shown that groundwater is entering the shoreline of the South Lagoon at varying rates of up to 4 m/d, but typically averaging ~0.1 -- 0.2 m/d within a ~30 m band along the shoreline of the South Lagoon during both summer and winter conditions. Simple models using measured piezometer water levels confirmed this observation for Jack Point.

The near-surface geophysical LoupeEM survey results showed that there was very low subsurface resistivity (Ohm-m) (high conductivity) in the nearshore environment, as expected given the very saline conditions of the Coorong. Inverted resistivity depth slices and sections from the JP and NSL sites showed some interesting spatial heterogeneity in resistivity in the near surface, which may be associated with the regional groundwater discharge into the lagoon. There was also some well-defined low resistive layering in the subsurface at an elevation of about -1 to -3 mAHD as well as the very low resistivity (high conductivity) material beneath this layer that extended much further eastwards from the nearshore of the Coorong. This may be super-saline water from the Coorong extending beneath less saline groundwater from the regional aquifer.

Physical water chemistry measurements helped to identify locations of groundwater. The EC of the regional groundwater was typically <20 mS/cm, and therefore it was easy to observe and locate areas of groundwater discharge, groundwater-Coorong water mixes, and Coorong water. The three water types were also clearly visible in the stable isotope data. Sampling of groundwater wedges east of the Coorong confirmed that the salinity and nutrient concentrations measured in the piezometers near the shoreline was indicative of regional concentrations, and that groundwater nutrient levels are roughly equivalent to Coorong concentrations.

Several further studies would greatly improve our understanding of the groundwater component of the South Lagoon water and nutrient balances:

- This study has shown that groundwater discharges along much of the South Lagoon shoreline, although the flux rates for these discharges are typically relatively low. One possibility that was not explored was the role of wave forcing in recycling water through the subsurface, and how that may impact nutrient cycling. We could envision that the waves would force oxygenated Coorong water into the shallow subsurface that would combine with the regional groundwater discharging along the shoreline. This topic warrants further investigation.
- Construction and installation of several shallow piezometers (up to 30 m depth) along the groundwater flow path of the regional aquifer towards the Coorong would be useful to evaluate the hydraulic gradient towards the Coorong and also provide appropriate water quality sample locations. This information would also assist in validating the near-surface geophysical data and changes in the stratigraphy and water quality with depth.

- We have previously met with Airborne Research Australia (ARA) based at Parafield airport to discuss
 possibilities for upscaling groundwater discharge estimates based on available remote sensing
 datasets and high-resolution aerial imagery. We believe aerial imagery may be a promising method
 for this, but it would require imagery analysis for temperature or visual anomalies in the locations
 where groundwater discharge has been observed. Multi-spectral imagery has also been collected in
 the area of interest but would require further processing and calibration by ARA.
- Simple models of the Jack Point and North South Lagoon sites were built for this project. While this worked well for the summer conditions when the Coorong water level was very low and the gradient of the groundwater, combined with the sediment hydraulic conductivity, were the primary drivers of groundwater discharge, we are less confident in the winter models, where salinity differences between the groundwater and Coorong would need to be investigated further.

4.4 How are nutrients moving within the system?

For the 2019-2020 period there was evidence of an export of nutrients from the North Lagoon out to the Murray Mouth and into the ocean. The majority of this water and nutrients represents what entered the Coorong from the barrages previously. Overall, nutrients enter the North Lagoon from October to March, and exit the North Lagoon out the Murray Mouth from April to September, likely reflecting seasonal patterns linked to river discharge and sea level fluctuations. The apparent flushing of nutrients in winter, despite increased nutrient inputs from the Murray-Darling Basin, is likely due to better mixing with higher water levels (driven by both inflows, tides and sea level increase in winter), with the net effect of water with lower nutrient concentrations coming into the Coorong, and nutrient-rich waters leaving the lagoon. Thus even though River Murray (barrage) water inflows are the primary source of nutrients, they are also the primary nutrient-removal process.

Nutrient budgets calculated at both annual and seasonal scales show nutrients enter the South Lagoon from both the North Lagoon (ocean and barrages) and from Salt Creek. It seems that rather than being exported out of the South Lagoon most of these nutrients are being retained in the water of this 'closed basin', with a portion deposited and stored in the sediment, which thus has a high nutrient stock. This supports previous findings that the North Lagoon is still being flushed but that the South Lagoon is gaining and retaining nutrients (Mosley et al. 2020) due to the limited flushing out through Parnka Point.

These seasonal flushing processes were evident in the nutrient budgets calculated for barrage low-flow (2009) and barrage high-flow (2016) conditions. There was net import of nutrients throughout the Coorong during the Millennium Drought low-flow conditions, and net export of nutrients throughout the Coorong during the high-flow conditions, which is consistent with Grigg et al. (2009). In fact, the large barrage inflows in 2016 led to flushing and removal of previously retained nutrients from both the South Lagoon and the North Lagoon. This highlights the critical importance of large River Murray inflows for flushing the South Lagoon of nutrients. The frequency of these flows has greatly declined over recent decades due to water extraction and river regulation (Maheshwari et al. 2005).

