

**CENTRE FOR FRESHWATER
ECOSYSTEMS (CFE)**

**River Murray Water Quality
Monitoring Program
(RMWQMP) Data Trends
Analysis 2021**

Report prepared for Murray-Darling Basin
Authority

August / 2022
CFE Publication No. 276

ENQUIRIES

Name: Ewen Silvester
Title: Associate Professor
La Trobe University
Victoria 3086

T +61 2 6024 9885
E E.silvester@latrobe.edu.au
W latrobe.edu.au/freshwater-ecosystems

Document history and status

VERSION	DATE ISSUED	REVIEWED BY	APPROVED BY	REVISION TYPE
Draft	30/08/2022	Aleicia Holland		
Revised	28/10/2022			

Distribution of copies

VERSION	QUANTITY	ISSUED TO

Report citation

Insert report citation, use authors' full names without reverting to the use of *et al.*

Ewen Silvester, Andre Siebers, Luke McPhan, Michael Shackleton, Julia Mynott, Nick Bond, Alison King, Aleicia Holland, River Murray Water Quality Monitoring Program (RMWQMP) Data Trends Analysis 2021, CFE Publication No. 276.

Traditional Owner acknowledgement

La Trobe University proudly acknowledges the Traditional Owners and Custodians of the Country. We pay our respects to the Elders past, present and emerging and respect their cultural heritage, beliefs and relationship with the land, waters and community.

Disclaimer

The information contained in this publication is indicative only. While every effort is made to provide full and accurate information at the time of publication, the University does not give any warranties in relation to the accuracy and completeness of the contents. The University reserves the right to make changes without notice at any time in its absolute discretion, including but not limited to varying admission and assessment requirements, and discontinuing or varying courses. To the extent permitted by law, the University does not accept responsibility of liability for any injury, loss, claim or damage arising out of or in any way connected with the use of the information contained in this publication or any error, omission or defect in the information contained in this publication.

La Trobe University is a registered provider under the Commonwealth Register of Institutions and Courses for Overseas Students (CRICOS). La Trobe University CRICOS Provider Code Number 00115M

Table of Contents

LIST OF FIGURES	5
EXECUTIVE SUMMARY	9
GLOSSARY	12
INTRODUCTION	15
REVIEW OF PROCESSES THAT IMPACT WATER QUALITY	16
Tributary effects	16
Physical effects	17
Chemical effects	17
Floodplain channel interactions (Blackwater)	18
Wildfire	18
Runoff (Climate variability)	19
Emerging contaminants	20
Metals and pesticides	20
Microplastics	20
Polyfluoroalkyl substances (PFAS) and their derivatives	20
Pharmaceuticals and Personal care products (PPCPs)	21
DATA ANALYSIS METHODS	21
Data sources	21
Spot data	21
Telemetry data	21
Site selection	22
VARIABLES (Parameters) analysed	23
Trend analysis	24
Step 1. Data interpolation	24
Step 2. Seasonal and/or autocorrelative de-trending	25
Step 3. Data imputation	26
Step 4. GAM spline fits	28
Step 5. GLMM fits	28
RESULTS	30
Longitudinal changes in water quality in River Murray	30
Trends by parameter	34
Discharge	34
Field pH	35
Water temperature	36
Dissolved Oxygen	37
Electrical conductivity at 25 °C	38
Turbidity	40
Alkalinity	41
Dissolved Organic Carbon (DOC)	43
Total Kjeldahl Nitrogen (TKN)	45
Nitrogen oxides (NO _x ; NO ₃ ⁻ + NO ₂ ⁻)	47

Total Phosphorus	49
Soluble Reactive phosphorus (SRP)	51
Dissolved Silicon	53
Generalised linear mixed-model (GLMM)	55
SCENARIOS	59
Tributary effects	59
Main stem-tributary discharge ratios	59
Murray@Heywoods-Kiewa confluence	60
Murray@Heywoods -Ovens confluence	61
River Murray d/sYarrowonga-Goulburn confluence	63
River Murray at Merbein-Darling confluence	64
Role of tributaries in controlling River Murray water quality	65
Blackwater	66
Seasonal patterns: Water temperature, DO, DO-% (Murray main channel sites)	66
Detection of Floodplain return water	67
Wildfire	69
COMMENTS ON RMWQMP	72
sampling Frequency	72
WQ parameters	73
Data resolution, data precision and detection limits	74
COMMENTS ON THE WQ TELEMETRY NETWORK	76
Post-fire response	76
Blackwater response	76
OPPORTUNITIES FOR NEW TECHNOLOGIES AND FURTHER INVESTIGATIONS	77
REFERENCES	79

List of Tables

Table 1. Processes and events likely to impact water quality in the River Murray and tributaries.....	16
Table 2. Site ID; site name; sampling class (see footnote); environment type and whether part of the 28 MDBA sites.....	22
Table 3. Key analysis steps in the trend analysis and development of a global model	24
Table 4. Stations where key water quality parameters are currently not recorded in the RMWQMP dataset.....	73
Table 5. Typical ranges for key water quality parameters in the RMWQMP dataset; recommended recording precision; achievable analytical precision; achievable detection limits; stations currently recording low precision data.....	74

List of Figures

Figure 1. Map of the River Murray and major tributaries. The light shaded envelope represents the 50km buffer applied for site selection. All water quality monitoring sites within the 50 km buffer shown on figure; flowing sites used in this report marked in red.	23
Figure 2. Example of imputed missing values, as Kalman filtered and smoothed data (red dots), calculated to fill in missing sections of the original, measured data (black dots) for dissolved organic carbon (River Murray at Murray Bridge site).....	25
Figure 3. Example of seasonally detrended values (blue dots) in comparison with the original, measured data (black dots) for dissolved organic carbon (River Murray at Murray Bridge site)...	25
Figure 4. Conceptualisation of the process by which random forest models were used to take the entire set of seasonally-detrended values for each site (left graphs) to impute the seasonally-detrended data (blue dots, upper right graph) into a continuous time series of monthly mean data (red dots, bottom right graph) for dissolved organic carbon sampling at the Murray Bridge site on the River Murray.	27
Figure 5. Example of generalised additive model (grey and red line; \pm 95% confidence interval) predicting smoothed trends in the long-term, seasonally detrended monthly average data (see text for details), in comparison with the original, measured data (black dots) for dissolved organic carbon (River Murray at Murray Bridge site). Colours for the model prediction line indicate periods of significant change (red sections) and no change (grey sections) in monthly mean concentrations, identified from analysis of additive model first derivatives. R^2 value indicates additive model fit to imputed monthly mean data.	28
Figure 6. Boxplot of seasonal patterns in water quality parameters in River Murray sites (main channel only). All data (except pH) plotted as logarithm (base-10). Dataset includes all water quality measurements available for the 1978-2021 period and does not reveal trends in these parameters over this period.	31
Figure 7. Correlation plot for water quality variables in River Murray sites (main channel only; all seasons combined; same data as Figure 6). Dataset includes all water quality measurements available for the 1978-2021 period.	32
Figure 8. Principal components analysis (PCA) plots of water quality data for River Murray (main channel) sites, separated by season. Shown are data for: (a) Summer (top left); (b) Autumn (top right); (c) Winter (bottom left); (d) Spring (bottom right). Dataset includes all water quality measurements available for the 1978-2021 period and does not account for trends in these parameters over this period.	33
Figure 9. Linear trend component derived from a general linear model (GLM) for changes in discharge at River Murray and tributary sites, plotted as effect size (GL/yr). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.....	35
Figure 10. Linear trend component derived from a general linear model (GLM) for changes in pH at River Murray and tributary sites, plotted as effect size (Δ pH/yr). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.....	36
Figure 11. Linear trend component derived from a general linear model (GLM) for changes in water temperature at River Murray and tributary sites, plotted as effect size ($^{\circ}$ C/yr). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.....	37
Figure 12. Linear trend component derived from a general linear model (GLM) for changes in dissolved oxygen concentrations at River Murray and tributary sites, plotted as effect size (mg- O_2 /L.yr). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.....	38

Figure 13. Linear trend component derived from a general linear model (GLM) for changes in electrical conductivity at River Murray and tributary sites, plotted as effect size ($\mu\text{S}/\text{cm}.\text{yr}$). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.	39
Figure 14. Linear trend component derived from a general linear model (GLM) for changes in TDS loads at River Murray and tributary sites, plotted as effect size (tonnes/yr), for the period 1978 – 2021. Note non-linear (square-root) x-scale.....	40
Figure 15. Linear trend component derived from a general linear model (GLM) for changes in turbidity at River Murray and tributary sites, plotted as effect size (NTU/yr). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.....	41
Figure 16. Linear trend component derived from a general linear model (GLM) for changes in alkalinity at River Murray and tributary sites, plotted as effect size ($\text{mg-CaCO}_3/\text{L}.\text{yr}$). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.....	42
Figure 17. Linear trend component derived from a general linear model (GLM) for changes in alkalinity loads at River Murray and tributary sites, plotted as effect size (tonnes- CaCO_3/yr), for the period 1978 – 2021. Note non-linear (square-root) x-scale.....	43
Figure 18. Linear trend component derived from a general linear model (GLM) for changes in dissolved organic carbon (DOC) concentrations at River Murray and tributary sites, plotted as effect size ($\text{mg-C}/\text{L}.\text{yr}$). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.....	44
Figure 19. Linear trend component derived from a general linear model (GLM) for changes in DOC loads at River Murray and tributary sites, plotted as effect size (tonnes-C/yr), for the period 1978 – 2021. Note non-linear (square-root) x-scale.....	45
Figure 20. Linear trend component derived from a general linear model (GLM) for changes in total Kjeldahl nitrogen (TKN) concentrations at River Murray and tributary sites, plotted as effect size ($\text{mg-N}/\text{L}.\text{yr}$). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.....	46
Figure 21. Linear trend component derived from a general linear model (GLM) for changes in TKN loads at River Murray and tributary sites, plotted as effect size (tonnes-N/yr), for the period 1978 – 2021. Note non-linear (square-root) x-scale.	47
Figure 22. Linear trend component derived from a general linear model (GLM) for changes in nitrogen oxides (NO_x) concentrations at River Murray and tributary sites, plotted as effect size ($\text{mg-N}/\text{L}.\text{yr}$). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.	48
Figure 23. Linear trend component derived from a general linear model (GLM) for changes in NO_x loads at River Murray and tributary sites, plotted as effect size (tonnes-N/yr), for the period 1978 – 2021. Note non-linear (square-root) x-scale.	49
Figure 24. Linear trend component derived from a general linear model (GLM) for changes in total phosphorus (TP) concentrations at River Murray and tributary sites, plotted as effect size ($\text{mg-P}/\text{L}.\text{yr}$). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.....	50
Figure 25. Linear trend component derived from a general linear model (GLM) for changes in TP loads at River Murray and tributary sites, plotted as effect size (tonnes-P/yr), for the period 1978 – 2021. Note non-linear (square-root) x-scale.....	51
Figure 26. Linear trend component derived from a general linear model (GLM) for changes in soluble reactive phosphorus (SRP) concentrations at River Murray and tributary sites, plotted as effect size ($\text{mg-P}/\text{L}.\text{yr}$). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.....	52

Figure 27. Linear trend component derived from a general linear model (GLM) for changes in SRP loads at River Murray and tributary sites, plotted as effect size (tonnes-P/yr), for the period 1978 – 2021. Note non-linear (square-root) x-scale.....	53
Figure 28. Linear trend component derived from a general linear model (GLM) for changes in dissolved silicon concentrations at River Murray and tributary sites, plotted as effect size (mg-SiO ₂ /L.yr). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.	54
Figure 29. Linear trend component derived from a general linear model (GLM) for changes in silica loads at River Murray and tributary sites, plotted as effect size (tonnes-SiO ₂ /yr), for the period 1978 – 2021. Note non-linear (square-root) x-scale.....	55
Figure 30. Predicted linear relationships between Standardised Discharge (SI Discharge) and water quality parameters from Generalised Linear Mixed Model (GLMM) relationships measured at the main channel sites selected for this trends analysis (mean slopes shown with shaded areas indicating 95% confidence intervals).....	56
Figure 31. Predicted linear relationships between Standardised Discharge (SI Discharge) and water quality parameters from Generalised Linear Mixed Model (GLMM) relationships measured at tributary sites selected for this trends analysis (mean slopes shown with shaded areas indicating 95% confidence intervals).	58
Figure 32. Boxplot of tributary-main channel discharge ratios for the confluences: (a) Kiewa-Murray (data period: 1970-2021), (b) Ovens-Murray (data period: 1998-2021), (c) Goulburn-Murray (data period: 1977-2021), and (d) Darling-Murray (data period: 1976-2021). Data presented on a seasonal basis as log (base-10) of the tributary (Q _T) to main channel (Q _R) mean daily discharge ratio (i.e., log ₁₀ (Q _T /Q _R) = 0, corresponds to equal discharge in both rivers); outliers removed.....	59
Figure 33. Boxplot of seasonal patterns in water quality variables in the River Murray at Heywoods and Kiewa River at Bandiana (Murray-Kiewa confluence). All data (except pH) plotted as logarithm (base-10). Dataset includes all water quality measurements available for the 1978-2021 period and does not show trends in these parameters over this period; outliers removed.....	61
Figure 34. Boxplot of seasonal patterns in water quality variables in the River Murray at Heywoods and Ovens River at Peechelba (Ovens-Murray confluence). All data (except pH) plotted as logarithm (base-10). Dataset includes all water quality measurements available for the 1978-2021 period and does not show trends in these parameters over this period; outliers removed.....	62
Figure 35. Boxplot of seasonal patterns in water quality variables in the River Murray downstream of Yarrawonga weir and Goulburn River at McCoys bridge (Murray-Goulburn confluence). All data (except pH) plotted as logarithm (base-10). Dataset includes all water quality measurements available for the 1978-2021 period and does not show trends in these parameters over this period; outliers removed.	63
Figure 36. Boxplot of seasonal patterns in water quality variables in the River Murray at Merbein and the Darling River at Burtundy (Murray-Darling confluence). All data (except pH) plotted as logarithm (base-10). Dataset includes all water quality measurements available for the 1978-2021 period and does not show trends in these parameters over this period; outliers removed.	64
Figure 37. Boxplot of seasonal patterns in: (a) water temperature, (b) dissolved oxygen concentration (mg-O ₂ /L) and (c) dissolved oxygen saturation (%) for River Murray sites (main channel only). Dataset includes all water quality measurements available for the 1978-2021 period and does not show trends in these parameters over this period.	66
Figure 38. Response of dissolved oxygen (DO) to dissolved organic carbon (DOC) pulse over the time period 2006 – 2015 for River Murray main channel and tributary sites between Yarrawonga and Merbein. Shown are: (a) DOC concentration time series, (b) measured (black) and calculated (red) DO concentrations, based on 90% atmospheric saturation, and (c) DO deviation from 90% saturation.	68

Figure 39. Post-fire water quality response at the River Murray at Jingellic site. Shown are: (a) discharge (ML/d), (b) turbidity (NTU), (c) electrical conductivity (EC; $\mu\text{S}/\text{cm}$), (d) dissolved oxygen (DO; $\text{mg-O}_2/\text{L}$) and (e) field pH; grey points correspond to telemetry data (15 minute) and red markers to spot measurements. Also shown are the approximate period of fire activity in January 2020) and the first post-fire event at which all telemetry variables were available (see Figure 40).

..... 70

Figure 40. Water quality at the River Murray at Jingellic site in response to a single post-fire event (03-03-2020 to 11-03-2020) (see: Figure 39). Shown are (LHS): (a) discharge (ML/d), (b) turbidity (NTU), (c) electrical conductivity (EC; $\mu\text{S}/\text{cm}$), (d) dissolved oxygen (DO; $\text{mg-O}_2/\text{L}$) and (e) field pH; RHS: concentration-discharge (C-Q) plots for two discrete spates that form part of this post-fire event. 71

Executive summary

Highlights and recommendations

The data record for the River Murray Water Quality Monitoring Program (RMWQMP) was analysed for long-term change and potential system drivers over the 1978 – 2021 period.

We show the general pattern is one of decreasing levels across the majority of water quality (WQ) constituents and parameters, across all sites; the exception is water temperature which is generally increasing at all sites.

For many WQ constituents, concentrations increase with river discharge (standardised run-off), suggesting that landscape connectivity is a key driver of water quality; decreasing run-off may provide an explanation for the observed long-term decrease in the majority of WQ constituents

An analysis of the capacity of the RMWQMP to detect landscape scale processes revealed that: (i) tributaries likely have an important role in restoring WQ in the River Murray downstream of storage reservoirs, (ii) the duration of hypoxic blackwater events is captured by spot measurements, but detection of the downstream propagation of low dissolved oxygen conditions is limited by the absence of data for lower Murray sites, and (iii) post-fire run-off events in upper catchment sites are not captured due to the rapid nature of these processes.

We make the following recommendations:

- The MDBA be more prescriptive in the expectations of data reporting (i.e., data resolution, detection limits, parameter naming conventions) in order to assist in future analyses and to enhance the general utility of the RMWQMP dataset; similarly, we also recommend that WQ monitoring be maintained at the 28 key sites, as recommended to the MDBA in previous reports from other agencies.
- High frequency data available through the WQ telemetry network be more closely integrated into river management and future WQ data analysis. Key opportunities to utilise these data are in: (i) capturing rapid pulse events in upper catchment sites, (ii) the management and response to floodplain inundation at mid-Murray sites, and (iii) the calculation of more accurate load data throughout the system.
- Further studies be conducted into: (i) the role of tributaries in maintaining WQ in the River Murray, and (ii) the potential occurrence of emerging contaminants at sites proximate to where such contaminants are known (or suspected) to occur.

The routine measurement of physico-chemical parameters in the River Murray (known as the River Murray Water Quality Monitoring Program; RMWQMP) has been operating since 1978. This program seeks to understand long-term changes in water quality in this system and assess conditions under which water quality guidelines and targets may be exceeded. The dataset is reviewed every 10 years (approximately) with respect to the analysis of trends, and how these trends might change over time. This report represents the analysis of the RMWQMP dataset for the period 1978 – 2021.

The data used in this report is that contained within the RMWQMP dataset, with the addition of some state-based data as well as an additional (partially curated) dataset kept by the MDBA. We have applied a 50 km river distance buffer around the main channel of the River Murray and collected data from all sites within this buffer. A generalised approach for the harmonisation of data across different time periods and from different jurisdictions was used to create a single database with common site names, preferred parameter names and preferred analytical units. The consolidated data set was further interrogated to determine whether the sampling points were in flowing water, pooled environments or drains; this main report is restricted to flowing water sites although an analysis of trends has been conducted for all sites within the 50 km river distance. In addition to standard water quality (WQ) metrics, the RMWQMP dataset includes measurements of algal abundance as well as herbicide/pesticide and heavy metal concentrations. Both the algal and herbicide/pesticide data were excluded from this analysis; heavy metals were

retained but the results are not presented in this main report. The WQ parameters included in the main report are: (see: Glossary for parameter details)

- Discharge
- Field pH
- Water temperature
- Dissolved oxygen (DO)
- Electrical conductivity @ 25 °C (EC@25°C)
- Turbidity
- Alkalinity
- Dissolved organic carbon (DOC)
- Total Kjeldahl nitrogen (TKN)
- Nitrogen oxides (NO_x)
- Total phosphorus (TP)
- Soluble reactive phosphorus (SRP)
- Dissolved silica

The analysis of trends in the data for each parameter and at each site was achieved by first creating a complete data record across the 1978 - 2021 data period; this was achieved by using a random-forest approach to impute seasonally-detrended, mean monthly data across each of the time series. The trends in this imputed data were analysed through (i) generalised additive models (GAMs), that identified non-linear trends and change-points; and (ii) generalised linear models (GLMs) that yielded a linear component giving the direction and magnitude of the data trend; these linear trend coefficients are presented in the report to understand changes in trend across all sites for each water quality parameter. GLMs were applied for four (4) different time periods: 1978 – 2021 (representing the entire RMWQMP dataset to date), 1978 – 2012 (corresponding to the entire dataset at the previous analysis of trends (Henderson et al., 2013), as well as two shorter (10-year) periods (2003 – 2012 and 2012 – 2021). The shorter time periods were included in response to the suggestion in the previous trends report (Henderson et al., 2013) that short time series may provide a more reliable indication of trends; we show that this is unlikely to be the case. The dataset was further analysed using a generalised linear mixed model (GLMM) to determine whether WQ across the sites could be explained by parameters relating to landscape run-off and water temperature, representing the key factors of connectivity within catchments and process (biogeochemical) rates.

We show the general pattern for WQ parameters is one of decreasing levels across the majority of WQ parameters and sites (except water temperature). In general, the magnitude of change is similar when analysed across the two long-term periods (1978 – 2012 and 1978 – 2021); by contrast, trend coefficients are much larger across the two 10-year data periods and have a common pattern of trend reversal between these two periods. For several parameters (discharge, water temperature and DO) there appears to be a weak climate change signature with decreasing discharge, increasing water temperature and decreasing DO concentrations. Across some parameters (e.g., EC, turbidity, alkalinity, DOC) there is a general pattern of increasing trend coefficients downstream, keeping in mind that the overall levels of these parameters also increase downstream; an important exception to this pattern is the water temperature, with larger increases observed at upstream sites. Relatively large trend coefficients are observed for the EC, particularly for sites downstream of the Goulburn River confluence. This observation is confirmed by closer examination of the EC data, which shows that for lower Murray sites, EC has more than halved over the period of the RMWQMP, with particularly strong decreases since 2010, and likely indicating the success of salt interception schemes that are now operating in the River Murray.

The GLMM built for the dataset, with standardised runoff index and water temperature as explanatory variables shows that the levels of WQ parameters generally increase with increasing run-off, likely reflecting the importance of landscape connectivity in driving the water quality of rivers. This dependence was particularly strong for sites in mid-Murray, reflecting stronger floodplain connectivity and the transfer of large quantities of materials at high flows. The only exceptions to this positive dependence were DO and field pH (particularly for upper Murray sites). The negative dependence for DO was particularly evident for mid-Murray sites and likely reflects the depletion of DO that can occur under high DOC conditions (i.e., blackwater); the decrease in pH with increasing run-off may

reflect the influence of soil acidity on main channel WQ in the upper Murray. While the dependencies of WQ variables on run-off were generally consistent across sites in the main channel of the River Murray, much more variability was observed across the tributary sites, likely reflecting more complexity in the factors which drive water quality as these scales.

As part of this report we investigated the capacity of the spot data program to detect WQ processes and events that occur in the River Murray; these processes/events were: (i) tributary junctions, (ii) blackwater, and (iii) wildfire. We considered four (4) tributary junctions (Kiewa-Murray, Ovens-Murray, Goulburn-Murray and Darling-Murray) and found for the upstream confluences that there were strong seasonal differences in key nutrients (NO_x and SiO_2) between the tributary and main channel. Specifically, significant depletion of SiO_2 (and to a lesser extent NO_x) occurred in the main channel over the summer-autumn period, with recovery occurring over winter-spring. This depletion is likely related to reservoir processes and may be critical in understanding algal dynamics at these sites. For the lower Murray confluences that strongest pattern was the higher level of most WQ parameters provided by the tributary compared to the main channel; this effect was particular evident for the Darling-Murray confluence and is likely responsible for the step change increase in the concentration of most of the WQ constituents in the River Murray below the Darling River confluence.

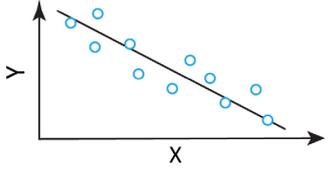
Our analysis of the ability of the RMWQMP to detect blackwater events focused on the 2010 – 2012 period (as well as the years before and after) when significant floodplain inundation occurred in the mid Murray. The production of floodplain DOC and the associated depletion of DO from the water column was well captured for this period, represented here as the 'deviation from saturation', this being a seasonally independent way of considering DO depletion from the water column. While the DO depletion that occurred during 2010-2011 (as well as the smaller event in 2011-2012) was captured at all sites downstream of Yarrawonga, the absence of any DO spot data downstream of Merbein prevents the spatial extent of DO depletion from being assessed.

In our analysis of the detection of wildfire, we focused on the 2019-2020 period and the impact on WQ at the Jingellic site. As part of this analysis we incorporated data from the WQ telemetry network to assess whether the high frequency nature of these data could provide additional information to the spot data program. We found that the spot data measurements were generally unable to detect any of the post-fire run-off events that occurred at the Jingellic site, due to both the low frequency (weekly) of the measurements and the suspension of the program for a short period following the fire. The WQ telemetry network on the other hand was extremely well suited to capturing post-fire run-off, with the detection of elevated levels of EC and turbidity and decreased levels of DO and pH, generally consistent with that expected for post-fire response. By way of example, a concentration-discharge (C-Q) analysis of the telemetry data was applied to demonstrate the richness of data that can be obtained from high frequency measurements.

Overall, we believe that the RMWQMP is well-suited to its primary purpose of detecting long-term changes in WQ in the River Murray and tributaries. Our key recommendations for the program are: (i) the re-commencement of WQ sampling at key sites where it appears that measurements have recently ceased, (ii) the reporting of dissolved oxygen at main channel sites downstream of Merbein, and (iii) stricter contractual arrangements around the reporting (and analytical) precision for key WQ parameters. We have identified some opportunities to (project-based) extensions to the program around: (i) tributary junctions and a more detailed analysis of dissolved and particulate organic carbon characteristics, directed towards understanding the influence of tributaries on main channel productivity, (ii) the seasonal depletion of silicon from sites downstream of Lake Hume and Lake Mulwala, and the potential link to algal community structure in the main channel, (iii) a more detailed investigation into the incorporation of WQ telemetry data into the monitoring program and the ways in which these data can be used to understand river function in real time, (iv) opportunities to utilise telemetry data for more accurate loads calculations, and (v) focused studies on the occurrence of emerging contaminants proximate to known or potential sources.

Glossary

STATISTICAL ANALYSIS TERMINOLOGY	
Increasing trend	
Decreasing trend	
Trend coefficient / effect size (interchangeable)	
Increasing (positive) effect size	
Increasing (negative) effect size	
Positive dependence	

Negative dependence	
GLM	Generalised Linear Model: A linear regression which accounts for the fact that the variance of each measurement is dependent on its predicted value
GAM	Generalised Additive Model: A GLM with a smoothing function that allows for multiple changes in the direction and/or effect size of trends within that regression
GLMM	Generalised Linear Mixed Model: A GLM which identifies predominant trends while accounting for "random" factors e.g., different trends at specific sampling sites

WATER QUALITY PARAMETERS			
WQ PARAMETER	ABBREVIATION	MEANING	UNITS
Discharge	NA	Volumetric water flow	ML/d
Field pH	pH	pH as measured on-site with a hand-held water quality meter	NA
Water temperature	Temp.	Temperature as measured on-site with a hand-held water quality meter	°C
Dissolved oxygen	DO	Concentration of oxygen dissolved in water, measured on-site with a hand-held water quality meter	mg-O ₂ /L
Dissolved oxygen saturation	DO-satn.	Comparison of the measured DO concentration against that expected for atmospheric equilibration, based on water temperature and atmospheric pressure	%
Electrical conductivity@25 °C	EC@25°C	Electrical conductivity of the water as measured either on-site with a hand-held water quality meter or in a laboratory, both corrected to 25 °C	µS/cm
Turbidity	Turb.	Turbidity ('cloudiness') of water, as measured with hand-held water quality meter	NTU

Alkalinity	Alk.	Acid neutralising capacity (resistance to pH change) as measured by laboratory titration	mg-CaCO ₃ /L
Dissolved organic carbon	DOC	Concentration of dissolved carbon (C) present in the form of organic material	mg-C/L
Total Kjeldahl nitrogen	TKN	Concentration of dissolved nitrogen (N) present in the form of ammonium (NH ₄ ⁺) and/or organic material	mg-N/L
Nitrogen oxides	NO _x	Concentration of dissolved nitrogen (N) present in the form of nitrite (NO ₂ ⁻) and/or nitrate (NO ₃ ⁻)	mg-N/L
Total phosphorus	TP	Concentration of all forms of phosphorus (P) (dissolved and particulate)	mg-P/L
Soluble reactive phosphorus	SRP	Concentration of dissolved phosphate (P)	mg-P/L
Dissolved silica	SiO ₂	Concentration of dissolved silica (SiO ₂)	mg-SiO ₂ /L

Introduction

The routine measurement of physico-chemical parameters in the River Murray (known as the River Murray Water Quality Monitoring Program; RMWQMP) has been operating since 1978. The intention of this program is broadly to understand long-term changes in water quality in this system and assess conditions under which water quality guidelines and targets may be exceeded. Over the 44 years since the inception of this program there have been changes to the suite of parameters recorded at sites, the number of sites that are monitored and the frequency at which sampling occurs. As a general comment the general trend in the monitoring program has been towards a reduced set of maintained sites and a reduced suite of physico-chemical parameters recorded at each site. The scope of the RMWQMP was last reviewed in 2013 (Biswas and Lawrence, 2013) with the recommendation to reduce the number of maintained sites (28 sites), removal of parameters that are not providing clear signals around water quality changes (e.g., ionic composition) and a reduction in frequency at some sites. The latter recommendation was largely driven by an earlier study that identified a potential risk in reducing sampling frequency with respect to estimating loads (Baldwin et al., 2013); reductions in sampling frequency were therefore restricted to tributary systems where load information was considered less critical.

The data collected by the RMWQMP is reviewed periodically (approximately every 10 years) for the purpose of understanding long-term trends in levels and concentrations of physico-chemical parameters. This review process allows some assessment of the success of river management interventions as well as providing the opportunity to consider further improvements in the program. The trends analysis also allows the impact of any longer-term climate drivers to be revealed. The previous analysis of the RMWQMP data (Henderson et al., 2013) identified a range of water quality (WQ) components (largely nutrients) that were decreasing over the (35 year) data record, but with high variability between sites. In this report we have conducted an analysis of the current dataset (1978 – 2021), spanning a period of 43 years. The techniques used in assessing these trend patterns are broadly similar to that implemented in previous analyses, recognising that advances in data analysis have occurred over the past 10 years.

In addition to the analysis of trends, this report includes the following elements:

- An investigation of potential explanatory variables (run-off and temperature) for water quality across the RMWQMP sites
- Assessment of the capacity for the program to detect environmental processes and disturbances typical of that which occur in this river system (tributary junctions, blackwater, wildfire).
- Consideration of how data collected from the water quality telemetry network can be used to augment data collected by the RMWQMP, and how this network could be usefully expanded to achieve MDBA management goals.
- Consideration of the analytical detection and precision applied to chemical analyses in light of the parameter concentrations typically encountered across the WQ network.

Review of processes that impact water quality

Water quality (WQ) programs are typically framed around the specific 'questions' relevant to that region. A range of processes can impact the WQ in the Murray Darling Basin (MDB), including (but not limited to): changing land-use, drought, flood; fire, river regulation, and to a lesser degree, aquatic contaminants. Superimposed on these system disturbances are the likely effects of climate change that will result in higher temperatures, reduced run-off, prolonged drought, more intense rainfall events and more frequent fire in the landscape. The key question is whether the current RMWQMP is fit for purpose. Specifically, does it measure WQ parameters that are relevant to the likely disturbances in this system and are there new developments in WQ monitoring which may improve the information acquired.

In this section we review four (4) processes that likely impact on water quality in the River Murray, including: tributary effects, floodplain-channel interactions ('blackwater'), wildfire and run-off (climate variability such as drought) (**Table 1**).

Table 1. Processes and events likely to impact water quality in the River Murray and tributaries

EVENT TYPE	TIMESCALES	WATER QUALITY PARAMETERS
Tributary effects	Constant / Seasonal	Temperature, suspended solids, particulate organic carbon (POC), Dissolved organic carbon (DOC), nutrients (N, P, Si, Fe)
Blackwater	Days → Weeks	Dissolved organic carbon (DOC), dissolved organic nitrogen (DON), dissolved oxygen
Wildfire	Hours → Days	Temperature, nutrients (smoke)
	Days → Weeks	(First flush) Suspended solids, electrical conductivity (EC), DOC, DO, base cations (Ca ²⁺ , Mg ²⁺), alkalinity
	Years	(Seasonal run-off) Nitrate, EC
Run-off	Months → Years	EC, DOC, nutrients (all)

TRIBUTARY EFFECTS

The water quality of regulated rivers are strongly controlled by the effects of reservoirs, as explained by the Serial Discontinuity Concept (SDC) (Ward and Stanford, 1995). The SDC recognises that reservoirs act as particulate trapping systems and are environments where 'lake processes' (i.e., lentic environments) dominate. The confluence of an unregulated tributary with a regulated river downstream of a reservoir can assist in the restoration of the regulated river to the natural gradient (river continuum conditions) due to modification of stream water quality conditions. This so-called 'tributary effect' (TE) can be due to a range of factors, including: (i) physical effects, (ii) chemical effects or (iii) biological effects (e.g., 're-seeding'). TE recognises that some water quality components may be provided by unregulated rivers that impact on (potentially increase) system productivity in the regulated river. The likely impact of an unregulated river on the water quality of a regulated river is best considered in terms of the volumetric mixing ratio of tributary (Q_T) and regulated (Q_R) flows (i.e., Q_T/Q_R).

Physical effects

Reservoirs typically exhibit reduced seasonality in water temperatures due to high hydraulic retention times (mixing and averaging) and reduced contact of water with the atmosphere (deeper and stratified water) (Vinson, 2001). Reservoirs are commonly colder than unregulated flows but can be warmer during periods of snowmelt run-off into the unregulated system or as a result of the abstraction of hyperlimnion water from the reservoir. The confluence of a regulated river with an unregulated tributary can result in direct thermal effects due to the wider seasonal temperature range of the unregulated system impacting biochemical reaction rates and system productivity.

Particulate trapping occurs in reservoirs as a consequence of reduced flow rates and results in reduced export of particulate matter downstream (Kennedy and Walker, 1990). Included in these trapped materials are: particulate organic carbon (POC) (Maavara et al., 2017, Maavara et al., 2015), particulate-bound nutrients (e.g., phosphorus; see below) and mineral particles. The export of POC from reservoirs is likely seasonally variable, with the continuous trapping of terrestrial POC contained in reservoir inflows and the seasonally variable export of algal POC, suspended in the reservoir water column (Maavara et al., 2017). The confluence of a regulated river with an unregulated tributary therefore likely represents one of the strongest contrasts encountered in systems, with mixing of terrestrial POC (unregulated) with low POC (or algal POC) from the regulated system. The chemical composition of POC is not commonly measured in aquatic systems, so the impact of reservoirs on this water quality component is largely unknown. POC can contain a range of biomolecule groups that are generally considered highly bioavailable, such as: carbohydrates, proteins, peptides and free amino acids, long-chain unsaturated fatty acids and short-chain organic acids. Included amongst these are compounds that are essential in the dietary context (e.g., essential amino acids (Dwyer et al., 2018) and long-chain fatty acids (Arts et al., 2001, Kainz et al., 2004).

Mineral particles contain a range of trace nutrients (including Fe and Si) that are essential for algal growth (e.g. Fe is essential in photosystem development; Si is essential in diatom cell wall structure) (Wetzel, 2001) and are likely lower in abundance in regulated rivers due to physical sedimentation (Friedl and Wüest, 2002, Walker, 1985). The confluence with an unregulated river may provide an important source of these trace elements.

Chemical effects

Dissolved nitrogen in surface waters can be in the form of dissolved inorganic nitrogen (DIN; NO_3^- , NO_2^- and NH_4^+) and dissolved organic nitrogen (DON; proteins, peptide, nucleic acids and amino-sugars); in many systems DON is the majority dissolved form (Harris et al., 2018, Kortelainen et al., 2006, Mattsson et al., 2009) but may not be the dominant bio-available form. Nitrogen in surface waters additionally occurs in living organisms as well as biogenic particles (as part of POC). Nitrate is the dominant form of DIN in most surface waters and is typically seasonally and event variable in response to run-off, immobilisation and uptake mechanisms as well as antecedent catchment conditions (Duncan et al., 2015, Ohte et al., 2010). Nitrogen speciation in reservoirs is more complex, with strong sedimentary anoxia driving de-nitrification and nitrogen (N_2) loss, countered by N_2 uptake and fixation by cyanobacteria (Wetzel, 2001). Seasonally strong algal growth can occur in surface layers during spring-summer, followed by sedimentation of dead algal cells in late summer-autumn. Reservoir mixing (turnover) in autumn-winter can make nutrients available for the following summer. The chemical form and concentrations of nitrogen released from reservoirs to river flow will therefore depend upon a range of factors, including: reservoir characteristics (depth, fill state), time of year and off-take position.

Phosphorus is more strongly associated with the particulate fraction in surface waters, in the form of biogenic particles, living organisms or adsorbed onto mineral particles (Stumm and Morgan, 1981). Consequently, dissolved P in unregulated catchments, particularly undisturbed (forested) land areas, will generally be low, with the bulk of P-transport via particulate materials with higher mobilisation during high flow events. Seasonally high dissolved P levels can occur in reservoirs, linked to sediment redox processes and reservoir mixing that would typically occur in autumn-winter (Wetzel, 2001). As a result, N&P from reservoirs may be more important in driving autotrophic production under steady state conditions whereas P from unregulated rivers may be more important under pulse flow conditions or when the mixing ratio (Q_T/Q_R) is high.

As noted previously, organic carbon characteristics (both dissolved (DOC) and particulate (POC)) likely differ markedly between unregulated and regulated catchments as a consequence of higher terrestrial OC delivery in the unregulated systems and dominant algal C formation in reservoirs (Maavara et al., 2017). The characteristics of DOC (or POC) can be described in terms of a range of 'quality' parameters, such as: aromaticity (Johnson et al.,

2011, McKnight et al., 2001), C:N ratios (Goldman and Dennett, 2000), or protein composition (Hollibaugh and Azam, 1983, Lee, 1993, Tupas and Koike, 1990) and is expected to differ between unregulated and regulated systems, reflecting the dominance of terrestrial and algal sources, respectively. DOC and POC provide energy for microbial decomposition as well as direct food sources for detritivores (filter feeders); marine studies indicate a strong link between algal carbon and microbial energy pathways (Azam et al., 1983). The direct utilisation of algal-fixed carbon by fungi and bacteria has also been demonstrated through carbon isotope tracer experiments (Kuehn et al., 2014). DOC/POC also serve as a nutrient source for autotrophic production, either through nutrient liberation from decomposition processes (mineralization), or directly as a nutrient source (Liu et al., 2012).

Question 1: How does the tributary-main channel mixing ratio (Q_T/Q_R) change seasonally at key tributary junctions in the River Murray? Do these tributary systems provide water quality components that are depleted in the regulated channel flow?

FLOODPLAIN CHANNEL INTERACTIONS (BLACKWATER)

The interaction of lowland rivers with floodplains is a natural process that allows exchange of carbon, nutrients and water, benefiting both the river system and the floodplain; this channel-floodplain interaction is represented theoretically by the flood-pulse concept (Junk et al., 1989). Floodplain inundation occurs as a consequence of high river discharge (overbank events) that will occur periodically in an unregulated river. In regulated river systems overbank events can be less frequent resulting in the accumulation of floodplain litter over longer periods. So-called 'blackwater events' occur when these high levels of accumulated litter are inundated, resulting in the leaching of dissolved organic carbon (DOC) into the overlying water and the transfer of this DOC to the main channel (Kerr et al., 2013, Whitworth et al., 2012). The released DOC places an oxygen demand on the water column and can result in oxygen depletion when the rate of oxygen utilisation exceed the rate of re-aeration from the atmosphere.

The likelihood of a blackwater event occurring is a combination of a range of factors, including: the quantity of floodplain litter (i.e., accumulation time, leaf deposition rates, forest type), litter age (i.e., the period of time litter has been on the floodplain floor), the hydrology of the overbank event (i.e., extent, duration and main channel return paths) and the physical conditions (i.e., water temperature, reaeration rates) (Kerr et al., 2013). In general, the most severe blackwater events occur in response to the inundation of floodplains that are infrequently connected to the main channel and at warmer times of year when the saturation levels of dissolved oxygen are at a minimum (and therefore can be reduced to very low levels more easily) and bacterial growth at its highest. Based on known rate parameters for: DOC leaching, oxygen consumption and reaeration, the effects of floodplain inundation on main channel levels of DO can be largely predicted. The models used for this purpose range from whole of system ('box' models; (Whitworth and Baldwin, 2016)) to more sophisticated linked hydrodynamic-chemical models (Holland et al., 2020).

The propagation of a DOC pulse in a river channel arising from the inundation of an upstream floodplain may result in a low DO 'slug' (aka. 'oxygen sag' in the wastewater literature (Kiely, 1997)) that impacts aquatic ecosystems over large river distances. The recovery from these oxygen depleted conditions is a function of a range of factors, including: the duration of the blackwater delivery to the main channel, the DOC utilisation rate (i.e., consumption of the bioavailable component of the mobilised DOC) and the atmospheric reaeration rate.

Question 2: Does the RMWQMP capture the spatial and temporal extent of blackwater events, including the downstream return to atmospheric oxygen saturation?

WILDFIRE

Wildfires are predicted to become more frequent and of higher intensity in South Eastern Australia (Abram et al., 2021), particularly in forested landscapes. Fire modifies the timing of delivery of materials from terrestrial to aquatic environments and changes the form of these materials. Immediate impacts of fire on aquatic systems are localised increases in water temperatures from radiant heat as well as ash deposition and smoke diffusion into streams, effects which occur on timescales of hours-days (Harper et al., 2019, Spencer and Hauer, 1991). Subsequent run-off events (days-weeks) transfer large quantities of material from the terrestrial landscape due to

losses in soil cohesion and run-off interception (Certini, 2005). The materials transferred however, are significantly transformed compared to the pre-fire state. The characteristics of run-off depend in a large part on fire intensity; fire converts nutrients (N & P) from organic to inorganic forms, releases base metals (alkalinity) associated with plant biomass as well as potentially toxic metals, increases aromaticity and hydrophobicity of soil organic carbon (OC; including the formation of black carbon and potentially toxic compounds) and phase-transforms soil minerals (Certini, 2005). Fire also disturbs microbial communities in soils, reducing biomass and interrupting nutrient cycling processes, with the extent of the disturbance penetrating further into the soil profile with higher temperatures (Certini, 2005). For many of these processes, higher fire intensity results in more complete conversion (e.g., OC to aromatic and inorganic forms) (Gresswell, 1999).

As a consequence of these landscape changes, run-off from fire affected catchments will typically have higher nutrient levels through mobilisation of nitrate, ammonium (to a lesser extent) and particle-bound phosphate, as well as higher pH (and alkalinity), higher suspended solids and higher EC (Certini, 2005, Emelko et al., 2016, Harris et al., 2015, Reale et al., 2015, Schindler et al., 1980). OC exported to aquatic systems will be less bioavailable although the loads of bioavailable OC may initially increase leading to significant oxygen depletion (Dahm et al., 2015). Changes to mineral phases likely impact on both mineral dissolution and (nutrient) adsorption processes through modification of surface properties (Stumm, 1987). The resulting changes within aquatic systems can lead to increases in pelagic algal growth as well as changes in algal community composition in response to elevated nutrient availability, but may inhibit benthic productivity due to scouring and siltation of stream beds (Planas et al., 2000, Verkaik et al., 2013). While run-off from fire affected landscapes can cause significant disturbance of aquatic systems, potential downstream benefits of these inputs are increasing stream complexity through increased heterogeneity of stream habitats (Harris et al., 2015, Kleindl et al., 2015). Over longer timescales the return to pre-fire conditions follows catchment recovery including: vegetation regrowth and litter generation, recovery of vegetation overstory in riparian corridors, re-establishment of soil nutrient cycles, re-generation of available base cations through mineral weathering processes, all of which depend on the extent to which these systems have been disturbed (Bixby et al., 2015, Britton, 1990, Diemer et al., 2015).

Question 3: Are wildfire water quality run-off components detected by the RMWQMP and/or the WQ telemetry systems over the day → week timescales?

RUNOFF (CLIMATE VARIABILITY)

Irregular inflows are a feature of the River Murray, as driven by short and long-term climate cycles in South Eastern Australia (King et al., 2020). The connections between terrestrial and aquatic environments are largely driven by run-off from catchments, with this connection being stronger during wetter periods. The interaction of run-off with catchment surface is controlled in part by land condition and the movement of water across the landscape (i.e., interflow, overland) and reflecting antecedent conditions, land use and time between run-off events. Longer periods between run-off events allows greater accumulation of materials in the landscape (e.g., rock weathering, litter accumulation). The flux of material from the terrestrial environment to drainage streams will therefore be a product of the amount of accumulated material in the terrestrial environment, how the water moves across the landscape and through the soil profile as well as the intrinsic mobilities of the accumulated material.

During periods of low run-off (hydrological drought) the connections between terrestrial and aquatic environments are restricted. Under these low run-off conditions water quality in streams and rivers are more strongly controlled by in-stream processes and water loss (evaporative concentration) (Peña-Guerrero et al., 2020). Groundwater contributions to stream flow become relatively more important under these conditions, with some WQ components controlled by groundwater composition. Evaporative water losses (typically higher under low run-off conditions) results in higher concentrations across many WQ components, although instream processes such as nutrient uptake may lead to depletion of some WQ components (e.g., nutrients) (Mosley, 2015). Given that low run-off conditions may also be associated with higher temperatures, dissolved oxygen concentrations may be lower. Additionally, while evaporation effects may increase suspended particle concentrations in the water column, decreased movement of particulate materials from the landscape may lead to reduced turbidity.

Under high run-off conditions, stream WQ is more strongly controlled by landscape connectivity. As noted above, the movement of materials from the terrestrial environment will depend upon the period of time since previous run-off events as well as the water path through the landscape. Prolonged periods of low run-off prior to a high run-off event will likely result in large amounts of material being mobilised and temporarily high concentrations of these

WQ components in the receiving stream/river. Over longer periods of high run-off conditions, stronger dilution effects may result in reduced concentrations of WQ components. Increased run-off from terrestrial environments can also result in mobilisation of particulate materials, potentially manifested as increased turbidity as well as elevated concentrations of particle-associated compounds (e.g., phosphorus). Under these conditions diffuse source pollutants (agricultural chemicals, fertilisers) from farmland areas are more likely to be transferred to aquatic environments.

EMERGING CONTAMINANTS

Contamination of freshwaters is increasing globally due to increased urbanisation, mining, agriculture and other anthropogenic pressures (Pinheiro et al., 2021). Contamination of aquatic ecosystems can have adverse impacts on biota, overall ecosystem function and also lead to significant human health issues. The Murray Darling Basin (MDB) has been identified as one of the top five watersheds globally at risk of pollution especially from pesticides (Tang et al., 2021). Contaminants such as pesticides, metals and other emerging contaminants such as microplastics (MP), perfluoroalkyl or polyfluoroalkyl substances (PFAS), pharmaceuticals and personal care products (PPCPs), and endocrine disrupting chemicals (EDC) are not routinely monitored within the MDB. With limited data available on concentrations in water, sediment and biota and direct effects to native species, especially regarding emerging contaminants of concern, this poses a significant risk to aquatic biota, ecosystems and human health.

Metals and pesticides

Metals and pesticides have been monitored inconsistently throughout the basin with some data available, however the analysis of trends with regard to these parameters have been excluded from this report due to the lack in frequency of monitoring. A brief look at the data available however indicates metals such as copper and zinc have at times throughout the basin exceeded the ANZG Water Quality Guidelines for these metals, with concentrations generally higher during drought periods. This poses significant risk to aquatic biota. Pesticides also pose a significant risk throughout the basin with the MDB rated in the top 5 at risk watersheds globally (Tang et al., 2021).

Microplastics

Microplastics (MPs) can enter freshwater systems in a variety of ways, including through weathering of larger plastic litter, wastewater treatment plants, drainage systems and through wind transport (Li et al., 2020). MP concentrations in freshwaters have been reported to range from less than 1 particle/L up to over 20,000 particles/L (Li et al., 2020). The responses of aquatic organisms to MP exposure often include reduction in survival, reproductive fitness (ability and success of offspring) and growth rates (Li et al., 2020). Limited studies have investigated the amount of MP in Australian freshwaters. Kowalczyk et al. (2017) found that the Maribyrnong and Yarra Rivers contained 2867 particles per litre in surface water. Little is known about MPs concentrations and effect on aquatic biota within the MDB, with preliminary studies finding MP particles within the water and sediment of the Murray River at Albury (Holland, pers comm.)

Polyfluoroalkyl substances (PFAS) and their derivatives

Polyfluoroalkyl substances are highly soluble in water, that do not degrade under typical environmental conditions and can readily leach from soil to surface water and groundwater, where they can potentially cause toxic effect on biota or accumulate and biomagnify up the food chain posing a direct risk to aquatic biota and human health (2020). Recent studies on the Kiewa River, Jack and Boz Creek catchments have shown elevated levels of PFAS in groundwater, river water and in carp (Ebsary, 2021). Concentrations in carp were found to be as high as 17,000 ug/kg significantly exceeding the food standard of 5.2 ug/kg (Ebsary 2021). Concentrations in oxbows of the Kiewa River floodplain contained 12.8 ug/L of PFHxS and PFOS, significantly exceeding the guidelines for recreational water (0.7 ug/L) and draft water quality guideline values (PFOS: 0.13 ug/L) for 95% protection of aquatic life (2020). However, due to the potential of PFAS to bioaccumulate and biomagnify up the food chain via its ability to directly bind to proteins, it is recommended that the 99% protection water quality guideline value for PFOS of 0.00023 ug/L be used instead of the 95% which is typically applied to slightly modified aquatic environments (EPA 2020). PFAS has also been found to be present in Australian waterbirds serum and excrement at concentration of 120 ug/L and 0.11 ug/g respectively (Szabo et al., 2022). A study of 19 wastewater treatment plants across Victoria found that PFAS concentrations increased through the wastewater treatment process, with concentrations high in effluent than in the influent. The mean PFAS concentration was 0.11 ug/L and ranged from 0.0093-0.520 ug/L (Coggan et

al., 2019). Recently PFAS has also been shown to be present globally in rain water and often exceeding recommended levels, making no freshwater ecosystem safe from potential contamination (Cousins et al., 2022).

Pharmaceuticals and Personal care products (PPCPs)

Pharmaceuticals and Personal care products (PPCPs) find their way into aquatic ecosystems through wastewater treatment plants, landfill leaching and use of biosolids as fertilisers (Ebele et al., 2017). Most PPCPS are not completely and/or consistently removed from conventional wastewater treatment processes. PPCPs generally been reported to occur in the ng or ug concentration in freshwater systems. Although they often occur at low concentrations many have been designed to cause direct effects at low concentrations and have the potential to bioaccumulate and potentially biomagnify up the food chain (Ebele et al., 2017). Many PPCPs can also be considered EDCs. During a national survey of trace organic contaminants in Australian rivers, the most commonly detected contaminants were pharmaceuticals such as: salicylic acid, paracetamol, carbamazepine, and caffeine at maximum concentrations of 1530 ng/L, 7150 ng/L, 682 ng/L and 3770 ng/L respectively (Scott et al., 2014). Aquatic invertebrates and riparian spiders from streams near Melbourne have been reported to contain over 60 PPCPs (Richmond et al., 2018). The removal efficiency and concentrations of PPCPs were monitored at a sewage treatment plant with effluent outfall into the lower Molonglo/upper Murrumbidgee catchment and found that removal of most PPCPs was incomplete and effluent loads of PPCPS such as carbamazepine, venlafaxine and sotalol could be as high as 64g/day (Roberts et al., 2016). Information regarding concentrations and composition of PPCPs and possible impacts in the MDB is limited.

Future research is needed to determine the risk posed by emerging contaminants in the MDB by determining concentrations throughout the basin, determining the risk they pose to biota at environmentally relevant concentrations and assessing accumulation across the food web. Initial sampling should include enough resolution to determine temporal and spatial variations with regard to concentrations of contaminants of concern in water, sediment and biota and toxicity bioassays should be conducted on native species relevant to the MDB to assess potential risk.

Data analysis methods

DATA SOURCES

Spot data

Spot data were retrieved from three separate sources. The MDBA RMWQMP dataset included 422 sites with unique latitude-longitude combinations. A further 28 sites were obtained by direct request to NSW Water. A previously curated dataset kept by the MDBA ('Hinton' dataset) provided data records for 1,879 locations with unique site identifiers. The Hinton data included some site locations that overlapped with sites in the previous two datasets. Where this occurred, Hinton data were only incorporated if they provided unique data points. Due to discrepancies between the Hinton data and the other data sets in terms of the dates that samples were collected, Hinton data were excluded if they fell within the same week as data recorded in the other datasets.

Telemetry data

Water quality telemetry data is available for a number of sites in the River Murray and tributaries, with collection of up to five (5) physical parameters (pH, dissolved oxygen (DO), electrical conductivity (EC), turbidity and water temperature). Active telemetry sites with high parameter coverage are skewed towards the upper Murray and associated tributaries; lower Murray sites with active telemetry are largely restricted to the measurement of EC and temperature. The available water quality parameters and date ranges over which data has been collected are summarised in Table A1. In general, EC and temperature records extend from as early as 1991 to current; pH, DO and turbidity data tends to be more recent and more fragmented, likely reflecting the difficulty in maintaining these sensor types. Telemetry data has not been used in the trends analysis, but is used in one of the scenarios considered below (wildfire response).

SITE SELECTION

Geofabric v2.1.1 (Bureau of Meteorology, 2014) was used to define river reaches. A 50km buffer around the River Murray was calculated in R using the buffer function of the sf package (Pebesma, 2018). The st_intersection function of the R package sf was used to identify sites that fell within the buffer. Water quality from sites that did not fall within the 50km buffer were removed from further analyses. Site locations were imported into QGIS (QGIS Development Team, 2021) with a google satellite background and their locations manually reviewed. In many instances, multiple stations were present at what may be regarded as the same location, i.e., within the same reach and within approximately 400 m of each other. These sites were aggregated by creating new variables of site names, latitudes, and longitudes, with common values/names set across the aggregated sites.

The type of aquatic environment for each site was determined (i.e., upstream or downstream of a weir, within lake or weir pool, drainage lines or in the main channel of a river). Only those data that were either: (i) within main channels and downstream of weirs or (ii) pooled sites that are part of the 28 sites currently supported by the RMWQMP, were retained for further analyses. Pooled sites are treated separately here and not included in the main trends report. The final water quality dataset for flowing sites included data from 73 stations (**Figure 1**). While an analysis of trends was carried out at all stations, this report (main section) is restricted to 25 sites that are currently supported by the RMWQMP as well as the additional flowing sites included to replace pooled sites. The flowing and pooled sites are listed in **Table 2**.