4.5 What contribution does Salt Creek make to nutrient loads to the South Lagoon?

As indicated in sections 3.3.1 and 4.3, and shown in Figure 15, the concentrations of total dissolved nutrients (TDN and TDP) in Salt Creek waters (sampled at Salt Creek regulator) are comparable to those in River Murray Lower Lakes and barrages releases. However, the water inflows are about one order of magnitude lower compared to discharges from the River Murray and Lower Lakes through the barrages (Figure 12), and there is a much greater flux of North Lagoon water into the South Lagoon via Parnka Pt during the predominant low-moderate flow conditions (Fig. 47-48). Thus, Salt Creek brings in only a fraction (<1%) of the dissolved

nutrients to the South Lagoon. Hence discharges from Salt Creek do not present a significant risk to South Lagoon water quality from a management perspective, but also do not improve water quality to anywhere near the same degree as large River Murray flows (which flush the whole system). Consideration of infrastructure options that improve flushing of the South Lagoon similar to large River Murray flows would be beneficial.

4.6 What is the effect of redox (oxidation-reduction) processes on nutrients?

There is evidence of redox processes being more influential in the South Lagoon with lower dissolved oxygen levels, higher ammonium, and heavier sulfur isotope ratios that are indicative of active microbial redox processes such as bacterial sulfate reduction and ammonification. These in turn point to more anoxic nutrient pathways in this restricted, oxygen-depleted and hypersaline part of the Coorong. Bacterial sulfate reduction is also the driver of monosulfidic black ooze formation which is dominating sediment types in both lagoons as found in the T&I Activity 1.3 nutrient cycling and fluxes investigations. Sulfate reduction in sediments is promoted by high organic matter deposition and maintenance of anoxic conditions. Hence there is a strong link between the persistently high algae and organic nutrient levels in the water column and sediment redox processes.

5 Summary

The nutrient budget calculations for the Coorong suggest a majority of the nutrients, especially in the North Lagoon, are coming through the barrages from the River Murray and Lower Lakes, followed by inputs from the ocean. Compared to these sources, Salt Creek contributes only a fraction of the nutrients, but this local input is magnified in South Lagoon. Within the water column, most of the nutrients are residing in organic phases in the form of dissolved and particulate organic nutrient species derived from algal material. The majority of the total nitrogen and phosphorus is residing in the top sediment, with approximately 50 times more nutrients in the top 5 cm of sediment compared to the water column of the entire Coorong. Overall, under the low-moderate flow conditions in the study period nutrients entered the North Lagoon through the barrages and through the Murray Mouth from the ocean between October to March, and exited the North Lagoon to the Murray Mouth between April to September, reflecting the seasonal pattern linked to river discharge and sea levels. There is evidence of less oxic conditions being present in the South Lagoon, with lower dissolved oxygen levels, anoxic sediment, higher ammonium, and more sulfide ("black ooze") formation.

The nutrient sources and transport research outcomes have provided key data and information to help parameterise and validate the Coorong Dynamics Model. This will reduce key uncertainties on sources and transport so that the biogeochemical model can be used to more confidently assess scenarios to achieve a "regime shift" back towards an aquatic plant dominated ecosystem, rather than the current algal dominated ecosystem. The results will help inform future HCHB activities, such as T&I Activity 1.4 nutrient removal options of this Component and infrastructure feasibility assessments. The important role of the sediment nutrient processes and fluxes in influencing water nutrient availability is assessed in detail in T&I Activity 1.3 nutrient cycling and fluxes investigations. The results will also help inform optimised operations of the barrages, South East inflows and the Murray Mouth dredging regime to limit nutrient availability. Nutrient budgets highlighted the importance of large River Murray flows for flushing nutrients from the whole Coorong system, while there was a minor contribution of Salt Creek to overall nutrient stocks in the South Lagoon.