Table 2. Site ID; site name; sampling class (see footnote); environment type and whether part of the 28 MDBA sites.

Site ID	Site name	Class	Type	Part of 28 sites
401201A	River Murray at Jingellic	2	Channel	Y
401204A	Mitta Mitta River at Tallandoon	2	Tributary	Y
409016	River Murray at Heywoods	2	Channel	Y
402205A	Kiewa River at Bandiana	2	Tributary	Y
403241A	Ovens River at Peechelba	2	Tributary	Y
409025	River Murray D/S Yarrawonga Weir	2	Channel	Y
404214	BROKEN_CREEK_KATAMATITE	2	Tributary	N
405232	Goulburn River at McCoy Bridge	2	Tributary	Y
406202	Campaspe River at Rochester	1	Tributary	Y
409207B	River Murray d/s Torrumbarry Weir	2	Channel	Y
407209	Gunbower Creek at Koondrook	2	Tributary	Y
407205	LODDON_RIVER_APPIN_SOUTH	2	Tributary	N
409204C	River Murray at Swan Hill	1	Channel	Y
409034	Wakool River at Kyalite	2	Tributary	Y
410130	Murrumbidgee River at Balranald	2	Tributary	Y
414204	Murray River at Redcliff	3	Channel	Y
414206	River Murray at Merbein	2	Channel	Y
425007	Darling River at Burtundy	1	Tributary	Y
A4260501	River Murray at Lock 9	2	Channel	Y
A4260553	LAKE_VICTORIA_OUTLET		Tributary	N
A4260200	River Murray d/s Rufus River Junction	3	Channel	Y

A4260539	River Murray at Waikerie	3	Channel	Y
A4260554	River Murray at Morgan	1	Channel	Y
A4260522	River Murray at Murray Bridge	2	Channel	Y
A4260551	River Murray at Taillem Bend	2	Channel	Y
414209	River Murray U/S Euston Weir	2	Pool	Y
404210	Broken Creek at Rices Weir	2	Pool	Y
407202	Loddon River at Kerang	1	Pool	Y
A4260512	River Murray at Lock 5 D/S	2	Pool	Y
A4260524	Lake Alexandrina at Milang	3	Pool	Y
A4261034	Goolwa site	3	Pool	Y

Note: Class refers to the sampling frequency and range of parameters/analytes measured at each site (Biswas and Lawrence, 2013).

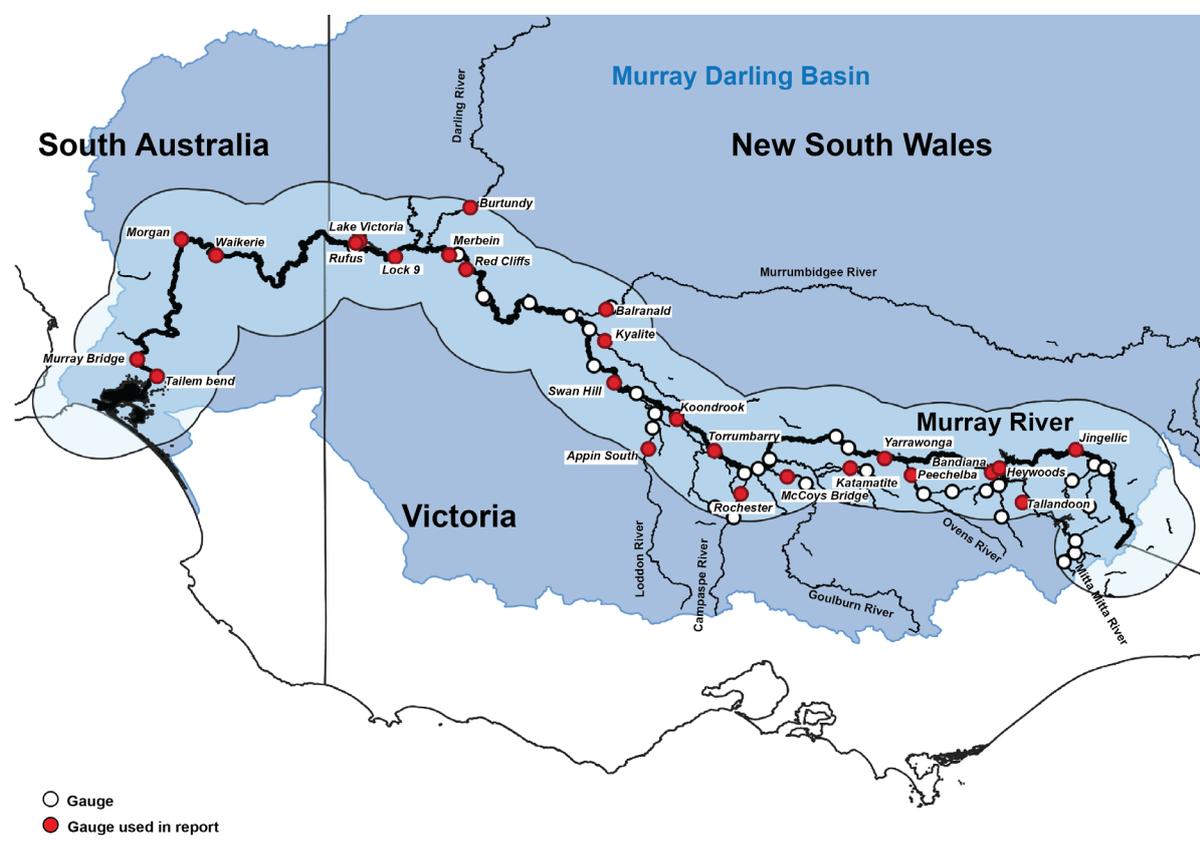


Figure 1. Map of the River Murray and major tributaries. The light shaded envelope represents the 50km buffer applied for site selection. All water quality monitoring sites within the 50 km buffer shown on figure; flowing sites used in this report marked in red.

VARIABLES (PARAMETERS) ANALYSED

There was some variation in the recorded parameter names, analytical methods and measurement units for water quality variables among and within the various datasets. For instance, reactive soluble phosphorus was present under five different variable names. A data harmonisation process was used to ensure that water quality data were comparable across datasets and that all potential data for a water quality variable were included in analyses. This

involved plotting each water quality variable and manually assessing whether variables were likely identical but with different names (i.e., measured at similar scales/units) or could be transformed to comparable units (e.g., g/m to mg/m). In order to automate the data harmonisation process, a 'data harmonisation table' was used to convert all measured parameters ('VARIABLES') to the preferred parameter name ('preferred name') and a preferred unit ('preferred_units'), at all sites.

Algal species, toxins and pesticides/herbicides were removed from the dataset and not considered further; algal data will be included as part of a separate project for the MDBA that considers long-term trends and drivers of blue-green algae in the River Murray. Metals were retained and analysed for trend patterns, but are not included in the main report. The water quality parameters included in this main report are: discharge, field pH, water temperature, dissolved oxygen (DO), electrical conductivity (EC), turbidity, alkalinity, dissolved organic carbon (DOC), total Kjeldahl nitrogen (TKN), nitrogen oxides (NO_x), total phosphorus (TP), soluble reactive phosphorus (SRP) and dissolved silicon (13 parameters in total).

TREND ANALYSIS

The steps involved in the trends analysis and the subsequent development of a global model for water quality in the selected RMWQMP sites are summarised in **Table 3**, and described in more detail below, by way of example.

Table 3. Key analysis steps in the trend analysis and development of a global model

Step No.	Analysis goal	Analysis step	Outcome
1	Replace missing data	Use Kalman filters for interpolation	Regular monthly time series without missing data points
2	Determine annual seasonality in parameters and account for moving average/autocorrelation	S/ARIMA models and extract the seasonal components of the models	Identification of seasonal or other regularly recurring patterns in the data – allowing the data to be 'de-trended' according to these patterns
3	Imputation of missing data across all sites and all seasonally-detrended (where appropriate) WQ parameters	Data imputation by Random Forest (RF) models	Regular, de-trended monthly time series of measured plus imputed values
4	Model the temporal trends of the parameter after accounting for site specific seasonality	GAM spline fits to determine trends over the data that was interpolated	Spline fits to datasets allowing trend coefficients to be extracted and identification of change periods
5	Model the observed parameter values and determine if site standardised discharge score and/or monthly mean temp were significantly correlated	GLMM fits of discharge and temperature to determine drivers of water quality changes	Global model for water quality

S/ARIMA=Seasonal/ AutoRegressive Integrated Moving Average; GAM = Generalised additive model; GLMM=generalised linear mixed model

Step 1. Data interpolation

The most commonly occurring sampling frequency, for most parameters and sites, was monthly. The original measurement data were therefore first consolidated into monthly means for each specific site and parameter

combination. Any missing data in these monthly time series were then imputed using a Kalman filter and smoothing (an algorithm which identifies the most probable values based on the measured data). This process filled in any gaps between the minimum and maximum measurement dates, for each site and parameter Figure 2.

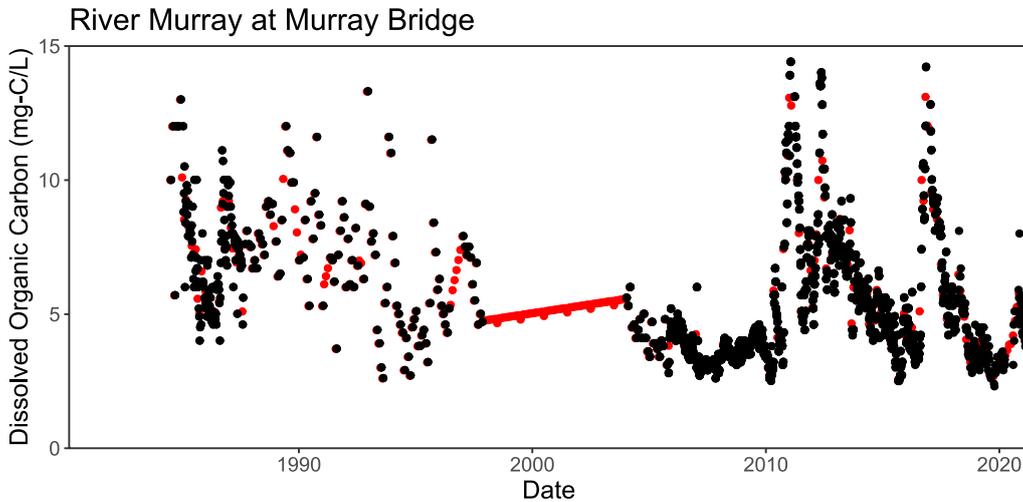


Figure 2. Example of imputed missing values, as Kalman filtered and smoothed data (red dots), calculated to fill in missing sections of the original, measured data (black dots) for dissolved organic carbon (River Murray at Murray Bridge site).

Step 2. Seasonal and/or autocorrelative de-trending

Once a continuous, monthly time series was produced, an automatic selection (via stepwise minimisation of model space) of the best-fitting Auto-Regressive Integrated Moving Average Model (ARIMA) for each specific time series was conducted. These models predict the time series values based on stationary (i.e., with long-term trends removed), linear regressions of past values, which potentially include both: (i) the auto-correlative function of the current and past values and (ii) a seasonal component (a.k.a., seasonal-ARIMA or SARIMA). We used this model selection to determine whether there were seasonal components present (i.e., whether the model selection chose an ARIMA or SARIMA model as the best fit). If seasonality was detected, we removed the seasonal component of the corresponding SARIMA model (i.e., the amount of variability in the data attributable to regular, seasonal variation in values) for the appropriate month from the original time series, resulting in a seasonally-detrended (where appropriate) series of values specific to each site and parameter (Figure 3).

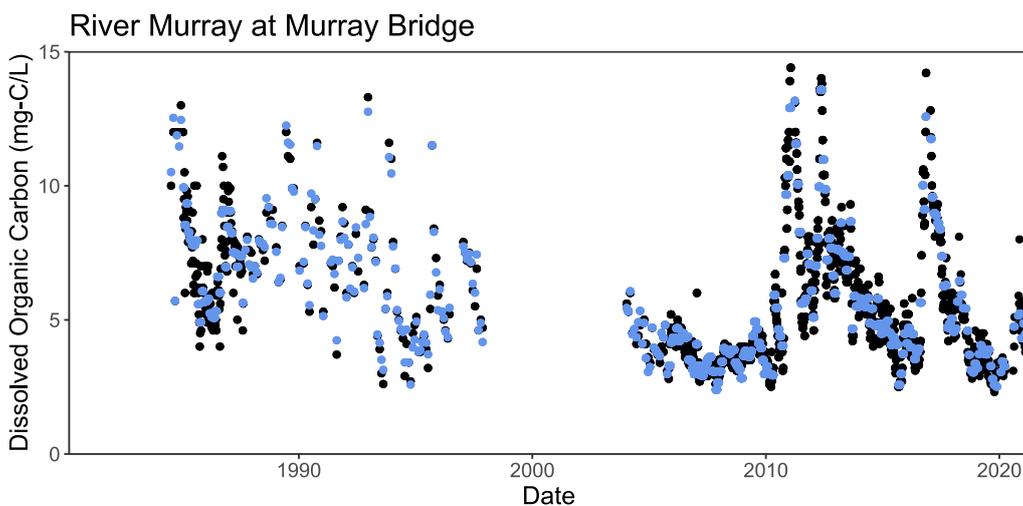


Figure 3. Example of seasonally detrended values (blue dots) in comparison with the original, measured data (black dots) for dissolved organic carbon (River Murray at Murray Bridge site).

Step 3. Data imputation

Next, we took the complete set of seasonally detrended time series for each parameter (i.e., all sites at which that parameter was measured), recalculated monthly, seasonally detrended means, and used chained random forest models (using data at all sites as predictors) to impute data across all sites, from the minimum to maximum dates at which the parameter was measured at any site. The result was a series of continuous, seasonally-detrended (where appropriate) series of monthly mean values for each site, across the entire measured period (Figure 4).

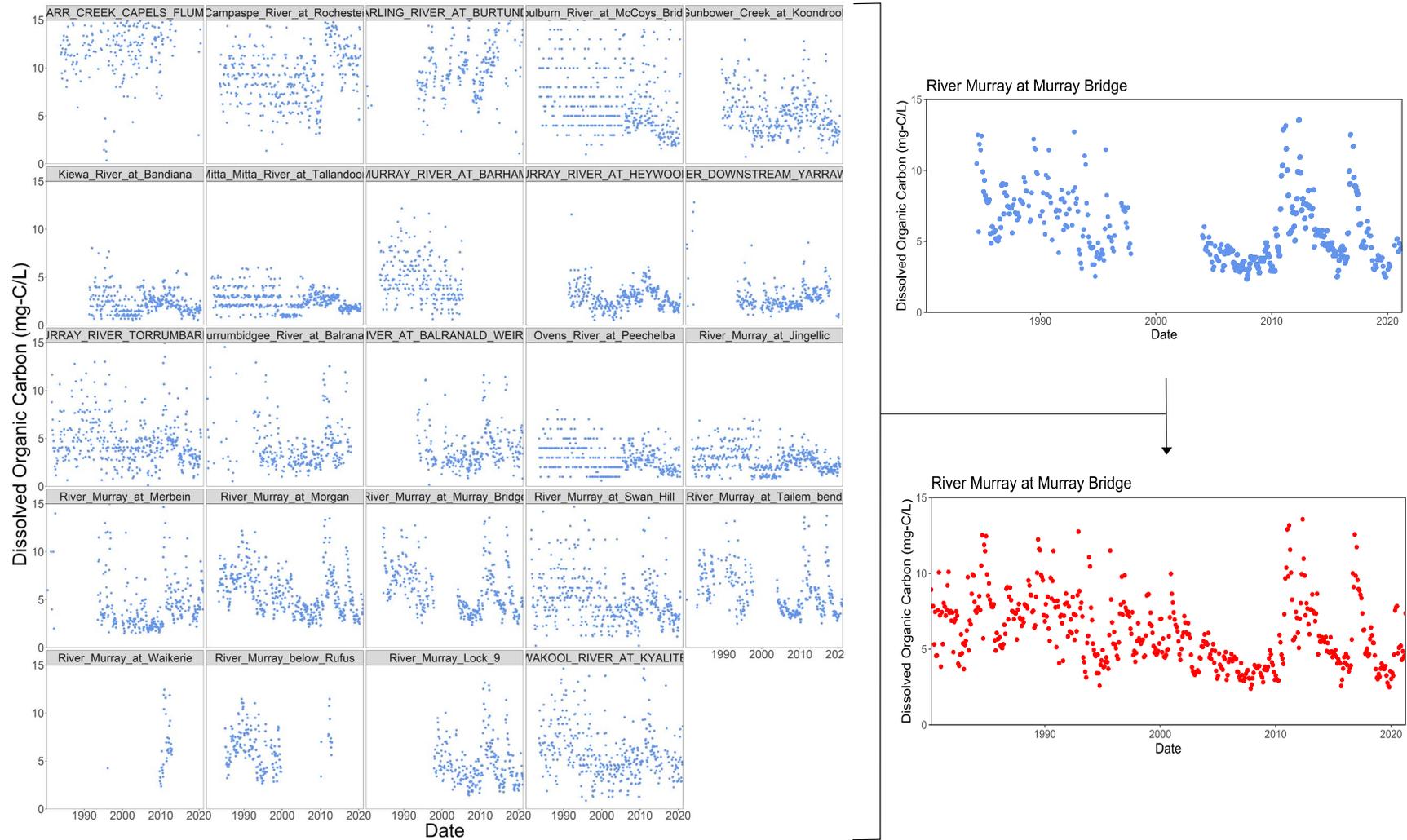


Figure 4. Conceptualisation of the process by which random forest models were used to take the entire set of seasonally-detrended values for each site (left graphs) to impute the seasonally-detrended data (blue dots, upper right graph) into a continuous time series of monthly mean data (red dots, bottom right graph) for dissolved organic carbon sampling at the Murray Bridge site on the River Murray.

Step 4. GAM spline fits

We then applied a generalised additive model (GAM; a smoothed prediction of trends in the parameter values based on date) to this monthly imputed data, which produces a prediction of the long-term trends in the data and the error around these predictions (Figure 5). We also calculated the overall, linear change in concentrations over for each monthly, imputed mean data set using generalised linear models (GLMs). Change point analysis was included in the GAM for each dataset, based on the first derivative of the non-linear GAM component. In GAMs, these derivatives are estimated using the method of finite differences; i.e., the difference between estimated values for two time points, separated by a very small time-shift, is an approximation of the true first derivative of the trend (Simpson, 2018). Significant periods of change (i.e., times at which monthly means were changing) were thus inferred from periods in which the 95% confidence interval for the estimated first derivative did not include zero (Figure 5). The GAMs calculated for all sites and water quality parameters are provided in electronic format; GAMs for the sites selected for trends analysis are provided in the Appendices of this report (details below).

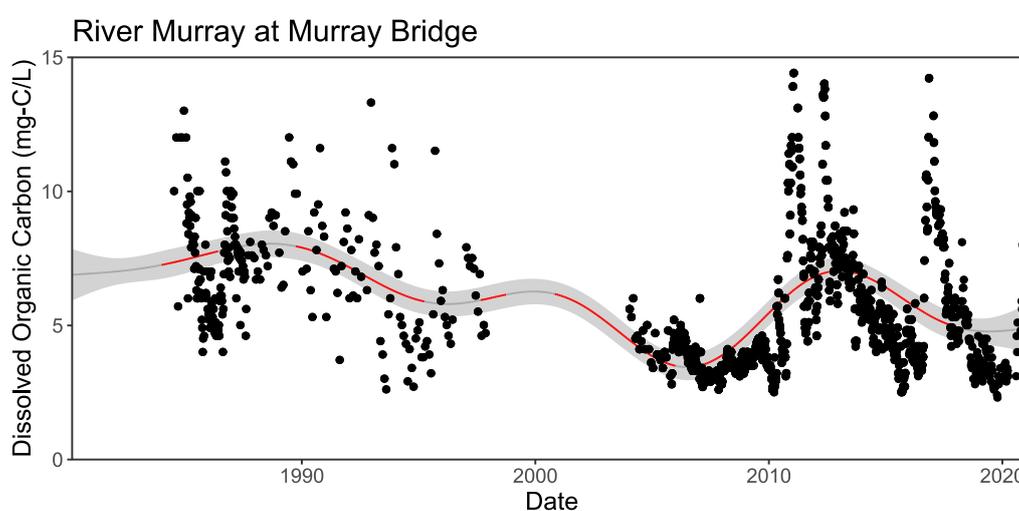


Figure 5. Example of generalised additive model (grey and red line; \pm 95% confidence interval) predicting smoothed trends in the long-term, seasonally detrended monthly average data (see text for details), in comparison with the original, measured data (black dots) for dissolved organic carbon (River Murray at Murray Bridge site). Colours for the model prediction line indicate periods of significant change (red sections) and no change (grey sections) in monthly mean concentrations, identified from analysis of additive model first derivatives. R^2 value indicates additive model fit to imputed monthly mean data.

Step 5. GLMM fits

Understanding if water quality parameters are driven by changes in climate, e.g. increasing wet and drying periods or increasing temperature, gives the ability to predict how water quality may change under future climates. To test these relationships a Generalised Linear Mixed Model (GLMM) was built using *glmmTMB* (v 1.1.4) (Brooks et al., 2017) for each water quality parameter. This modelled each selected water quality parameter as a normally distributed response variable and analysed its correlation with the relative hydrological conditions and mean temperature at each site.

Monthly mean discharge data was pre-processed via the *SPEI* package in R (v 1.7) (Vicente-Serrano et al., 2010) to generate the standardised runoff index. This parameter centre-standardises the mean discharge for each month to all months of that type (e.g. all January's) across the observed time period. This models the hydrological conditions as an indicator of the relatively wet or dry periods experienced at the site and was preferable to mean discharge given the high variability in flows across the catchment. Given that temperature has a more direct physical (and predictable) influence on biogeochemical reaction rates, the influence of water temperature was based on mean monthly values.

Discharge is likely to influence parameters different across the catchment, so to control for different responses of water quality parameters between sites a random intercept and slope term was included in the model. Specifically,

we allowed for a response intercept in the model that was variable by site (random intercept) and a coefficient of the relationship to discharge (SI_discharge) that was variable by site (random slope estimate). Temperature was assumed to have the same influence across sites and was left as a fixed factor in the model formula.

A chi-squared model comparison was used to test for the significance of random slopes and intercepts in addition to analysis of variance for determining the significance of the fixed effects of standardised runoff and temperature. Following this, predicted relationships were derived from the model using the *ggpredict* function of the *ggeffects* package (v 1.1.3) (Lüdtke, 2018) including random effect influences to give 95% confidence in our estimates of linear relationships for each parameter.

Results

LONGITUDINAL CHANGES IN WATER QUALITY IN RIVER MURRAY

Water quality changes along the River Murray were investigated using RMWQMP data from main channel sites (Jingellic – Tailem Bend; Figure 6), separated by season. All data (except pH) has been log-transformed (base-10) and plotted on a seasonal basis.

The main features of water quality changes along the River Murray are a general increase in pH and most WQ variables between Jingellic and Merbein as well as a step change (increase) downstream of Merbein, likely due to the influence of the Darling River (see: Darling-Murray confluence, section: Scenarios). These longitudinal changes along the main channel of the River Murray are broadly consistent with that reported previously for this system (Biswas and Mosley, 2019).

Across all sites the pH ranges between 6.5 – 8.3, without clear seasonality and with the largest change between Merbein and Waikerie. Conductivity increases 10-fold between Jingellic and Tailem Bend, with a step change increase between Merbein and Waikerie. Turbidity increases 10-fold between Jingellic and Tailem Bend, with the largest increases between Heywoods and Swan Hill as well as between Merbein and Waikerie. Total phosphorus (TP) follows a very similar pattern to turbidity; as discussed below, these two parameters are highly correlated for reasons likely related to the chemical forms of particulate phosphorus. Both dissolved organic carbon (DOC) and total Kjeldahl nitrogen (TKN) increase between Jingellic and Swan Hill, with a further step change increase downstream of Merbein. Soluble reactive phosphorus (SRP) levels are low throughout the River Murray, but show a step change increase below Merbein.

Both nitrogen oxides (NO_x ; $\text{NO}_2^- + \text{NO}_3^-$) and total dissolved silica (SiO_2) show strong seasonality for sites upstream of Merbein. For these sites a strong seasonal depletion occurs between spring – autumn, particularly pronounced between Yarrowonga and Swan Hill. Similarly, SiO_2 shows a strong seasonal depletion between Heywoods and Merbein sites, with the onset of this depletion occurring earlier for the more downstream of these sites. This seasonal depletion of SiO_2 and NO_x is investigated later in this report (Section: Scenarios).

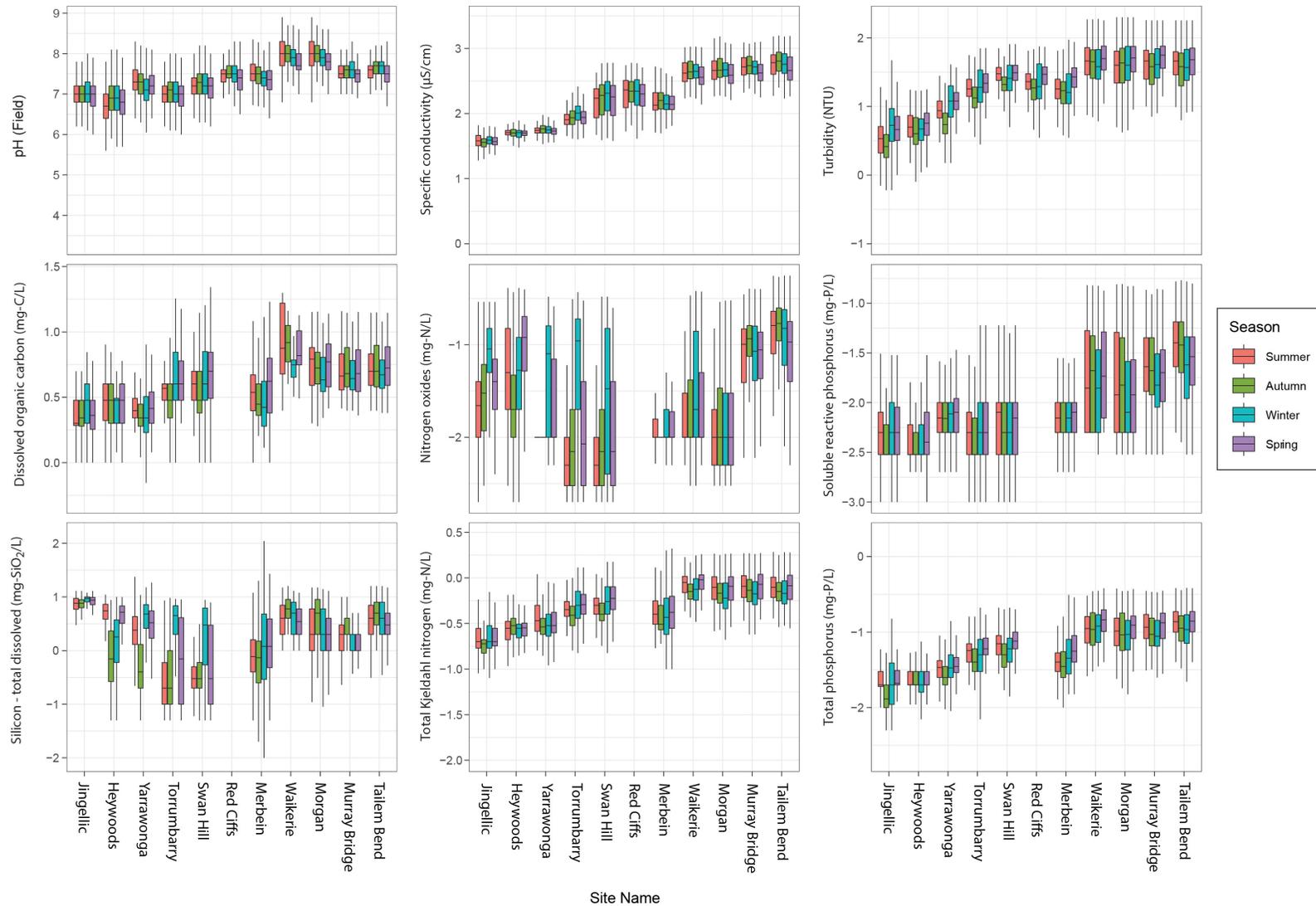


Figure 6. Boxplot of seasonal patterns in water quality parameters in River Murray sites (main channel only). All data (except pH) plotted as logarithm (base-10). Dataset includes all water quality measurements available for the 1978-2021 period and does not reveal trends in these parameters over this period.