6 List of shortened forms and glossary

T&I	Trials and Investigations project
Ammonification	A process that produces inorganic reduced ammonium NH_4^+ species
Ammonia gas production	Reaction that produces ammonia (NH $_3$) gas from ammonium
Anoxic	Sediment or water conditions where there is an absence of oxygen
Anoxia	Sediment or water that are depleted of dissolved oxygen
Chemoautotrophs	Are organisms that obtain energy by the oxidation of organic or inorganic molecule electron donors in their environments.
Chlorophyll-a	Photosynthetic pigment found in green algae
Coorong Dynamics Model	Coupled hydrodynamics-biogeochemistry model of the Coorong used for Coorong infrastructure and ecological restoration options assessment
DOC	Dissolved organic carbon
DO	Dissolved oxygen
Drivepoint piezometer	Can be inserted into the sediment to monitoring and sample shallow groundwater
Endorheic basin	A drainage basin that retains water and allows no outflow to other external bodies of water
Eutrophication	Elevated supply of organic matter and nutrients
Euxinic	Water conditions where the water is both anoxic (there is an absence of oxygen) and sulfidic (containing sulfide)
FRP	Filterable reactive phosphorus
FRP HCHB	Filterable reactive phosphorus Healthy Coorong, Healthy Basin
FRP HCHB Heterotrophs	Filterable reactive phosphorus Healthy Coorong, Healthy Basin Are organisms that cannot produce their own food. Instead they take nutrition from other sources of organic carbon, mainly plant or animal matter.
FRP HCHB Heterotrophs Hypereutrophic	Filterable reactive phosphorus Healthy Coorong, Healthy Basin Are organisms that cannot produce their own food. Instead they take nutrition from other sources of organic carbon, mainly plant or animal matter. Are very nutrient-rich waters characterised by frequent and severe nuisance algal blooms and low transparency
FRP HCHB Heterotrophs Hypereutrophic Isotope	Filterable reactive phosphorus Healthy Coorong, Healthy Basin Are organisms that cannot produce their own food. Instead they take nutrition from other sources of organic carbon, mainly plant or animal matter. Are very nutrient-rich waters characterised by frequent and severe nuisance algal blooms and low transparency Isotopes are atoms of the same element that have different numbers of neutrons but the same number of protons and electrons. The difference in the number of neutrons between the various isotopes of an element means that the various isotopes have different masses. The superscript number to the left of the element abbreviation indicates the number of protons plus neutrons in the isotope.
FRP HCHB Heterotrophs Hypereutrophic Isotope mAHD	Filterable reactive phosphorus Healthy Coorong, Healthy Basin Are organisms that cannot produce their own food. Instead they take nutrition from other sources of organic carbon, mainly plant or animal matter. Are very nutrient-rich waters characterised by frequent and severe nuisance algal blooms and low transparency Isotopes are atoms of the same element that have different numbers of neutrons but the same number of protons and electrons. The difference in the number of neutrons between the various isotopes of an element means that the various isotopes have different masses. The superscript number to the left of the element abbreviation indicates the number of protons plus neutrons in the isotope. Abbreviation for elevation in metres with respect to the Australian Height Datum
FRP HCHB Heterotrophs Hypereutrophic Isotope MAHD Millennium Drought	 Filterable reactive phosphorus Healthy Coorong, Healthy Basin Are organisms that cannot produce their own food. Instead they take nutrition from other sources of organic carbon, mainly plant or animal matter. Are very nutrient-rich waters characterised by frequent and severe nuisance algal blooms and low transparency Isotopes are atoms of the same element that have different numbers of neutrons but the same number of protons and electrons. The difference in the number of neutrons between the various isotopes of an element means that the various isotopes have different masses. The superscript number to the left of the element abbreviation indicates the number of protons plus neutrons in the isotope. Abbreviation for elevation in metres with respect to the Australian Height Datum An Australian drought which impacted the Murray-Darling Basin over the period 1996-2010, and substantially impacted the Coorong over the period 2001-2010.
FRP HCHB Heterotrophs Hypereutrophic Isotope mAHD Millennium Drought Monosulfidic Black Ooze (MBO)	 Filterable reactive phosphorus Healthy Coorong, Healthy Basin Are organisms that cannot produce their own food. Instead they take nutrition from other sources of organic carbon, mainly plant or animal matter. Are very nutrient-rich waters characterised by frequent and severe nuisance algal blooms and low transparency Isotopes are atoms of the same element that have different numbers of neutrons but the same number of protons and electrons. The difference in the number of neutrons between the various isotopes of an element means that the various isotopes have different masses. The superscript number to the left of the element abbreviation indicates the number of protons plus neutrons in the isotope. Abbreviation for elevation in metres with respect to the Australian Height Datum An Australian drought which impacted the Murray-Darling Basin over the period 1996-2010, and substantially impacted the Coorong over the period 2001-2010. Are black gel-like deposits enriched in acid volatile sulfur

Oxidation	Part of a reduction-oxidation (redox) reaction in which atoms lose electrons
PC	Particulate carbon
PON	Particulate organic nitrogen
PSU	Practical salinity units
Radiogenic	Produced by a process of radioactive decay
Redox	REDuction-OXidation reactions involving electron transfer
Reduction	Part of a reduction-oxidation (redox) reaction in which atoms gain electrons
Ruppia	Ruppia community, consisting of Ruppia tuberosa, Althenia cylindrocarpa and Ruppia megacarpa
Scintillant	Radioactive sample material
TDN	Total dissolved nitrogen
TDP	Total dissolved phosphorus
TKN	Total Kjehldahl nitrogen
TN	Total nitrogen
тос	Total organic carbon
ТР	Total phosphorus
Wedge	Open groundwater well

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