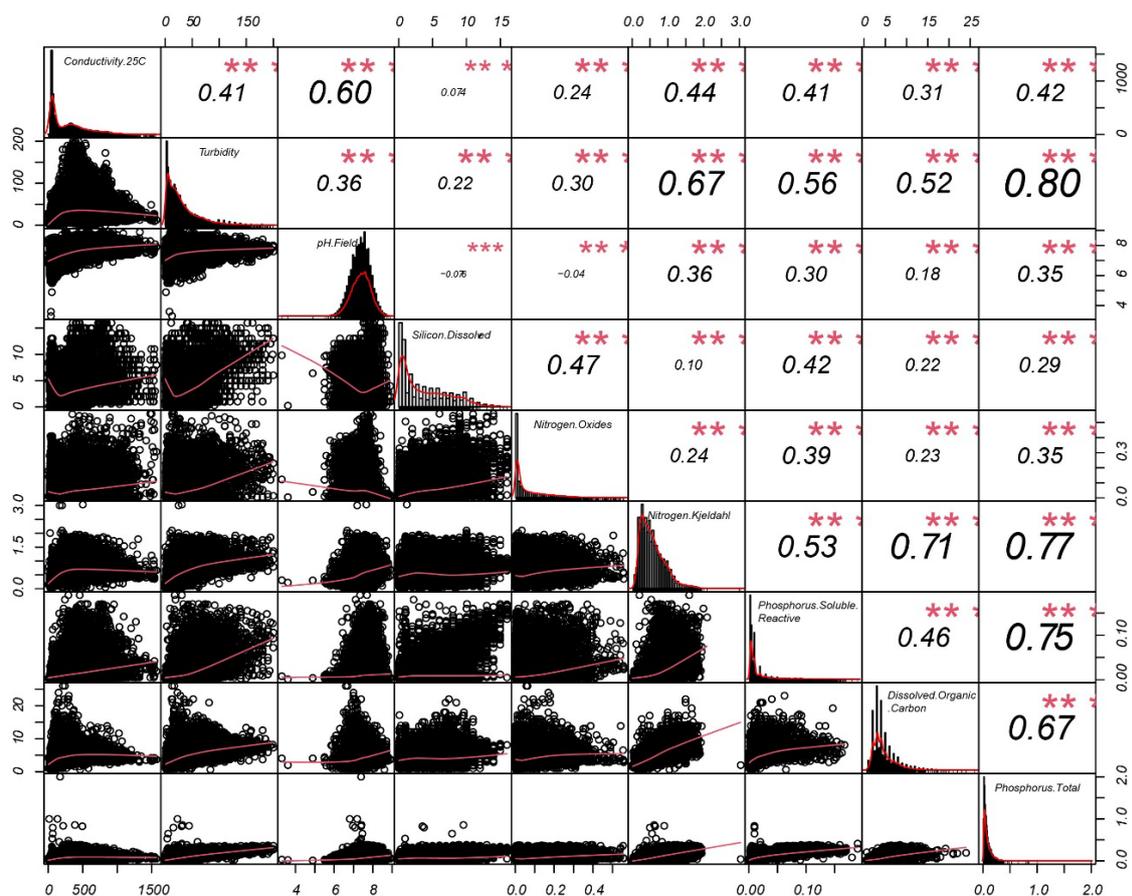


Figure 7. Correlation plot for water quality variables in River Murray sites (main channel only; all seasons combined; same data as Figure 6). Dataset includes all water quality measurements available for the 1978-2021 period.

The correlation plot for the River Murray sites (all seasons combined; main channel site only) reveals strong correlations between several sets of variables (Figure 7). These include: (i) conductivity – pH; possibly due to a link between the mobilisation of base cations and buffering capacity, (ii) turbidity – TP; likely due to the link between particulate organic and mineral phases that include adsorbed phosphorus, (iii) DOC – TKN – TP; linked through dissolved organic matter containing organically-bound C, N & P, (iv) SRP – TP; TP includes SRP, and for many samples SRP will be significant (dominant) proportion of TP.

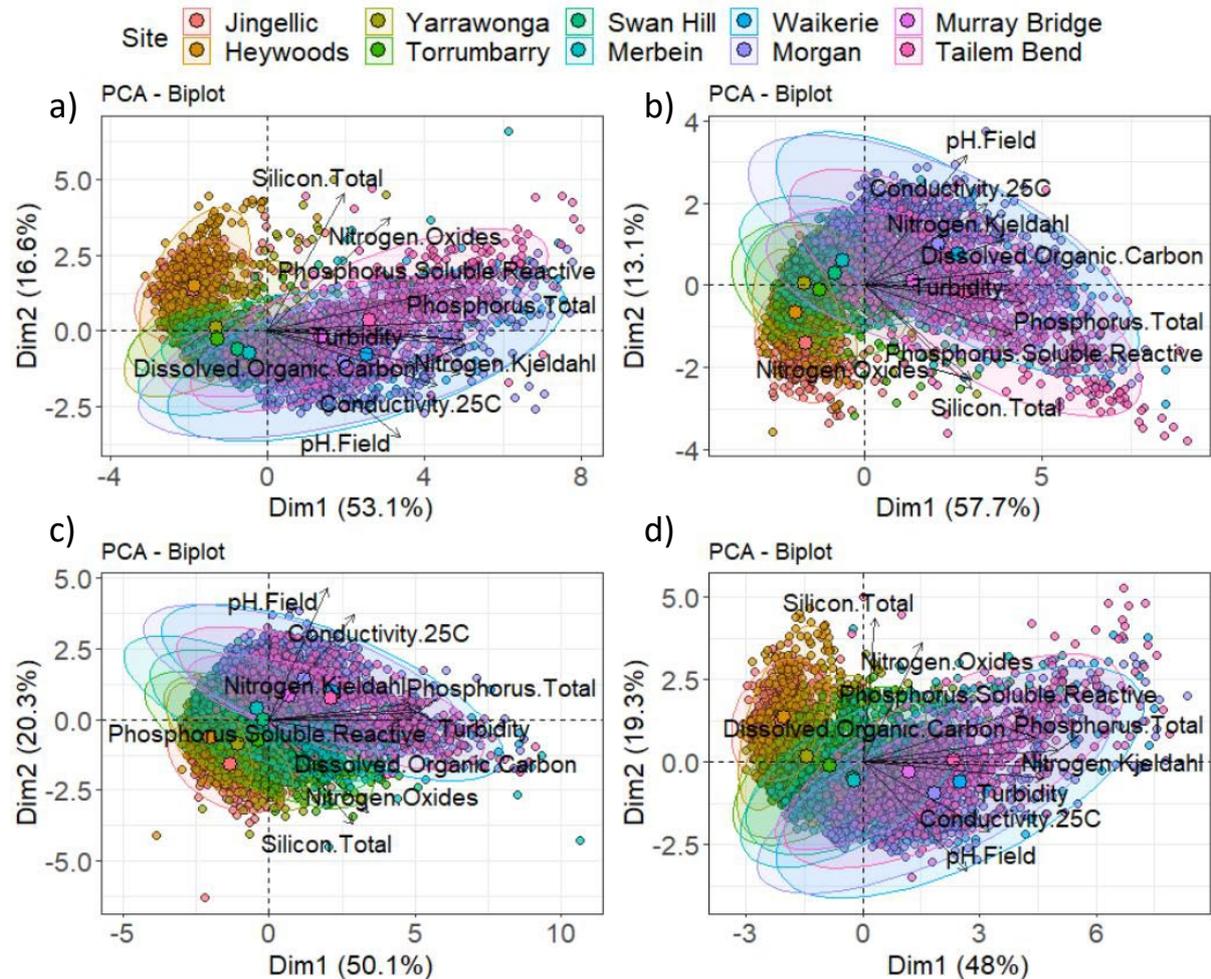


Figure 8. Principal components analysis (PCA) plots of water quality data for River Murray (main channel) sites, separated by season. Shown are data for: (a) Summer (top left); (b) Autumn (top right); (c) Winter (bottom left); (d) Spring (bottom right). Dataset includes all water quality measurements available for the 1978-2021 period and does not account for trends in these parameters over this period.

Visual examination of site differences by principal components analysis (PCA; Figure 8; each season plotted separately) shows a pattern of sites being more similar in their water quality characteristics in winter (more clustered) and less similar (more separated) in summer. In general, the site characteristics change in a sequential way between Jingellic and Tailm Bend, but with a clear separation of sites upstream and downstream of the Darling River confluence. The separation of sites in spring – autumn can be largely attributed to increasing differences in the levels of all water quality parameters between Jingellic and Tailm Bend (Dimension 1; Dim1) and seasonal depletion of SiO_2 and NO_x species between Heywoods and Merbein (Figure 6).

TRENDS BY PARAMETER

Trend patterns in the 13 selected parameters (discharge and 12 water quality parameters) in levels/concentrations are represented as 'change effect' bar charts for each of the 13 parameters at the 25 sites selected for this analysis, with the sites ordered by position in catchment. Load trends are also shown for parameters that can be represented as a quantifiable mass unit. Trends in load values were calculated using a 5-step process: (i) measured daily load values (mass/day) were calculated wherever possible (i.e., dates where both discharge and concentration data were measured at a site); (ii) missing load values were imputed using linear interpolation of discharge and concentration data (Cohn, 1995); (iii) total annual loads (mass/year) were summed from measured and estimated load values across each year; and (iv) linear trends in annual loads were calculated from the estimated slopes (trend coefficients) of generalised linear models (GLMs) predicting annual loads from year.

Trends in water quality levels/concentrations have been calculated over four (4) separate time periods: (i) 1978 – 2012, presenting the time period analysed by the previous trends report (Henderson et al., 2013); (ii) 1978 – 2021, the full RMWQMP dataset analysed in this report; (iii) 2003 – 2012, a 10-year data period analysed by (Henderson et al., 2013); (iv) 2012 – 2021, the subsequent 10 year period analysed in this report. Loads are calculated for the 1978 – 2021 period only.

Included for each parameter is a brief description of the ecological significance of the parameter, the natural controls, data availability (Appendix A) for the 25 selected sites, data resolution (Appendix B), GAMs (including change points and default trigger values from ANZG and/or River Murray specific targets; Appendix C) and the seasonal and/or autoregressive component (Appendix D).

Trend data for RMWQMP pooled sites excluded from this main report are shown in Appendix E.

Discharge

Discharge is currently measured at most (19/25) of the sites selected for trends analysis (Appendix: Figure A1), with some data records extending to before the year 1900. Discharge records for sites downstream of Swan Hill are less complete and particularly for South Australian sites where only four (4) sites have available data. A striking absence in the discharge record is the River Murray at Merbein (Class 2 WQ monitoring site); for the purpose of calculating loads at this site, discharge data from the River Murray at Colignan has been used.

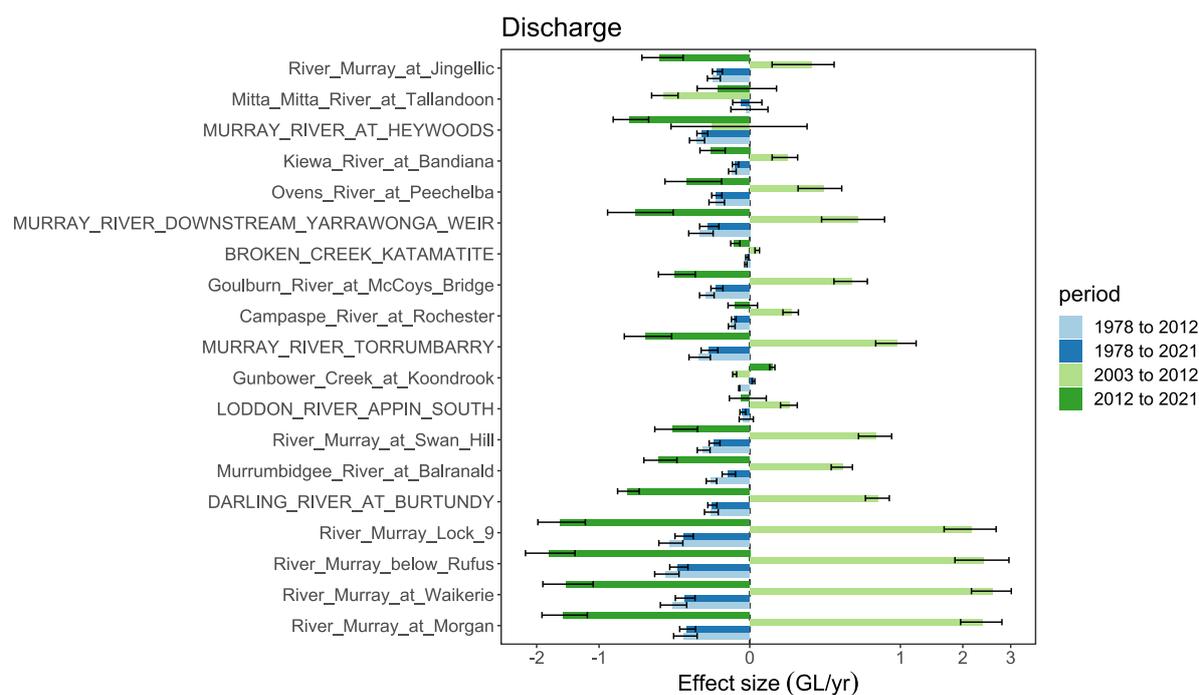


Figure 9. Linear trend component derived from a general linear model (GLM) for changes in discharge at River Murray and tributary sites, plotted as effect size (GL/yr). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.

Generalised additive models (GAMs) for discharge at the selected sites are shown in Figure C1. Over the full data period analysed here (1978 – 2021) a clear decreasing trend in discharge (range: 500 – 2000 ML/yr) is observed at all sites (except Gunbower Creek at Koondrook). The effect size is extremely similar between both long-term periods (1978 – 2012 and 1978 – 2021), representing the data periods analysed in this report and that analysed in the previous trends report (Henderson et al., 2013) (Figure 9). Again, the one exception to this consistency between data periods is the Gunbower Creek at Koondrook site where a decreasing discharge trend was observed for 1978 – 2012 and an increasing trend for 1978 – 2021. Over shorter data periods much larger effect sizes are observed, with a generally positive trend (range: 1500 – 2500 ML/yr) over the period 2003 – 2012 and negative trend (range: 1000 – 2500 ML/d/yr) over the period 2012 – 2021. The exceptions to this pattern are Mitta Mitta River at Tallandoon and Murray River at Heywoods (decreasing trends over both periods) and Gunbower Creek at Koondrook where the trends over the two periods were opposite to the majority of sites. Overall, the data show that discharge is decreasing at all sites (except Gunbower Creek at Koondrook).

Field pH

The pH of surface waters is critical parameter for a range of biotic and abiotic processes, controlling the partitioning of nutrients and contaminants between water and solid phases as well as influencing physiological processes in aquatic biota. Flowing surface waters (lotic systems) would typically experience pH in the range 6 – 8 (Boulton et al., 2014), with excursions outside this range possibly indicating environmental disturbance (e.g., algal blooms, acid-sulphate soils, bushfire run-off etc).

Field pH is measured at most (24/25) of the sites selected for trends analysis, with the data record extending from 1978 (pre 1970 for some South Australian sites; Figure A2). Data resolution across the data record is generally high (1 – 2 decimal places; Figure B2). Generalised additive models (GAMs) for field pH at the selected sites are shown in Figure C2 along with ANZG upper and lower pH limits, according to position in the catchment. In general, the measured (field) pH is within the ANZG limits, with periods of more acidic conditions in some upper Murray and upper tributary sites as well as periods of more alkaline (basic) conditions in lower Murray and Darling River sites.

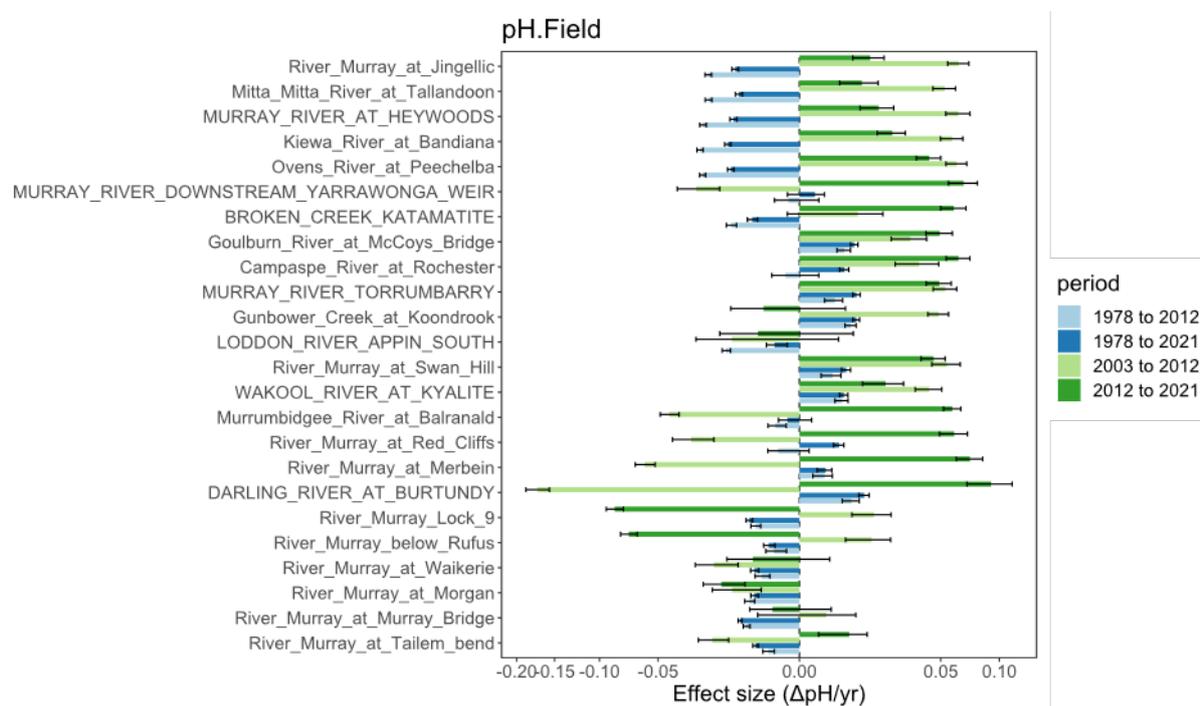


Figure 10. Linear trend component derived from a general linear model (GLM) for changes in pH at River Murray and tributary sites, plotted as effect size ($\Delta\text{pH}/\text{yr}$). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.

Changes in field pH over the full data period (1978 – 2021) are extremely small (<0.02 pH units/year), with the largest effect sizes observed in the upper River Murray and tributary sites where a decreasing trend is observed (Figure 10). Changes observed over the time period 1978 – 2012, corresponding to the previous trends analysis (Henderson et al., 2013) are broadly very similar to that observed for the full data record. Much larger effect sizes are observed for the shorter 9-year periods (2003 – 2012 and 2012 – 2021), with the majority of sites showing a positive trend over both time periods. Exceptions to this are some lower River Murray and tributary sites where a negative trend is observed over 2003 – 2012 and a positive trend over 2012 – 2021. Two lower Murray sites (River Murray at Lock 9, River Murray below Rufus) show distinctly different behaviour, with very little change over 2003 – 2012 and a strongly negative trend over 2012 – 2021.

Water temperature

The water temperature is a key physical parameter in aquatic systems, controlling abiotic and biotic (biochemical) rates, with higher rates at higher temperatures. Water temperature also controls the chemical equilibrium of physical processes, including gas exchange with atmosphere (e.g., oxygen solubility in water). Water temperature is largely controlled through heat exchange with the atmosphere and varies both diurnally as well as seasonally.

The water temperature data record for River Murray and tributary sites is near-complete (23/25) for the period 1978 – 2021, with the largest gaps for sites below Merbein (River Murray below Lock 9; Lake Victoria outlet; River Murray below Rufus River; River Murray at Waikerie) (Figure A3). A significant data gap is also present for Loddon River at Appin South; this site is not the standard MDBA site for this tributary (Loddon River at Kerang) but as noted previously, is used here as there is some uncertainty about whether the Kerang site is a 'pool' site. Data resolution for water temperature is typically 1-2 decimal places although lower resolution data is reported for lower Murray sites in South Australia (Figure B3). Generalised additive models (GAMs) for water temperature at the selected sites are shown in Figure C3.

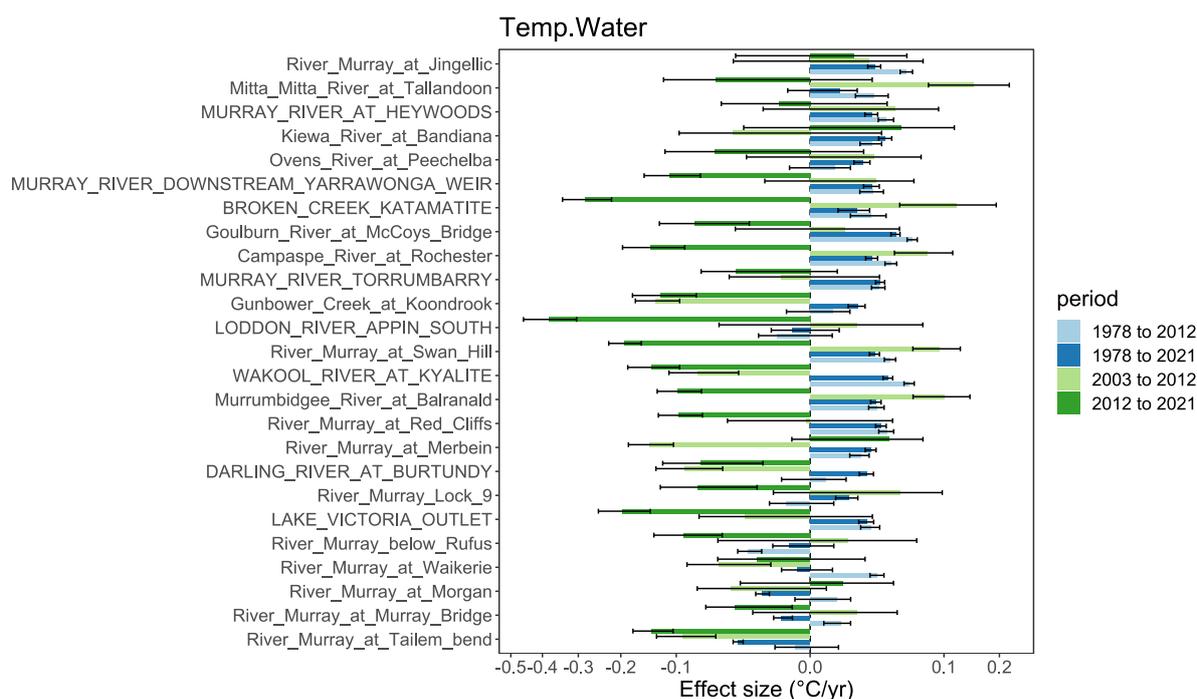


Figure 11. Linear trend component derived from a general linear model (GLM) for changes in water temperature at River Murray and tributary sites, plotted as effect size ($^{\circ}\text{C}/\text{yr}$). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.

Over the full data period (1978 – 2021) a general increase in water temperature is observed at all sites upstream of Waikerie; larger increases are generally observed at the upstream and tributary sites (Figure 11). The magnitude of the temperature increase is generally less than $0.05\text{ }^{\circ}\text{C}/\text{yr}$. Also shown in Figure 11 are trends in water temperature over the period 1978 – 2012 (matching the time period used in the previous trends report (Henderson et al., 2013)), with generally very similar values at all sites to that observed over the full data record. The two 9-year periods (2003 – 2012 and 2012 – 2021) show a common pattern across a number of water quality parameters, with a strong reversal in trend over these two periods, in this case manifested as a warming trend across most sites over the period 2003 - 2012 and a cooling trend over the past 9 years (2012 - 2021). Several sites (Gunbower Creek at Koondrook, Wakool River at Kyalite, Darling River at Burtundy, River Murray at Tailem Bend) show cooling trends over both 9-year periods. Overall, the data show a general warming trend in line with that expected with global climate trends. Comparison over different time periods show that much larger rates of change in water temperature can occur over short time scales compared to that observed over the entire 43-year data period.

Dissolved Oxygen

Dissolved oxygen (DO) in aquatic systems is essential for respiration by aquatic biota and for maintaining oxidizing redox conditions. Concentrations of DO are largely controlled by exchange with atmospheric oxygen, with a natural tendency towards equilibration. The equilibrium concentration of DO is dependent on water temperature, with lower concentrations of DO at higher water temperatures (Stumm and Morgan, 1981). Deviations from atmospheric equilibration typically occur in response to events where oxygen consumption or production processes occur faster than the rates of exchange with the atmosphere (e.g., blackwater events, algal blooms).

The data record for DO is highly fragmented at all sites, with extended periods of no data (Figure A4). A notable exception is Broken Creek at Katamatite with a near-continuous data record. Perhaps more surprising is the absence of any data at sites downstream of River Murray below Rufus River (i.e., nearly all SA sites). Due to the absence of a complete data record for DO there is a strong reliance on imputed data for the missing data periods in the calculation of trend values. Data resolution for the available data is generally high (1 – 2 decimal places; Figure B4). Generalised additive models (GAMs) for DO concentrations at the selected sites are shown in Figure C4.

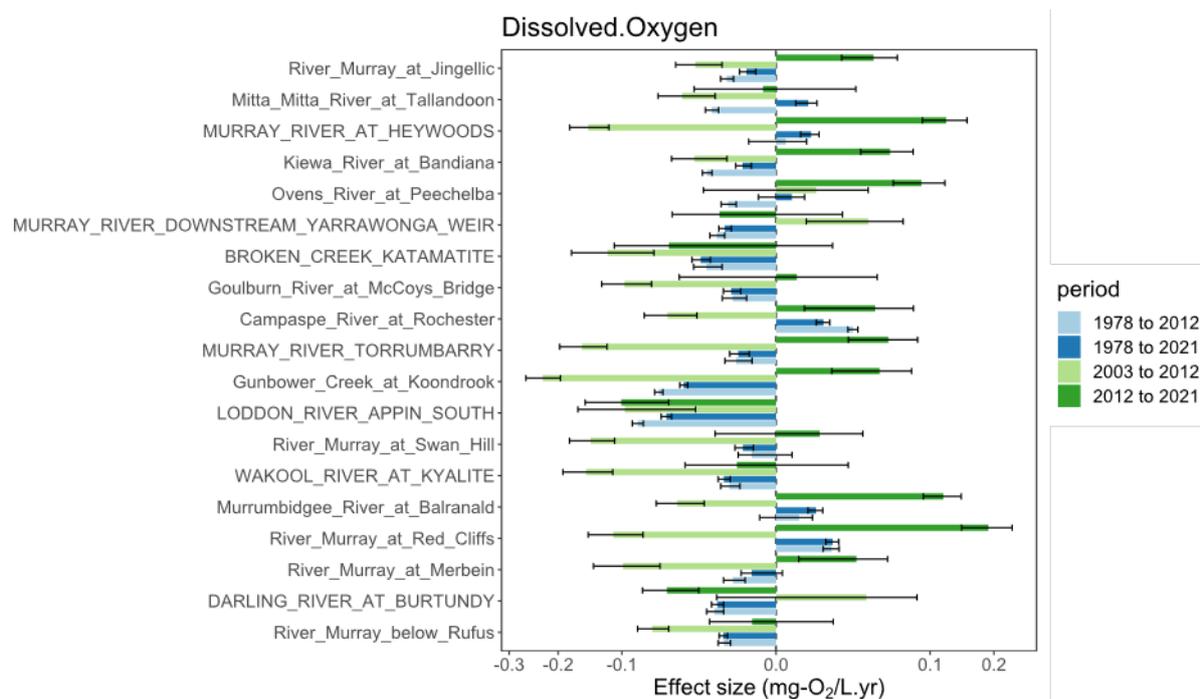


Figure 12. Linear trend component derived from a general linear model (GLM) for changes in dissolved oxygen concentrations at River Murray and tributary sites, plotted as effect size ($\text{mg-O}_2/\text{L.yr}$). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.

Trends in DO concentrations over the two longer periods (1978 – 2012 and 1978 – 2021) are very similar for each of the sites, and with the majority of sites showing a weak decrease in DO concentration (generally less than $-0.05 \text{ mg-O}_2/\text{L.yr}$) (Figure 12). Exceptions to this decreasing trend are the Campaspe at Rochester and the River Murray at Red Cliffs. Substantially larger decreasing trend values are observed at Gunbower Creek at Koondrook and Loddon River at Appin South. Much larger effect sizes are observed for the shorter time periods (2003 – 2012 and 2012 – 2021) and showing a common pattern across all sites with a strongly decreasing (negative) trend during the period 2003 - 2012 and strongly increasing (positive) trend during the period 2012 - 2021. These alternating trends can be directly related to the stronger increasing trend in water temperatures over the 2003 - 2012 period and decreasing water temperatures over the 2012 - 2021 period, noting the approximately inverse relationship between water temperature and equilibrium DO concentrations.

The overall trend pattern for DO in the River Murray and tributaries is decreasing concentrations of dissolved oxygen, commensurate with the long-term trend of increasing water temperatures. These trends are however small, keeping in mind that the sensitivity of DO concentrations to water temperature decreases with increasing temperature.

Electrical conductivity at 25 °C

The electrical conductivity (EC) is a general measure of ionic (salt) concentrations in water and broadly reflects the movement of salts from the landscape to aquatic systems (Berner and Berner, 2012). While the EC provides no specific information about the dominant ions (water type) it is an extremely important parameter for assessing the utility of the particular water resource for various human uses (e.g., irrigation, potable water supply).

The data record for EC is largely complete (25/25) for the sites selected in this trends study for the 1978 – 2021 data period, but with significant gaps for Loddon River at Appin South, River Murray at Lock 9 and Lake Victoria Outlet (Figure A5). Data resolution for EC is generally very uniform across the data record at 0 – 1 decimal places; exceptions include Murrumbidgee at Balranald where the reported precision is higher (2 – 3 decimal places; Figure B5).

Generalised additive models (GAMs) for EC (25 °C) at the selected sites are shown in Figure C5 along with ANZG upper and lower EC trigger values, set according to position in the catchment. Specific target values for River

Murray sites are also shown, where these exist (lower Murray sites only). Over full data record (1978 – 2021) the EC has generally been below the upper trigger value at nearly all sites, approaching the lower EC limit over the past 10 years. The only site to consistently exceed the upper EC limit is the Darling River at Burtundy, likely corresponding to low flow periods. Over the past 10 years, none of the specific River Murray EC target values have been exceeded at the sites where these targets exist.

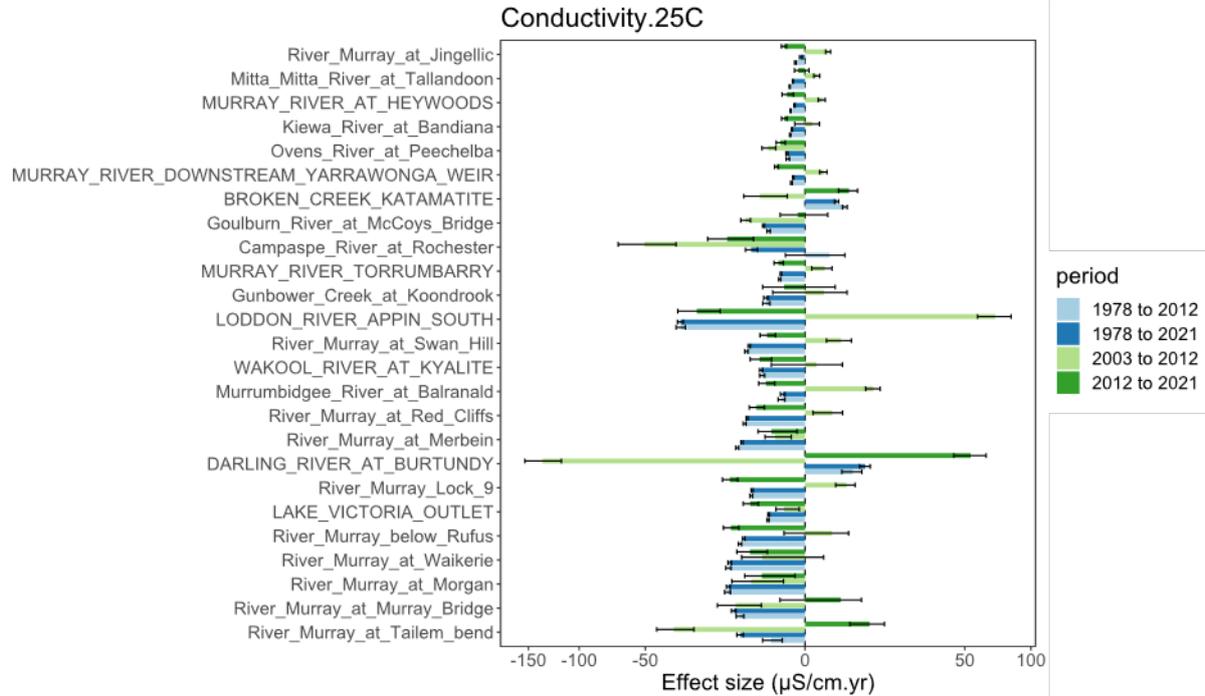


Figure 13. Linear trend component derived from a general linear model (GLM) for changes in electrical conductivity at River Murray and tributary sites, plotted as effect size ($\mu\text{S}/\text{cm.yr}$). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.

Over the full data period (1978 – 2021) there is a decreasing (negative) trend in EC for all River Murray sites and most tributaries; very similar trend values are observed over both the 1978 – 2012 and 1978 – 2021 time periods for all sites (Figure 13). The only sites to show an increasing (positive) trend are Broken Creek at Katamatite and Darling River at Burtundy. In general, the magnitude of the effect size increases downstream, with only small trend values for all sites upstream of Yarrowonga weir and substantially higher (and increasing) trend values for all sites downstream of Yarrowonga. Changes over shorter time periods (2003 – 2012 and 2012 – 2021) are more variable amongst the sites, with some sites showing similar direction trends over both periods (majority decreasing) and others showing reversal of trend direction. Examples of the latter include Loddon at Appin South where EC increased over the period 2003 – 2012 and decreased over the period 2012 – 2021, while the reverse was observed at Darling River at Burtundy, River Murray at Murray Bridge and River Murray at Tailem Bend.

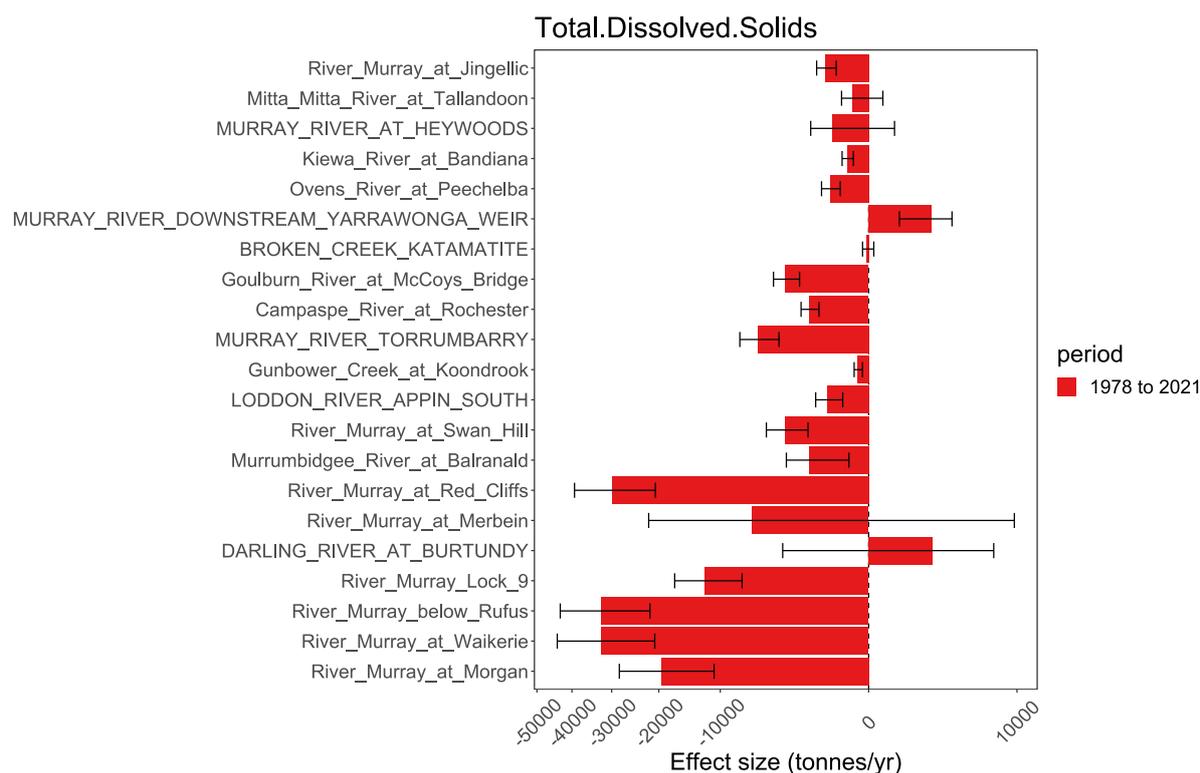


Figure 14. Linear trend component derived from a general linear model (GLM) for changes in TDS loads at River Murray and tributary sites, plotted as effect size (tonnes/yr), for the period 1978 – 2021. Note non-linear (square-root) x-scale.

The majority of sites show a decreasing trend in total dissolved solids (TDS; calculated from EC data) loads over the full data period (1978 – 2021), consistent with the decreasing trend in both discharge and EC over this same period (Figure 14). The magnitude of the TDS load trend changes markedly, from ~ -5000 tonnes/yr at River Murray at Jingellic to as high as ~ -40,000 tonnes/yr at River Murray at Waikerie.

Turbidity

Turbidity is a proxy measurement of suspended solid (particulate) concentrations in water, largely associated with mineral and organic particles mobilised from the landscape or resuspended from the riverbed. While the measurement of turbidity provides no specific information about the types of particles present, it is a valuable parameter in assessing the downstream movement of materials and the treatment of the water resource for potable water supply. In the ecological sense, turbidity provides important information around the transmission of light for primary production and increased sediment loads can also have direct effects on aquatic biota. As shown above there is a strong correlation of total phosphorus with turbidity, reflecting the strong association of phosphorus with particulate materials.

The data record for the 1978 – 2021 data period is largely complete (25/25) for sites selected in this trends analysis. Notable exceptions include the Loddon River at Appin South, River Murray at Lock 9 and Lake Victoria Outlet (Figure A6). Data resolution (Figure B6) shows a general pattern of higher resolution measurements (1 – 2 decimal places) at upper Murray and tributaries and lower resolution measurement (0 – 1 decimal places) at lower Murray sites. These differences likely reflect the much lower turbidity values generally observed at upper Murray sites compared to lower Murray sites (order of magnitude difference; see Figure 15).

Generalised additive models (GAMs) for turbidity at the selected sites are shown in Figure C6 along with ANZG upper and lower trigger values, set according to position in the catchment. For upper and mid-Murray sites (as well as upper tributary sites) the turbidity is generally below the upper trigger level, but with short-term elevated levels that are likely associated with high flow events. The majority of lower Murray sites (below the confluence with the Darling River), as well as Darling River at Burtundy site, are frequently above the upper trigger value.

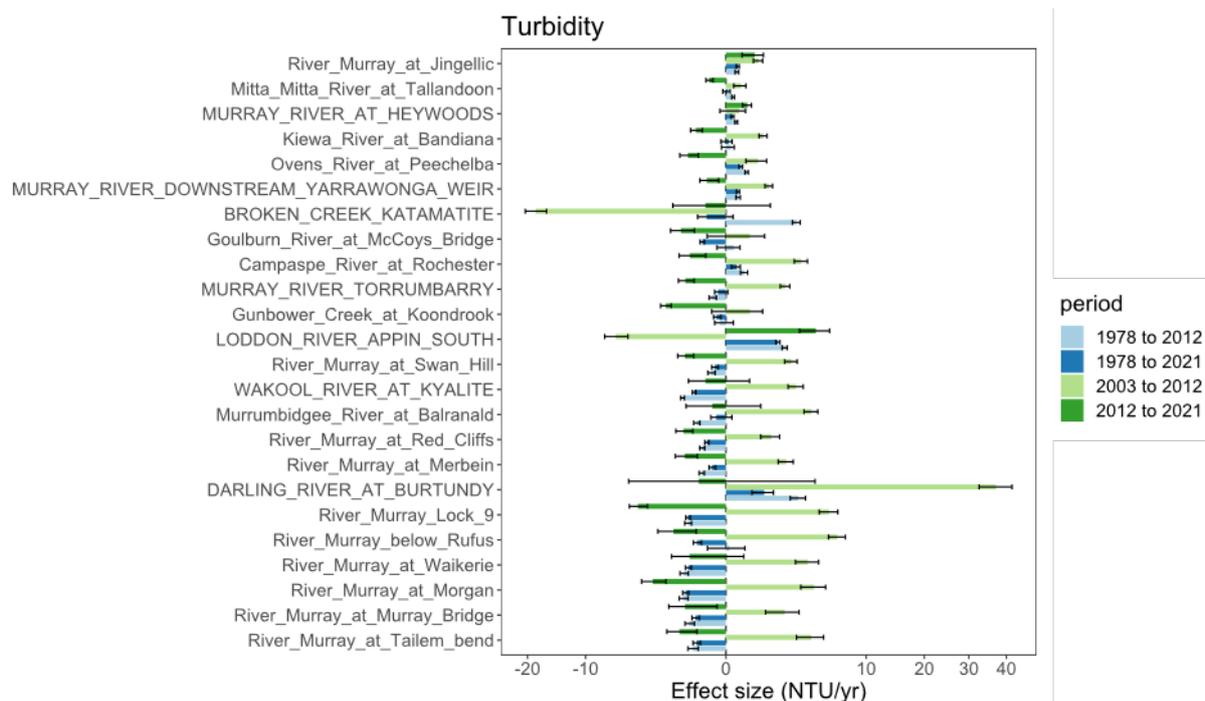


Figure 15. Linear trend component derived from a general linear model (GLM) for changes in turbidity at River Murray and tributary sites, plotted as effect size (NTU/yr). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.

The majority of sites show a decreasing (negative) trend in turbidity over the full data period (1978 – 2021); in general, the majority of sites also show very similar trend values over the reduced time period (1978 – 2012) (Figure 15). The only exception to this similarity between data periods is Broken Creek at Katamatite which showed an increasing trend over the period 1978 – 2012 and a weak decreasing trend over the period 1978 – 2021. Two sites (Loddon River at Appin South and Darling River at Burtundy) show positive trend values over both long term periods. In general, the magnitude of the effect size increases from upstream to downstream sites, but are all less than -5 NTU/yr. Over the shorter nine-year periods a strong reversal pattern is apparent for nearly all sites, with increasing (positive) trend values for the 2003 – 2012 period and decreasing (negative) trend values for the 2012 - 2021 period.

Alkalinity

Alkalinity is a measure of the (pH) buffering capacity of water and is important in understanding the resilience of a water body to ecological and environmental disturbances. The alkalinity of water is also important in assessing treatment requirements in the production of potable water. Alkalinity is generated in the catchment through rock weathering and also as part of biogeochemical cycling processes.

Alkalinity values are available for the majority of the sites selected for this trends analysis (20/25) but with a reduced period of data coverage (Figure A7). For the majority of sites upstream of Merbein, alkalinity measurements cease at 2005, although reporting of this parameter recommenced at some of these sites in 2018 - 2019. There is good data availability for some sites downstream of Merbein, with near complete data coverage at Darling at Burtundy and River Murray at Morgan sites. Data resolution is generally uniform across sites and data periods (2 decimal places; Figure B7), but with surprisingly much higher resolution data (6 decimal places) reported for some sites (Murray River d/s Yarrawonga, Murrumbidgee at Balranald, River Murray at Merbein and Darling River at Burtundy). Generalised additive models (GAMs) for alkalinity concentrations at the selected sites are shown in Figure C7; there are no associated ANZG trigger levels for this parameter.

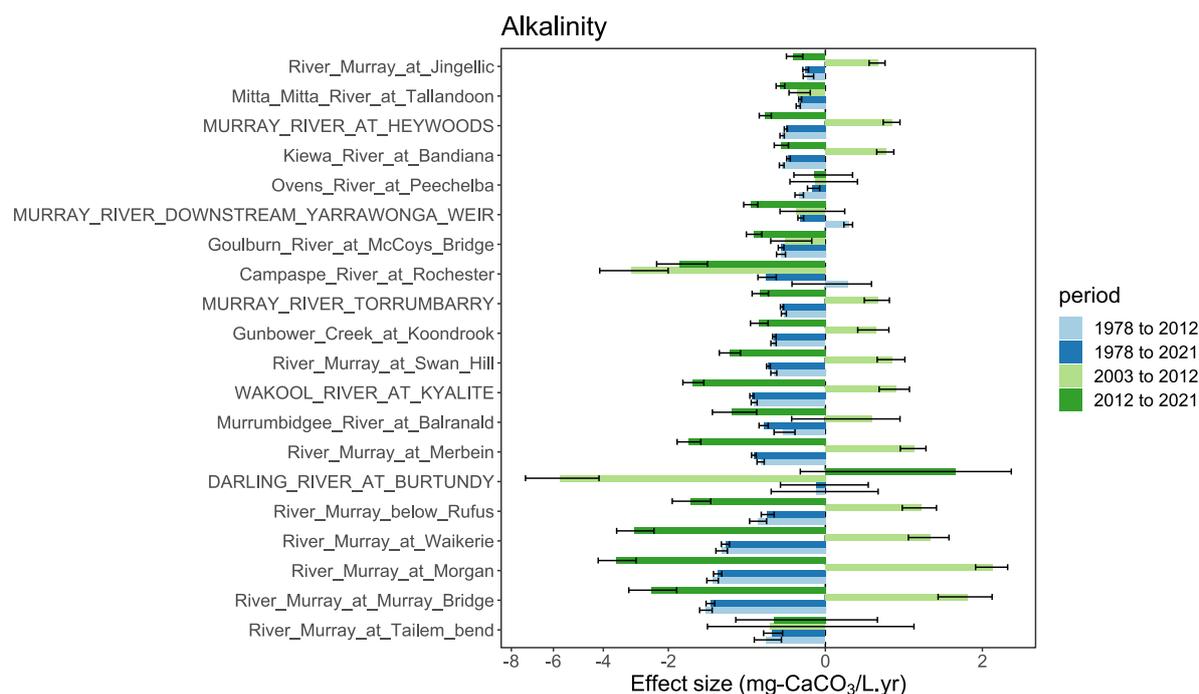


Figure 16. Linear trend component derived from a general linear model (GLM) for changes in alkalinity at River Murray and tributary sites, plotted as effect size ($\text{mg-CaCO}_3/\text{L.yr}$). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.

All sites show a decreasing (negative) trend over the longer-term data periods (1978 – 2012 and 1978 – 2021), with very similar values over both data periods (Figure 16). Long-term changes in alkalinity are extremely small in the upper Murray and tributary sites, increasing down-stream to approx. $-1.5 \text{ mg-CaCO}_3/\text{L.yr}$ at the lower Murray sites (with the exception of River Murray at Tailem Bend where the effect size is much smaller). Over the shorter nine-year periods a strong reversal of trend behaviour is observed, with the majority of sites showing an increasing trend over the 2003 – 2012 period and a decreasing trend over the 2012 – 2021 period. Notable exceptions to this pattern are the Campaspe at Rochester where a decreasing trend was observed over both time periods and the Darling River at Burtundy where the trend directions were opposite to River Murray sites.

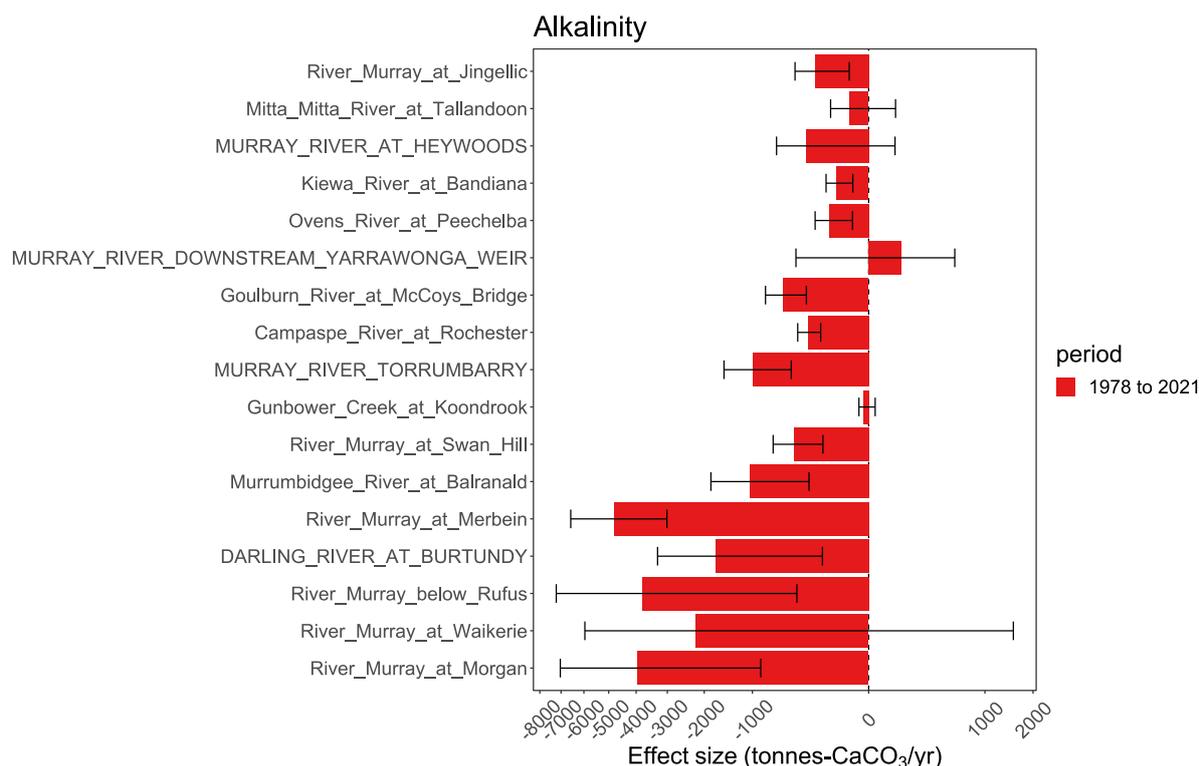


Figure 17. Linear trend component derived from a general linear model (GLM) for changes in alkalinity loads at River Murray and tributary sites, plotted as effect size (tonnes-CaCO₃/yr), for the period 1978 – 2021. Note non-linear (square-root) x-scale.

The majority of sites show a decreasing trend in alkalinity loads over the full data period (1978 – 2021), consistent with the decreasing trend in both discharge and alkalinity concentrations over this same period (Figure 17).

Dissolved Organic Carbon (DOC)

Dissolved organic carbon (DOC) is a measure of the concentration of carbon bound in dissolved organic matter (also containing organically-bound N, P, S etc). DOC plays a part in many abiotic and biotic processes and is an energy source for microbial processes in aquatic systems and supplied from both terrestrial (allochthonous) and in-stream (autochthonous) processes. Additional anthropogenic sources of DOC are urban stormwater and the treated effluent from wastewater treatment plants. Naturally high concentrations of DOC can occur as a result of floodplain-river exchange, and under extreme conditions can lead to O₂ drawdown (hypoxic blackwater).

There is a high coverage of DOC data for the sites selected in this trends analysis (21/25), with the data commencing from 1980 – 1996 across all sites (Figure A8). Notable gaps in the data are present at River Murray d/s Yarrowonga weir, Murrumbidgee at Balranald and several of the lower Murray sites in South Australia. Data resolution is highly variable across the sites, with low resolution data (0 decimal places) recorded for most of the upper Murray and tributary sites until 2015, switching to higher resolution data after this time (Figure B8). The most recent data (post-2018) for Wakool River at Kyalite, River Murray at Merbein and Darling River at Burtundy are also low resolution. Given that DOC concentrations in the River Murray and tributaries are typically low (<10 mg-C/L), the collection of low resolution data is highly problematic in the analysis of these data. Generalised additive models (GAMs) for DOC concentrations at the selected sites are shown in Figure C8; there are no associated ANZG trigger levels for this parameter.

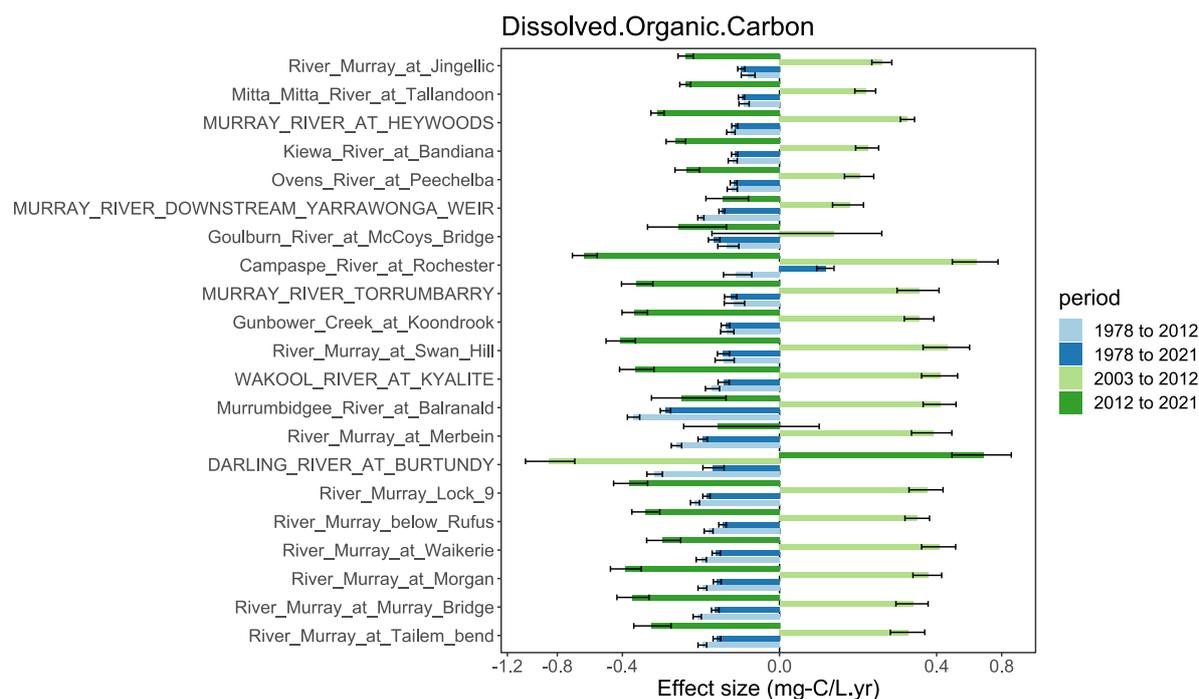


Figure 18. Linear trend component derived from a general linear model (GLM) for changes in dissolved organic carbon (DOC) concentrations at River Murray and tributary sites, plotted as effect size (mg-C/L.yr). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.

All sites show a decreasing trend in DOC concentration over the full data period (1978 – 2021), with very similar effect sizes over the reduced data period (1978 – 2012) (Figure 18). In general the trend values are less than -0.1 mg-C/L.yr, with larger effect sizes observed for more downstream sites. Substantially larger trend values are observed for the shorter nine-year data periods, with an increasing (positive) trend over the period 2003 – 2012 and decreasing (negative) trend over the period 2012 – 2021, for nearly all sites. The one exception to this pattern is the Darling River at Burtundy which shows the opposite behaviour.

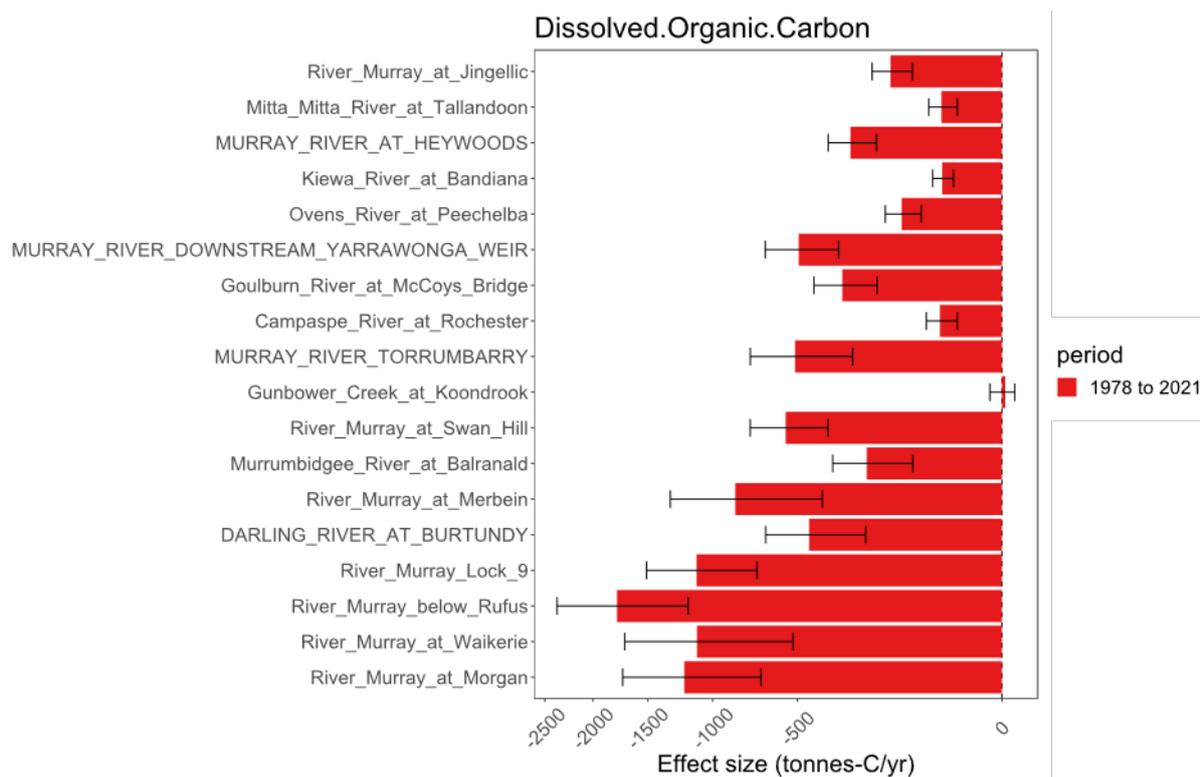


Figure 19. Linear trend component derived from a general linear model (GLM) for changes in DOC loads at River Murray and tributary sites, plotted as effect size (tonnes-C/yr), for the period 1978 – 2021. Note non-linear (square-root) x-scale.

DOC loads show a decreasing trend at nearly all sites over the period 1978 - 2021, consistent with the decreasing trends in both discharge and DOC concentrations over this period. The magnitude of the effect size is quite similar between upper and lower Murray sites, increasing from ~ 250 tonnes/yr (River Murray at Jingellic) to ~2000 tonnes/yr (River Murray below Rufus).

Total Kjeldahl Nitrogen (TKN)

Total Kjeldahl nitrogen (TKN) is a measure of reduced nitrogen compounds (ammonium + organically-bound N). Under most surface water conditions (i.e., unpolluted) concentrations of ammonium will be extremely low, with result that TKN approximates to a measure of dissolved organic nitrogen (DON). Given that DON forms part of dissolved organic matter, the origin and sources of DON largely mirror that for DOC (see above). In many aquatic systems DON represents the largest pool of dissolved nitrogen and may be an important source of N for in-stream processes (Harris et al., 2018).

There is good coverage of TKN data across the sites selected for the trends analysis (23/25) with the data record commencing pre-1980 for most sites (Figure A9). Notable gaps in the data record are evident at several sites for the period 1991 – 2005 (Murray River d/s Yarrowonga, River Murray at Merbein, Darling River at Burtundy) as well as after 2000 for some South Australian sites (River Murray below Rufus, River Murray at Waikerie). Data resolution is generally high (2 – 3 decimal places) but with some lower resolution data collected prior to 1996 at upper Murray and tributary sites (Figure B9).

Generalised additive models (GAMs) for TKN at the selected sites are shown in Figure C9 along with ANZG total nitrogen (TN) trigger values, set according to position in the catchment. For all sites the levels of TKN are close to the TN trigger values, with several of the mid-Murray and associated tributaries consistently above the trigger values.

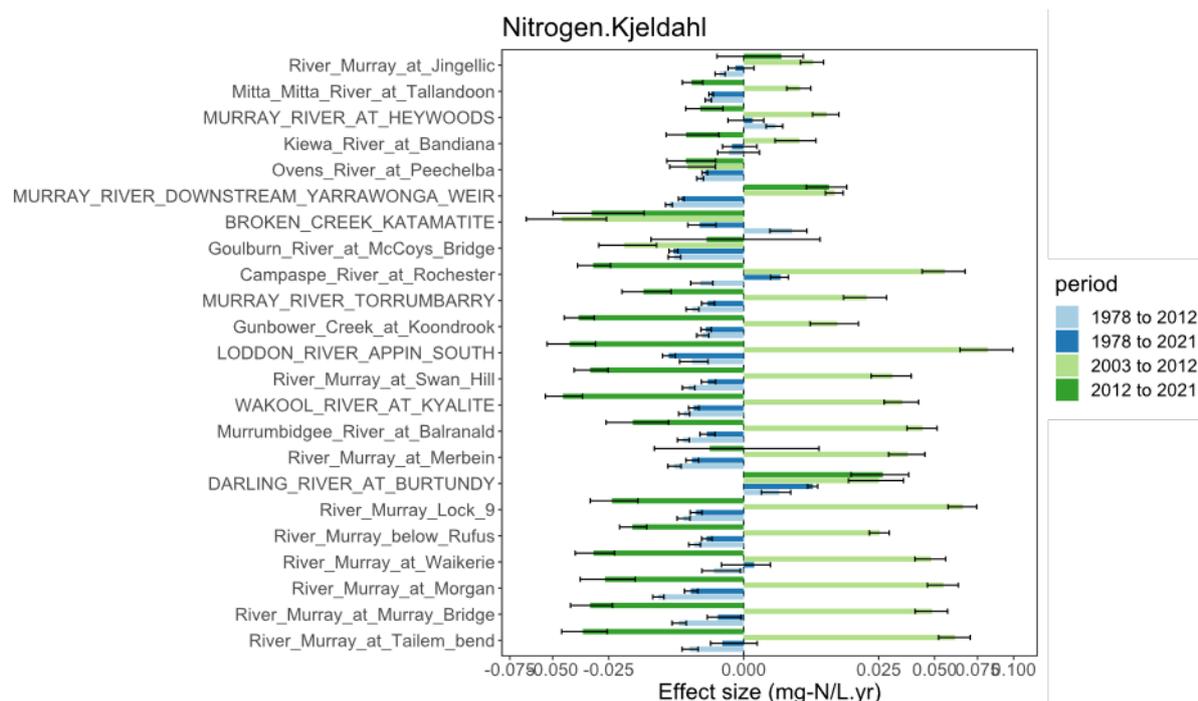


Figure 20. Linear trend component derived from a general linear model (GLM) for changes in total Kjeldahl nitrogen (TKN) concentrations at River Murray and tributary sites, plotted as effect size (mg-N/L.yr). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.

Nearly all sites show a (weak) decreasing trend in TKN over the full data period (1978 – 2021), with very similar effect sizes over the shorter data period (1978 – 2012) (Figure 19). The only site to show an increasing trend over these data periods is the Darling at Burtundy. Across all sites the magnitude of the effect size is less than 0.01 mg-N/L.yr, with smaller effect sizes for upper Murray and upper tributary sites. As expected, there is a close correspondence in trend patterns between TKN and DOC (see previous), with TKN trend values approximately one-tenth that of that observed for DOC, consistent with typical C:N ratios for dissolved organic matter in the range 10:1 – 20:1. Much larger effect sizes are observed for the shorter nine-year data periods, with the majority of sites showing an increasing trend over the 2003 – 2012 data period and a decreasing trend over the 2012 – 2021 data period. Exceptions to this pattern are Broken Creek at Katamatite where a decreasing trend is observed over both time periods and Darling at Burtundy with increasing trends over both periods.

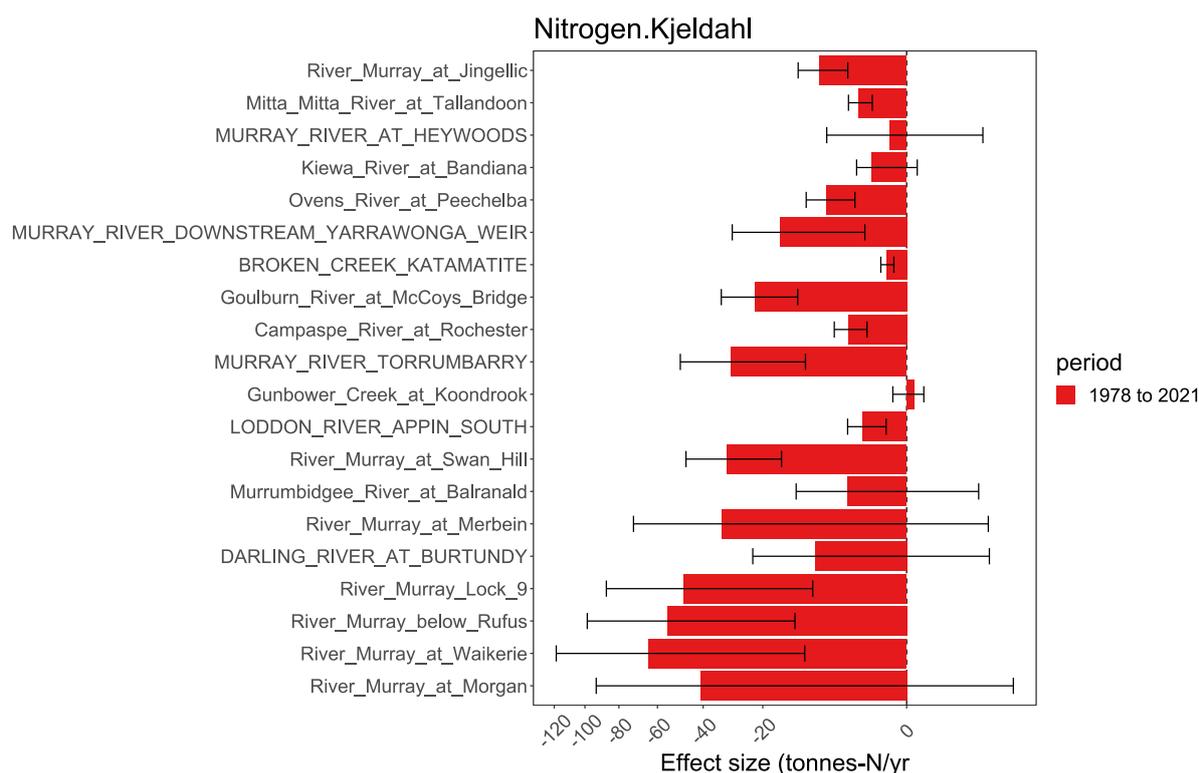


Figure 21. Linear trend component derived from a general linear model (GLM) for changes in TKN loads at River Murray and tributary sites, plotted as effect size (tonnes-N/yr), for the period 1978 – 2021. Note non-linear (square-root) x-scale.

TKN loads decrease at the majority of sites over the full data period (1978 – 2021), consistent with trend patterns in discharge and TKN concentrations (Figure 20). As observed for DOC loads, the magnitude of the size effect increases from upper Murray (~10 tonnes/yr for River Murray at Jingellic) to lower Murray (~60 tonnes/yr for River Murray at Waikerie) sites.

Nitrogen oxides (NO_x ; $\text{NO}_3^- + \text{NO}_2^-$)

Nitrogen oxides (NO_x), comprising nitrate (NO_3^-) and nitrite (NO_2^-), are bioavailable forms of nitrogen for in-stream and riparian productivity. NO_x species are formed through nitrification of organic matter and potentially lost to the atmosphere as N_2 gas through denitrification mechanisms. Sources of NO_x species include that formed through in-stream nitrification processes, nitrogen fixed from the atmosphere by some organisms (e.g., cyanobacteria) as well as NO_x species derived from terrestrial run off (Boulton et al., 2014).

The majority of the sites selected for the trends analysis (23/25) have some data reported for NO_x species (Figure A10). The data record for most sites commences after 1980, although some lower Murray (South Australian) sites extend from 1978. For a few sites (Murray River at Yarrowonga, River Murray at Merbein and Darling River at Burtundy) the data record commences much later (1995). Data resolution is generally high (and consistent) across all sites and time periods at 2 – 3 decimal places (Figure B10), keeping in mind that NO_x levels are typically very low (0.005 – 0.1 mg-N/L).

Generalised additive models (GAMs) for NO_x at the selected sites are shown in Figure C10 along with ANZG trigger values, set according to position in the catchment. For all upper Murray and associated tributaries the levels of NO_x species are well above the trigger values. Sites in the mid and lower-Murray (as well as the tributaries) tend to be close to the trigger values, but with peak levels well above the respective trigger values.

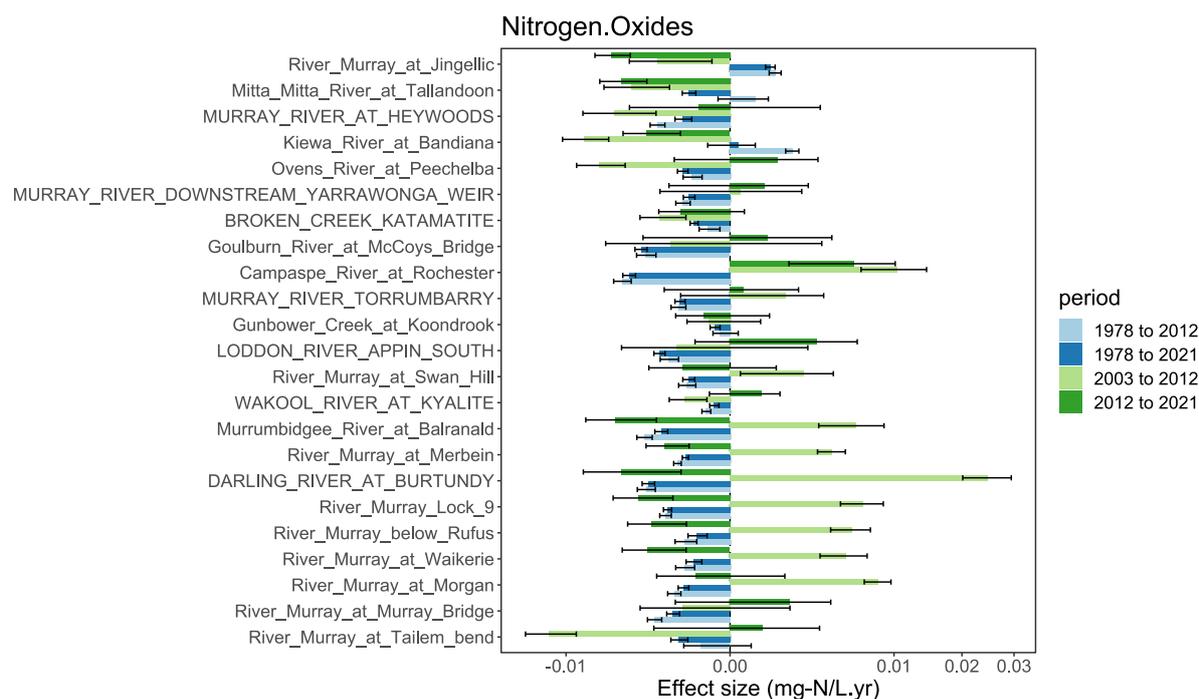


Figure 22. Linear trend component derived from a general linear model (GLM) for changes in nitrogen oxides (NO_x) concentrations at River Murray and tributary sites, plotted as effect size (mg-N/L.yr). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.

A weak decreasing (negative) trend is observed for the majority of sites across both long-term periods (1978 – 2012 and 1978 – 2021), with very close correspondence between these two data periods (Figure 21). The only exceptions to a decreasing trend are two upper Murray sites (River Murray at Jingellic and Kiewa at Bandiana) where a small increasing trend is observed. Overall, the magnitude of the effect sizes over the long term data periods are very small (typically smaller than -0.005 mg-N/L.yr). Larger effect sizes are observed for the shorter nine-year periods, although the directions of change vary between upper Murray and lower Murray sites. In general, upper Murray sites show a decreasing trend in NO_x species across both nine-year periods, while lower Murray (downstream of Merbein) generally show increasing NO_x concentrations over the 2003 – 2012 period and decreasing NO_x concentrations over the 2012 – 2021 period (with the exception of River Murray at Murray Bridge).

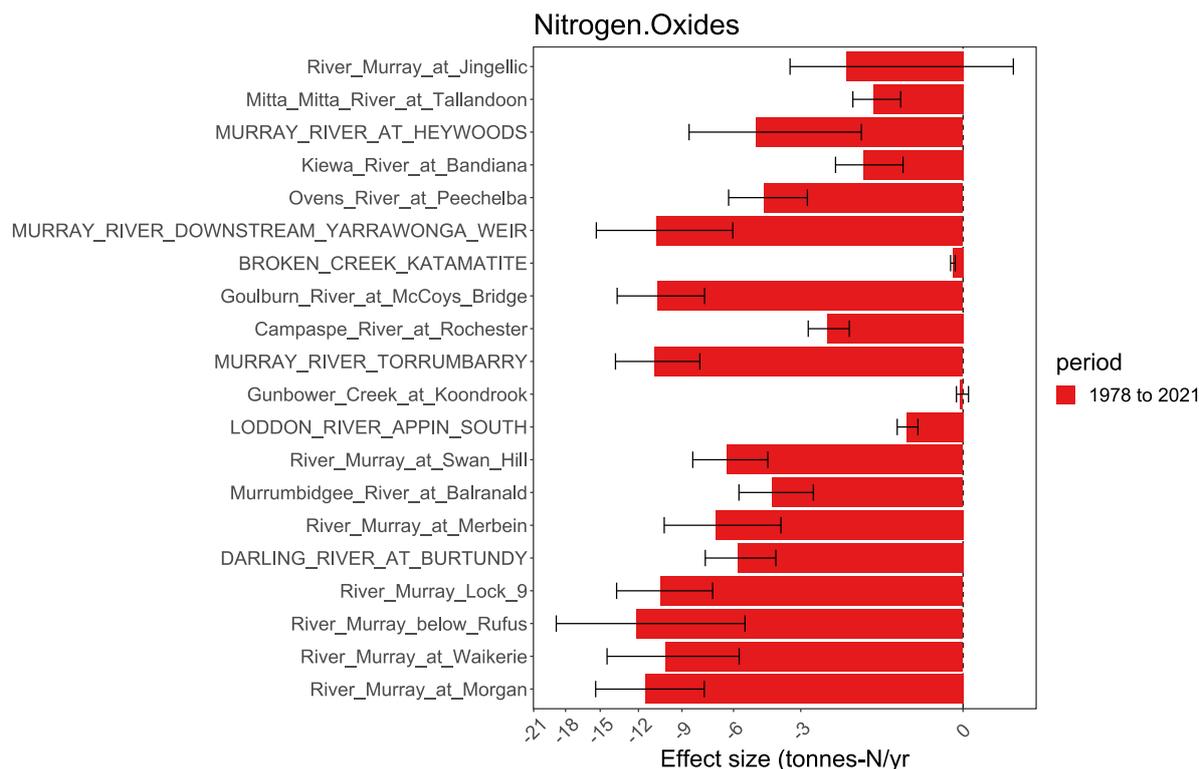


Figure 23. Linear trend component derived from a general linear model (GLM) for changes in NO_x loads at River Murray and tributary sites, plotted as effect size (tonnes-N/yr), for the period 1978 – 2021. Note non-linear (square-root) x-scale.

NO_x loads decrease at nearly all sites across the full data period (1978 – 2021), consistent with trend patterns in both discharge and NO_x concentrations (Figure 22). The magnitude of the size effect in River Murray sites is generally similar (range: 1 – 12 tonnes-N/yr); tributary sites are more variable with some sites showing effectively no change in NO_x loads over this period.

Total Phosphorus

The total phosphorus (TP) measurement includes all dissolved and particulate forms of phosphorus, in most cases dominated by dissolved phosphate ($\text{H}_n\text{PO}_4^{(3-n)}$) and polyphosphate ($\text{P}_x\text{O}_y^{n-}$) species as well as phosphorus species adsorbed on particle surfaces. The strong association of phosphorus with particles and particle surfaces is supported by the strong correlation between TP and turbidity across all sites (Figure 7). Sources of phosphorus include mineralisation of organic matter in aquatic decomposition processes and landscape run-off of particulate materials.

Total phosphorus data is available for the majority of sites used for the trends analysis (22/25), with most sites having data available from 1980 onwards; some lower Murray sites have data extending from 1973 (Figure A11). Significant data gaps are apparent for Murray River d/s Yarrowonga, Wakool River at Kyalite and sites between Merbein and Waikerie, with no data after 2013 and suggesting that this parameter is no longer measured at these sites. Data resolution is typically in the range 3 – 4 decimal places, although for all sites upstream of Swan Hill lower resolution data (1 – 2 decimal places) was collected prior to 2009 (Figure B11). TP measurements typically range between 0.01 – 0.1 mg-P/L (Figure C11).

Generalised additive models (GAMs) for TP at the selected sites are shown in Figure C11 along with ANZG trigger values, set according to position in the catchment. The majority of sites are close to (or slightly above) the TP trigger values, although levels at the Darling River at Burtundy site are well above the trigger values.

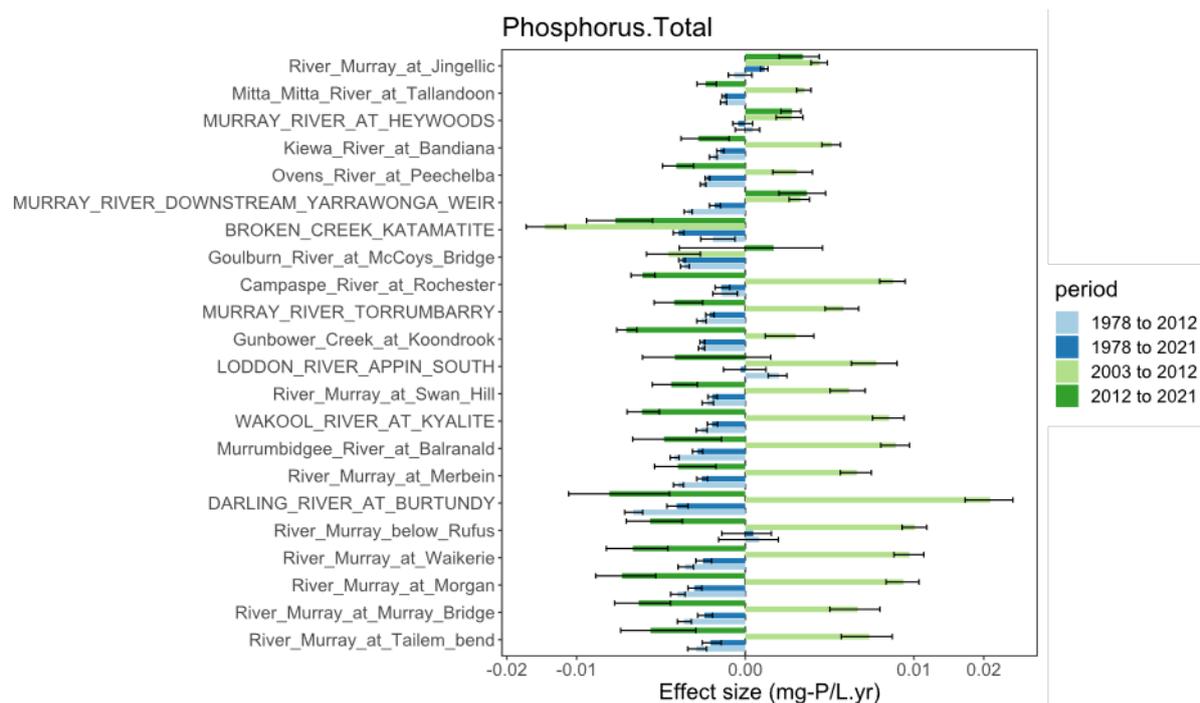


Figure 24. Linear trend component derived from a general linear model (GLM) for changes in total phosphorus (TP) concentrations at River Murray and tributary sites, plotted as effect size (mg-P/L.yr). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.

Total phosphorus concentrations show a decreasing trend (negative trend coefficient) at all sites and across both long-term data periods (1978 – 2012 and 1978 – 2021) (Figure 23). In general the effect size is extremely small (less than 0.002 mg-P/L.yr) but with slightly larger values (0.005 mg-P/L.yr) for Darling River at Burtundy. Across the shorter nine-year periods much larger effect sizes are observed and a common pattern of increasing TP concentrations over the 2003 – 2012 data period and decreasing TP concentrations over the 2012 – 2021 data period. The main exceptions to this reversal pattern are the Broken Creek at Katamatite site where TP decreases over both periods, and several of the upper Murray and upper tributary sites where extremely small effect sizes are observed.

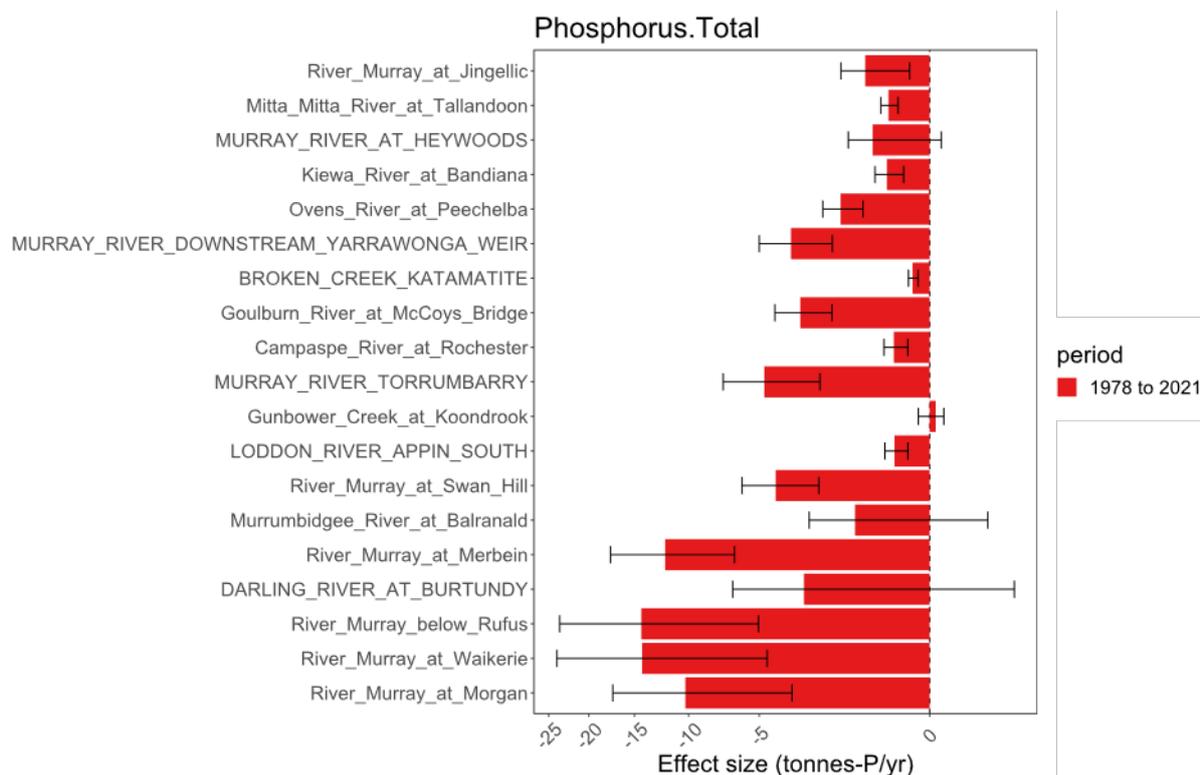


Figure 25. Linear trend component derived from a general linear model (GLM) for changes in TP loads at River Murray and tributary sites, plotted as effect size (tonnes-P/yr), for the period 1978 – 2021. Note non-linear (square-root) x-scale.

Total phosphorus loads decrease at nearly all sites over the 1978 – 2021 data period, consistent with the decrease in both discharge and TP concentrations over this same period (Figure 24). The magnitude of the size effect ranges from 0.5 – 15 tonnes/yr and increases from upstream to downstream sites.

Soluble Reactive phosphorus (SRP)

Soluble reactive phosphorus (SRP) is a measure of dissolved phosphate ($H_nPO_4^{(3-n)-}$), a bioavailable form of phosphorus for plant growth and in-stream productivity. SRP forms through the mineralisation of organic matter (i.e., decomposition) and is part of total phosphorus (TP) the sources of which are outlined in the previous section.

There is good data coverage for the majority of sites selected for the trends analysis (23/25), with the majority of sites having data from 1981 – 1983 onwards (Figure A12). As for other nutrient parameters, some South Australian sites have data available from 1978. Several data gaps are apparent in the data record, with at least four sites where SRP measurement appears to be discontinued (Murray River d/s Yarrowonga, Murrumbidgee at Balranald, River Murray below Rufus, River Murray at Waikerie). Data resolution is generally consistent across all sites and time periods at 3 – 4 decimal places, commensurate with the levels of SRP that are observed across all sites (range: 0.001 – 0.1 mg-P/L).

Generalised additive models (GAMs) for SRP at the selected sites are shown in Figure C12 along with ANZG trigger values, set according to position in the catchment. Upper Murray (and associated tributary) sites are generally below the SRP trigger values, while mid and lower Murray sites are closer (and slightly above) the trigger values. Concentrations of SRP at the Darling River at Burtundy site are well above the trigger value for this site.

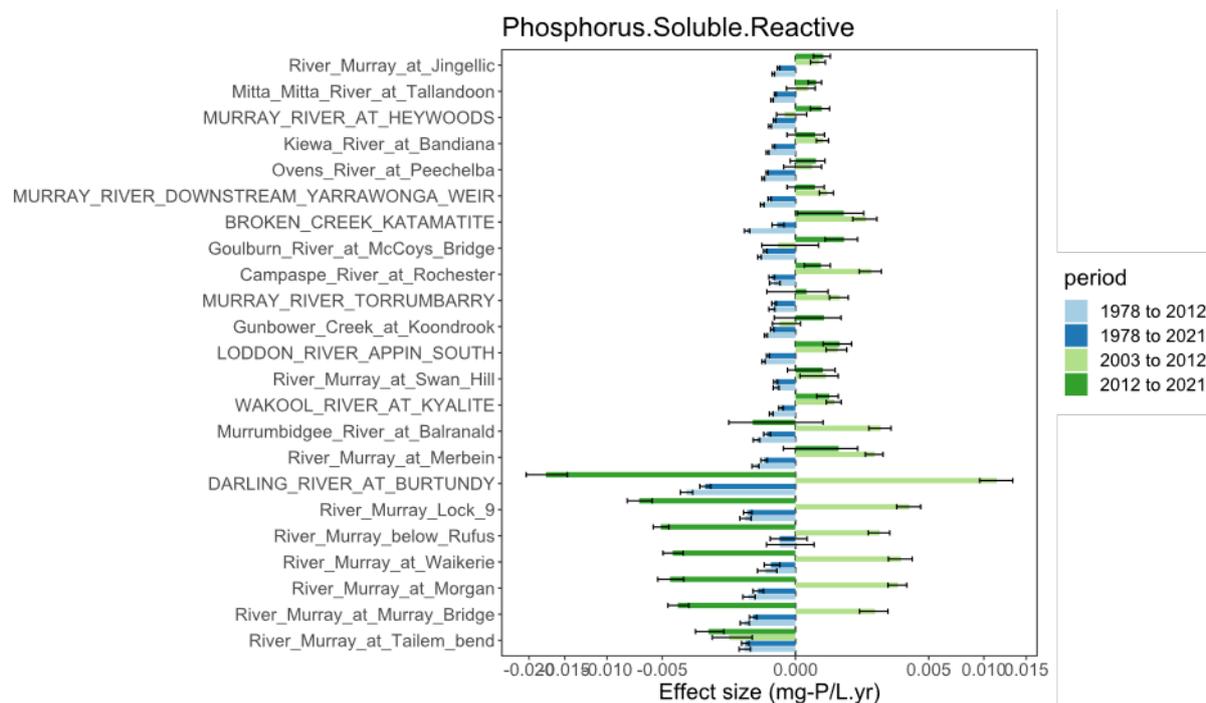


Figure 26. Linear trend component derived from a general linear model (GLM) for changes in soluble reactive phosphorus (SRP) concentrations at River Murray and tributary sites, plotted as effect size (mg-P/L.yr). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.

Extremely small changes are observed in SRP across all sites over the long-term data periods (1978 – 2012 and 1978 – 2021), and consistent with the very low concentrations of this parameter that are often close to method detection limits (Figure 25). For the majority of sites the trend is decreasing (negative) and less than 0.001 mg-P/L.yr. The largest effect size is observed for the Darling River at Burtundy at approx. -0.003 mg-P/L.yr. Over the shorter nine-year data periods much stronger effect sizes are observed for the Darling River at Burtundy and all River Murray sites below the Darling River confluence. For all of these sites SRP increased over the period 2003 – 2012 and decreased over the period 2012 – 2021.

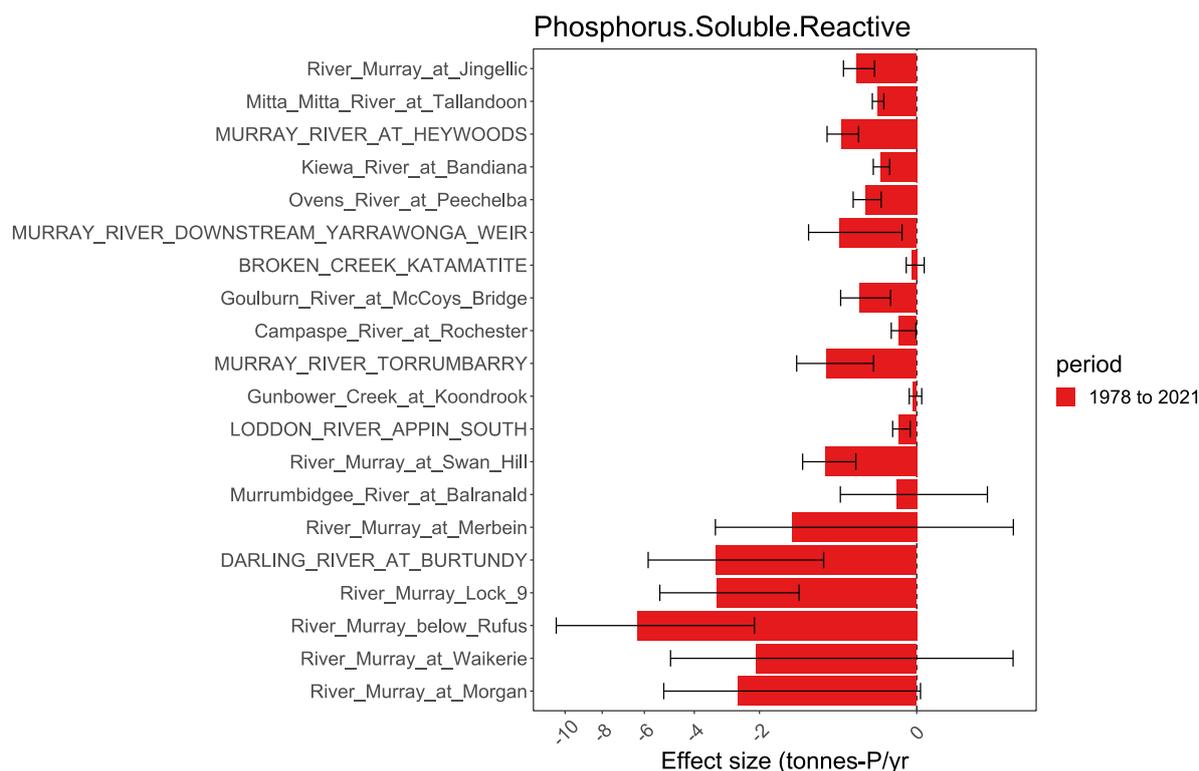


Figure 27. Linear trend component derived from a general linear model (GLM) for changes in SRP loads at River Murray and tributary sites, plotted as effect size (tonnes-P/yr), for the period 1978 – 2021. Note non-linear (square-root) x-scale.

Soluble reactive phosphorus loads decrease at all sites over the full data record (1978 – 2021), consistent with the observed decreasing trend in both discharge and SRP concentration across this time period (Figure 26). Annual changes in load range between 0 – 6 tonnes/yr, with a general trend of increasing size effect from upstream to downstream sites.

Dissolved Silicon

Dissolved silicon (in the form of SiO_2 ; silica) is an important nutrient for some organisms in aquatic environments, forming part of hard structures in diatoms and some invertebrates (Boulton et al., 2014). Silica is derived from the weathering and dissolution of quartz and silicate minerals, with an equilibrium concentration of $\sim 11 \text{ mg-SiO}_2/\text{L}$ (at 25°C ; native quartz) (Stumm and Morgan, 1981, Gunnarsson and Arnórsson, 2000). Environmental levels of silica are frequently lower, reflecting the slow dissolution and equilibration of silicate minerals and/or reservoir losses through deposition (Maavara et al., 2020).

There is good coverage of silica data for the sites selected in this trends analysis (21/25), with data commencing over the period 1980 – 1990 in the upper Murray sites and pre-1970 in the lower Murray (South Australian) sites (Figure A13). Reporting of this parameter has apparently been discontinued at some sites (Murrumbidgee at Balranald, River Murray below Rufus, River Murray at Waikerie). Data resolution is notably different between sites upstream of Merbein (2 – 3 decimal places) and lower Murray sites in South Australia (0 – 1 decimal places; Figure B13). Generalised additive models (GAMs) for silica at the selected sites are shown in Figure C13; there are no associated ANZG trigger levels for this parameter.

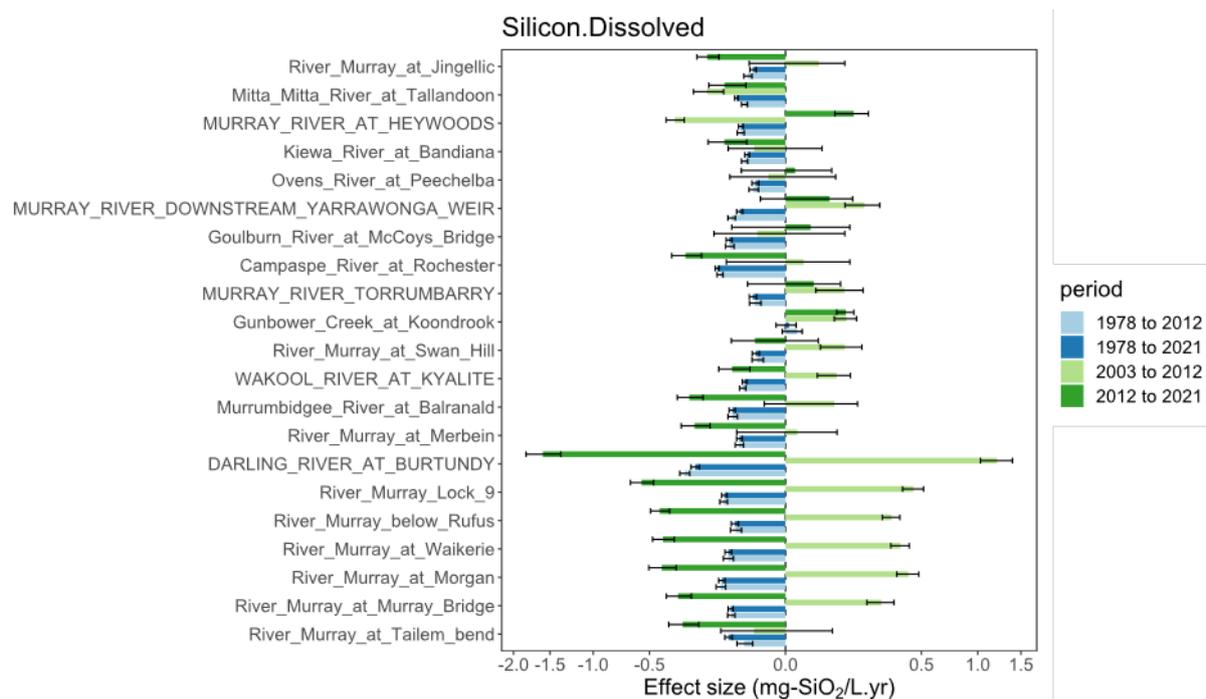


Figure 28. Linear trend component derived from a general linear model (GLM) for changes in dissolved silicon concentrations at River Murray and tributary sites, plotted as effect size (mg-SiO₂/L.yr). Shown are four time periods: (i) 1978 – 2012; (ii) 1978 – 2021; (iii) 2003 – 2012; (iv) 2012 – 2021.

A decreasing trend is observed at nearly all sites over the long-term data series (1978 – 2012 and 1978 – 2021), with generally very similar trend values obtained over both time periods (Figure 27). The magnitude of the size effect is generally small (smaller than -0.1 mg-SiO₂/L.yr) for most sites, particularly for the majority of upper Murray and upper tributary sites. Slightly higher magnitude trend values are observed for the Darling River at Burtundy (-0.3 mg-SiO₂/L.yr). Over the shorter nine-year timescales much larger trend values are observed, particularly for the Darling River at Burtundy and all River Murray sites below the Darling River confluence. For all of these sites there is a strong increasing trend in silica concentrations over the period 2003 – 2012 and a strong decreasing trend over the period 2012 – 2021.

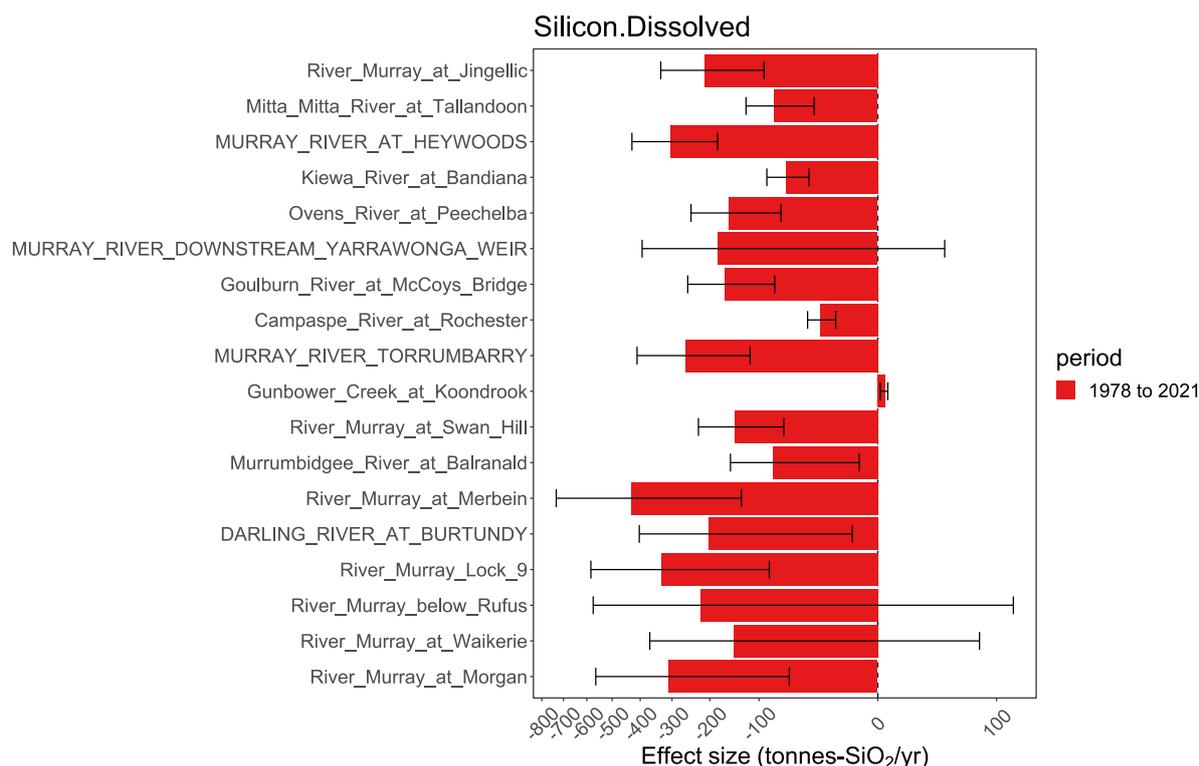


Figure 29. Linear trend component derived from a general linear model (GLM) for changes in silica loads at River Murray and tributary sites, plotted as effect size (tonnes-SiO₂/yr), for the period 1978 – 2021. Note non-linear (square-root) x-scale.

Dissolved silicon loads decrease at nearly all sites over the full data record (1978 – 2021), consistent with trends in both discharge and silica concentrations; note the very high uncertainty at some sites (Murray River d/s Yarrowonga, River Murray below Rufus, River Murray at Waikerie) (Figure 28). The magnitude of the effect size ranges between 50 – 500 tonnes/yr, with some of the higher trend values observed for upstream River Murray sites (River Murray at Heywoods, River Murray d/s Yarrowonga Weir).

GENERALISED LINEAR MIXED-MODEL (GLMM)

A generalised linear mixed model (GLMM) was constructed for each water quality parameter in order to determine if water quality in the River Murray and tributary sites could be explained through two explanatory variables: (i) the standardised run-off index (SI Discharge; a measure of the relative wetness and dryness) and (ii) mean monthly water temperature. The justification for choosing these two explanatory variables is that they provide metrics for the connectivity between terrestrial and aquatic systems (SI Discharge) as well as the effect of temperature on biogeochemical reaction rates (i.e., productivity, nutrient cycling, mineral dissolution). The model allowed for different linear correlations (random slopes and intercepts) of SI Discharge with water quality variables at each site and constant temperature correlations (fixed slope, random intercept) for each WQ parameter across all sites (details in Data Analysis Methods). The reasoning behind this approach is that the temperature dependence of abiotic and biotic processes will be broadly similar across all sites though absolute temperature will likely vary across the catchment, while the effect of landscape connectivity (SI discharge) on WQ will depend upon the type of landscape. GLMM results are separated here into main channel sites (Figure 29) and tributary sites (Figure 30).

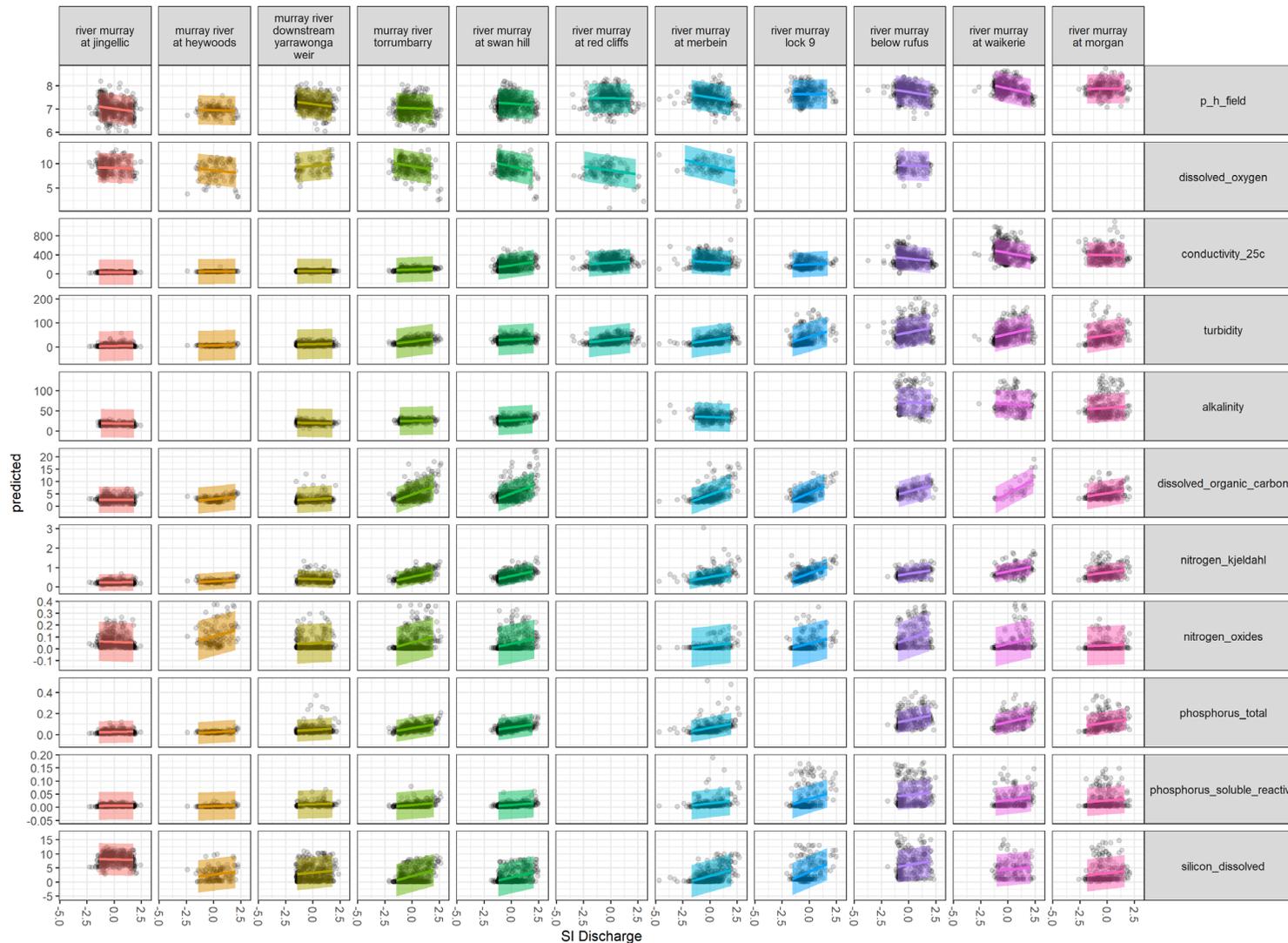


Figure 30. Predicted linear relationships between Standardised Discharge (SI Discharge) and water quality parameters from Generalised Linear Mixed Model (GLMM) relationships measured at the main channel sites selected for this trends analysis (mean slopes shown with shaded areas indicating 95% confidence intervals).

The GLMM for the River Murray sites provided a good description of the WQ for several parameters (e.g., EC, DOC, DO, TKN, TP, turbidity); WQ was less well described for WQ parameters linked to in-stream productivity and/or high seasonal variability (NO_x , SRP, pH, Silica). Alkalinity was well described at upper and mid-Murray sites, but poorly described at lower Murray sites, possibly due to the influence of the Darling River (see below).

The observed dependencies on SI Discharge can be broadly understood in terms of the link between run-off and landscape connectivity. The electrical conductivity (EC) shows a positive dependence on SI Discharge that increases from upper to mid-Murray sites, likely reflecting the transfer of landscape salts under higher run-off conditions; at lower Murray sites a negative dependence is observed that may be due to a de-coupling of landscape connectivity and increased dilution and/or the influence of tributary inflows (e.g., Darling River). Dissolved organic carbon (DOC) shows a positive dependence on SI Discharge across all sites, with maximum dependence at mid-lower Murray sites. As for EC, the positive dependence is likely due to increased connectivity with terrestrial environment, but with much higher sensitivity at the mid-Murray locations due to adjacent floodplains that provide higher levels of DOC under high flow conditions (i.e., floodplain inundation). Total Kjeldahl nitrogen (TKN) exhibits similar behaviour to DOC, which as noted previously is due to the strong association of organically bound carbon and nitrogen. Dissolved oxygen broadly shows the opposite dependence to DOC across all sites, reflecting that high DOC is strongly linked to DO depletion from the water column.

Turbidity shows a positive dependence on SI Discharge across all sites, with increasing dependence from upstream to downstream sites. The positive dependence of turbidity on run-off is entirely consistent with that expected for particle mobilisation from terrestrial environments as well as the effect of stream velocity (generally increasing with increasing discharge) on suspended solids loads. The similar dependencies for total phosphorus (TP) are consistent with the high correlation between turbidity and TP (Figure 7), reflecting that much of the TP is present as particulate and adsorbed P-containing materials.

The ability of the GLMM to describe WQ variations in the tributary systems is broadly similar to that observed for the main channel sites but with greater variability in the observed dependencies on SI Discharge. The mid-Murray tributaries (Goulburn, Campaspe, Gunbower, Loddon and Murrumbidgee) all show dependencies on SI Discharge that are broadly similar to that observed for the mid-Murray main channel sites, likely reflecting the stronger influence of floodplain interactions for these sites. The GLMM is less successful in describing WQ at the Darling at Burtundy site (with the exception of: EC, DOC and TKN). Further, the dependence on SI Discharge at this site is the opposite to that observed at other tributary sites for these same parameters, suggesting that dilution effects are stronger than landscape connectivity under high run-off conditions. Overall, the contrasting patterns (and poorer description of the WQ by the GLMM) for the Darling River at Burtundy site provide some explanation for the observed SI Discharge dependencies for the main channel sites below the Darling River confluence. The higher variability in the observed SI Discharge dependencies for the tributary sites suggests that the drivers of water quality are catchment specific and more complex than that which can be described by temperature and run-off alone.

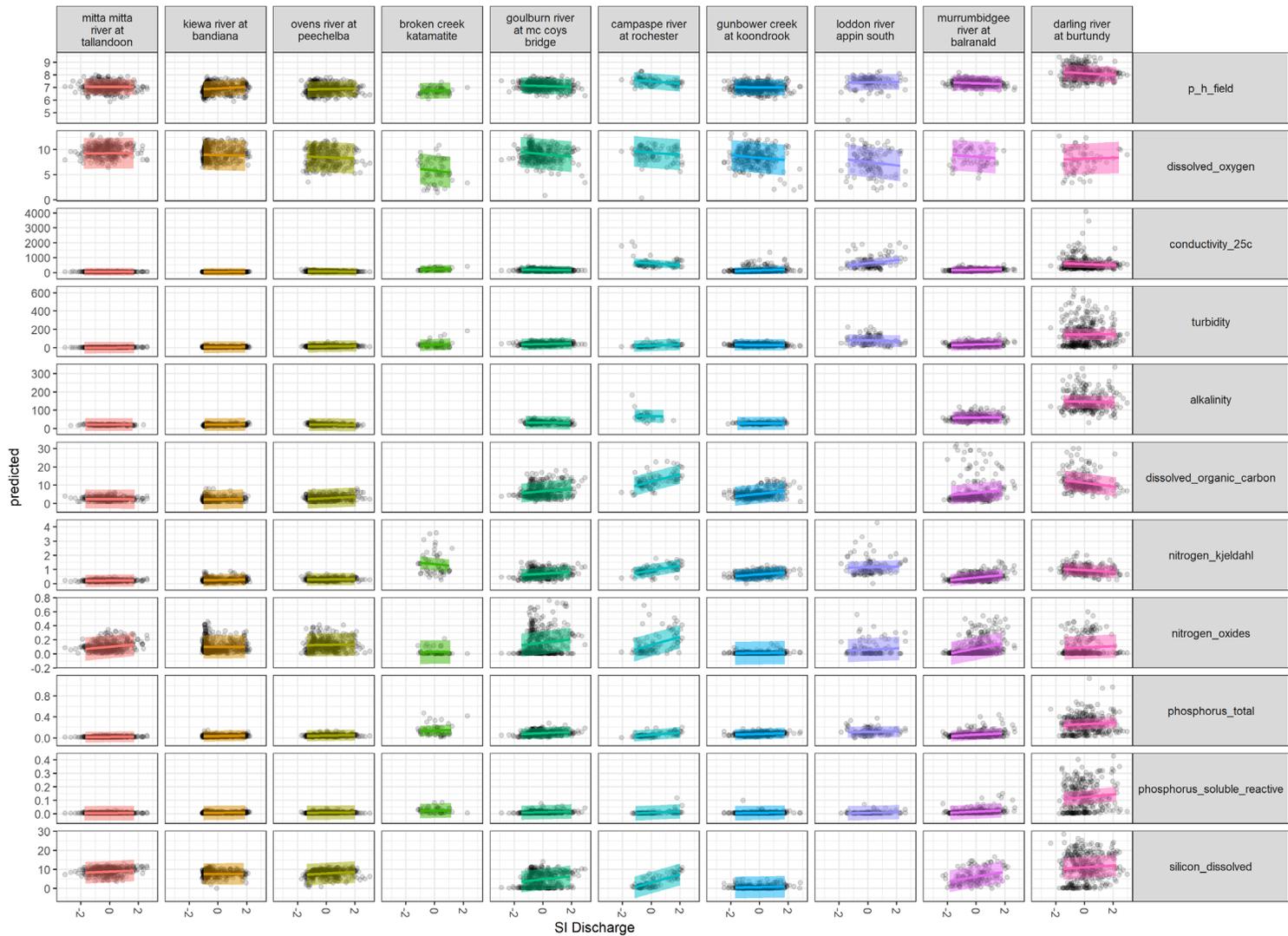


Figure 31. Predicted linear relationships between Standardised Discharge (SI Discharge) and water quality parameters from Generalised Linear Mixed Model (GLMM) relationships measured at tributary sites selected for this trends analysis (mean slopes shown with shaded areas indicating 95% confidence intervals).

Scenarios

As discussed above there are a range of processes that can impact on water quality in a regulated river. Here we consider three (3) of these processes to determine whether the water quality data obtained through the RMWQMP (and potentially in combination with data from the WQ telemetry network) is able to capture this information. The three processes investigated include: (i) tributary effects, (ii) floodplain-channel interactions ('blackwater') and (iii) wildfire.

TRIBUTARY EFFECTS

Main stem-tributary discharge ratios

We have considered four (4) tributary junctions in the River Murray, including: (i) Kiewa-Murray confluence, (ii) Ovens-Murray confluence, (iii) Goulburn-Murray confluence, (iv) Darling-Murray confluence. These tributary inflows represent a wide range of river types that may impact on main channel water quality, depending on differences in water quality between the two rivers and the relative discharges of the main stem and tributary. All data has been treated on a seasonal basis, recognising that both discharge and water quality likely vary seasonally.

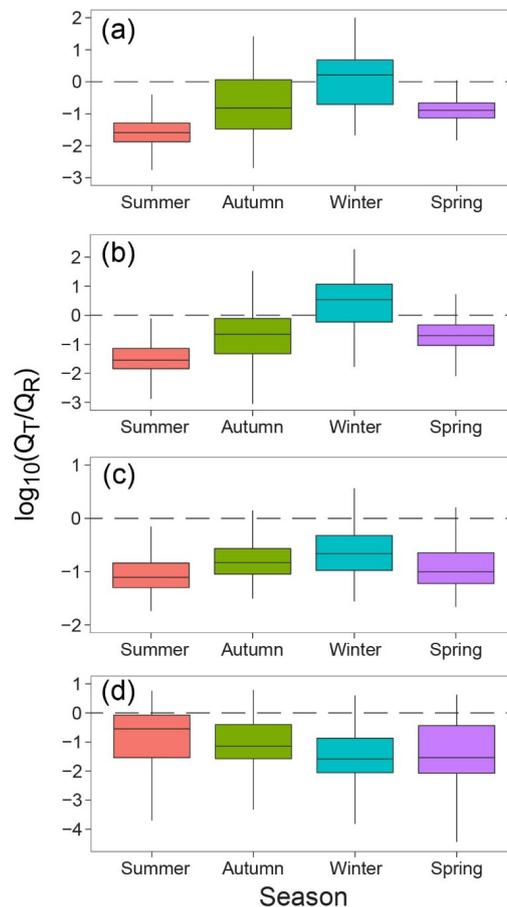


Figure 32. Boxplot of tributary-main channel discharge ratios for the confluences: (a) Kiewa-Murray (data period: 1970-2021), (b) Ovens-Murray (data period: 1998-2021), (c) Goulburn-Murray (data period: 1977-2021), and (d) Darling-Murray (data period: 1976-2021). Data presented on a seasonal basis as \log (base-10) of the tributary (Q_T) to main channel (Q_R) mean daily discharge ratio (i.e., $\log_{10}(Q_T/Q_R) = 0$, corresponds to equal discharge in both rivers); outliers removed.

Seasonal patterns in discharge ratios at Kiewa-Murray (Figure 32(a)) and Oven-Murray (Figure 32(b)) confluences are very similar, with maximum tributary influence during the Autumn to Winter period and with tributary flows in these seasons that are similar in magnitude to (or greater than) the main channel. Strong annual ranges in the discharge ratios are observed at both sites, with a two orders of magnitude difference in mean daily flow ratios between summer and winter. Both the Kiewa and Ovens rivers are partly regulated, although the storage-run-off ratios are extremely low in both systems and they effectively operate as unregulated rivers. The observed annual patterns in discharge ratios at these confluences reflects both the natural variation in discharge of these rivers, combined with the stronger regulation of the River Murray below Lake Hume.

The seasonal mean daily discharge ratios of the Goulburn-Murray confluence (Figure 32(c)) are broadly similar to that observed for the Ovens and Kiewa rivers, but with a much lower maximum and a much smaller range over the annual cycle (\log_{10} range ~ 0.5). This smaller range in discharge ratio likely reflects the higher regulation of the Goulburn River and seasonal controls on water releases that broadly mirror that of the River Murray. The seasonal mean daily discharge ratio pattern for the Darling-Murray confluence (Figure 32(d)) is the reverse of all other confluences shown in Figure 32, with maximum discharge contributions in spring-summer. The annual range in discharge ratio is relatively low (\log_{10} range ~ 1), skewed towards lower flow contributions from the Darling River.

Murray@Heywoods-Kiewa confluence

Water quality parameters for the Kiewa-Murray confluence were investigated using long-term data from the Kiewa at Bandiana ('Kiewa River') and River Murray at Heywoods ('Heywoods') sites (Figure 33).

WQ parameters for Heywoods and Kiewa River are broadly similar across a range of water quality variables (Figure 33). Across all seasons the Kiewa River has slightly lower conductivity and higher turbidity (especially in winter and spring). The lower conductivity of the Kiewa River may be due to hydroelectric 'pipe-to-pipe' transfers in the upper catchment that limit ionic uptake from the catchment. Similarly, higher natural flows in the Kiewa River in winter and spring likely lead to higher turbidity during these seasons through particle mobilisation. Seasonal variations in nitrogen oxides (NO_x) are observed at both sites, with lower levels in summer and autumn (i.e., during higher productivity periods). Dissolved silicon (silica) levels in the Kiewa River are always higher than at Heywoods, particularly during autumn when strong seasonal depletion of silica occurs. The depletion of silica at the Heywoods site likely reflects reservoir processes where silica is partitioned to sediment through biological (diatom) uptake and sedimentation (Maavara et al., 2020). Silica depletion at Heywoods is sustained during winter and recovers into spring-summer, likely through re-supply from upstream of Hume dam. Both DOC and TKN are slightly higher at Heywoods compared to the Kiewa River; as noted above, throughout the River Murray these two water quality variables are strongly correlated, likely because TKN largely represents organically-bound nitrogen (dissolved organic nitrogen; DON) that along with DOC form part of dissolved organic matter (DOM). Total phosphorus (TP) is slightly higher in the Kiewa River in winter-spring, similar to that observed for turbidity, and likely due to elevated levels of particulate organic material and particle-bound P. Maximum tributary influence at the Murray-Kiewa confluence occurs in autumn-winter (Figure 33a)), a period of time when the two rivers differ most strongly in dissolved Si and NO_x . The Kiewa River may therefore be important providing these nutrients over these periods, recognising that autumn-winter are generally periods of low productivity.

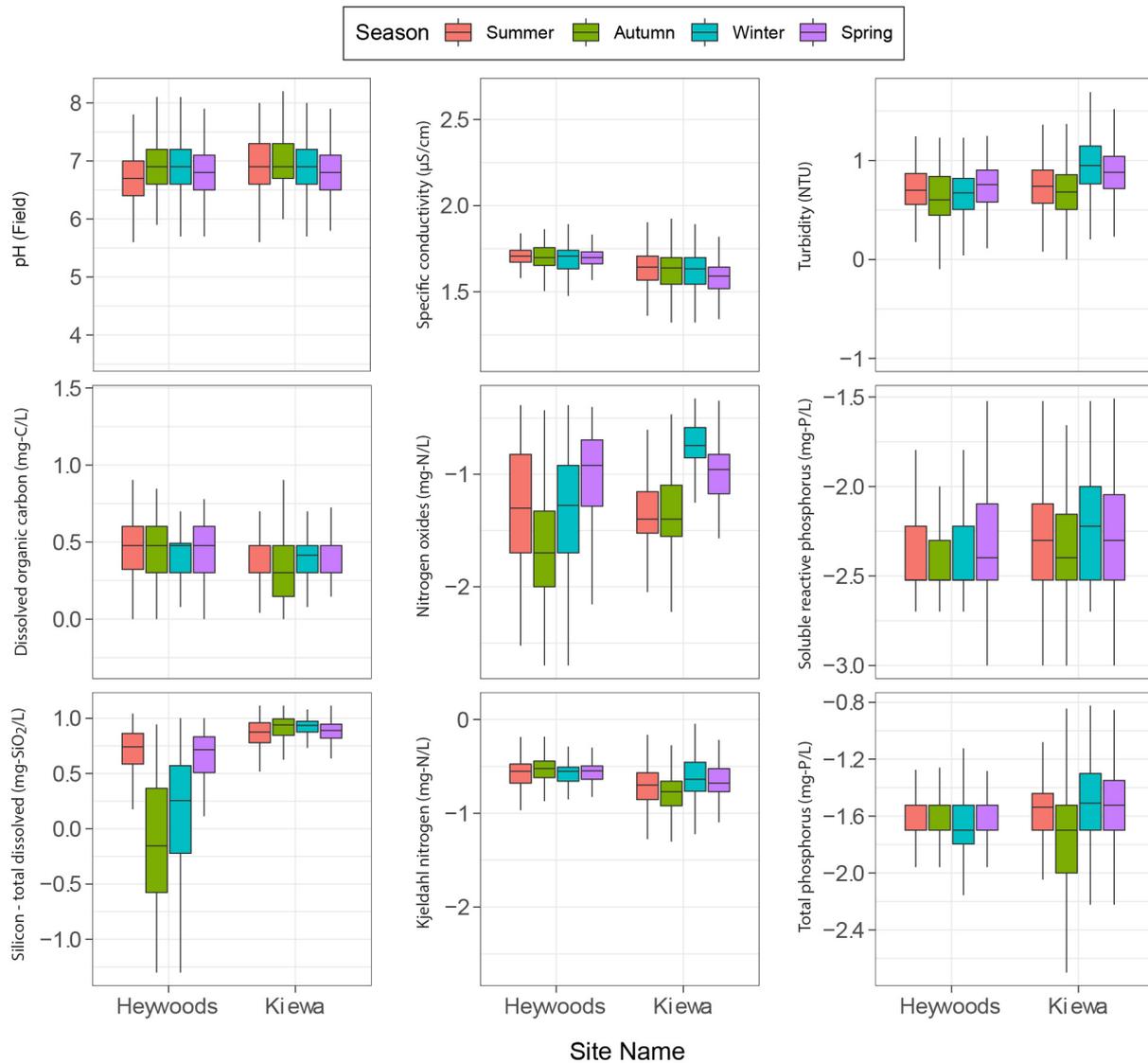


Figure 33. Boxplot of seasonal patterns in water quality variables in the River Murray at Heywoods and Kiewa River at Bandiana (Murray-Kiewa confluence). All data (except pH) plotted as logarithm (base-10). Dataset includes all water quality measurements available for the 1978-2021 period and does not show trends in these parameters over this period; outliers removed.

Murray@Heywoods -Ovens confluence

Water quality parameters for the Ovens-Murray confluence were investigated using long-term data from the Ovens at Peechelba ('Ovens River') and River Murray at Heywoods ('Heywoods') sites (Figure 34). Note that the River Murray @ Heywoods site is the most proximate water quality monitoring site upstream of the Ovens River confluence.

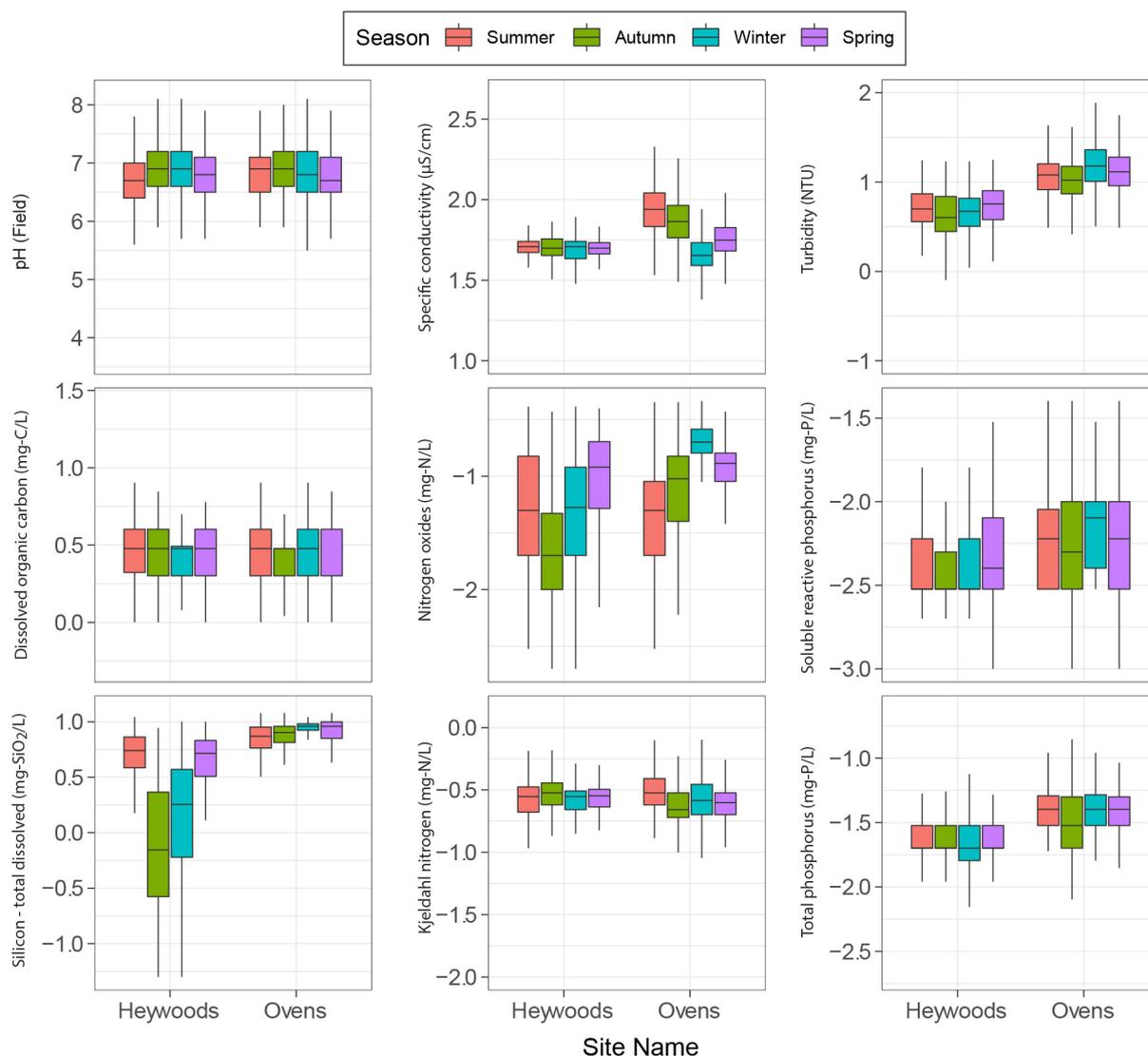


Figure 34. Boxplot of seasonal patterns in water quality variables in the River Murray at Heywoods and Ovens River at Peechelba (Ovens-Murray confluence). All data (except pH) plotted as logarithm (base-10). Dataset includes all water quality measurements available for the 1978-2021 period and does not show trends in these parameters over this period; outliers removed.

The differences in seasonal water quality patterns in the Ovens River compared to Heywoods are largely similar to that observed for the Kiewa-Murray confluence. Notable differences include the higher conductivities in the Ovens River, with a much stronger annual pattern. This annual variation in conductivity is likely driven by stronger catchment pick-up of ionic components (absence of hydro-electric water transfers) and higher conductivities in summer driven by water loss (evapotranspiration) and enhanced weathering processes. The Ovens River has much higher turbidity across all seasons, indicating higher particulate loads and consistent with the elevated levels of TP. As in the Kiewa River, a seasonal pattern is observed for NO_x species, with depletion in summer months. Silica levels are near-constant in Ovens River (slight summer depletion) compared to strong autumn-winter silica depletion observed (and noted previously) at Heywoods. As observed for the Kiewa-Murray confluence, the maximum (mean daily) discharge ratio for the Ovens-Murray confluence occurs in autumn-winter, a period of time where both silica and (to a lesser extent) NO_x are depleted in the Murray, again keeping in mind that this occurs during cooler periods of lower productivity.

River Murray d/sYarrowonga-Goulburn confluence

Water quality parameters for the Goulburn-Murray confluence were investigated using long-term data from the Goulburn at McCoy's Bridge ('Goulburn River') and River Murray downstream of Yarrowonga weir (Yarrowonga) sites (Figure 35).

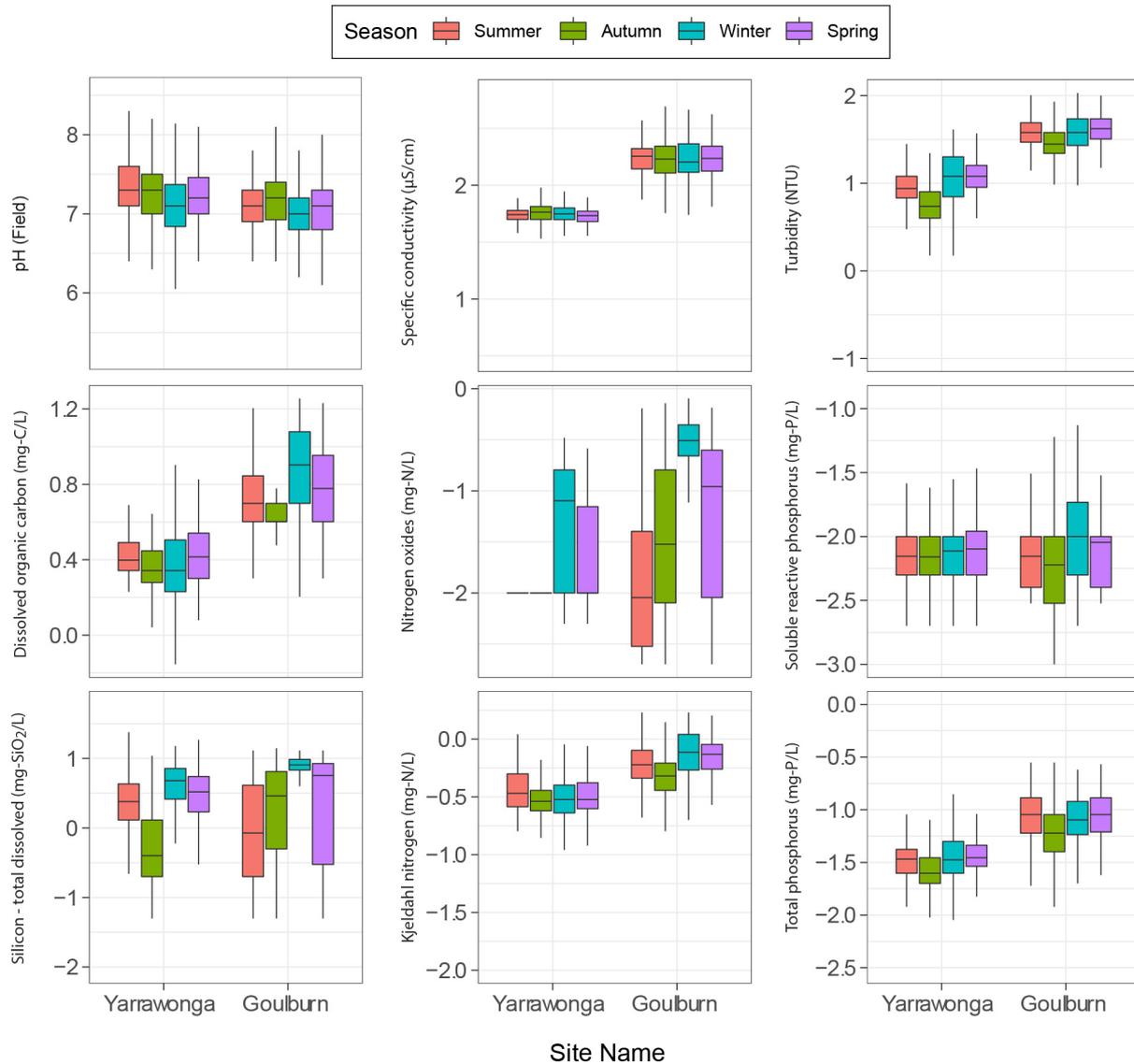


Figure 35. Boxplot of seasonal patterns in water quality variables in the River Murray downstream of Yarrowonga weir and Goulburn River at McCoy's bridge (Murray-Goulburn confluence). All data (except pH) plotted as logarithm (base-10). Dataset includes all water quality measurements available for the 1978-2021 period and does not show trends in these parameters over this period; outliers removed.

Seasonal water quality patterns at the Yarrowonga and Goulburn River sites differ strongly for a range of parameters. Conductivity at the Goulburn River site is substantially higher than for Yarrowonga, without any significant annual variation. This suggests that while there is greater ionic pick-up in the Goulburn catchment, there is stronger mixing across the annual cycle. Turbidity is also higher at the Goulburn River site and as for other sites, strongly correlated with TP. DOC is also higher at the Goulburn River site and closely coupled to TKN. Strong seasonality is observed in NO_x species at Goulburn, with higher values in winter and depletion in summer. The behaviour of NO_x at Yarrowonga is somewhat similar, with higher values in winter and spring compared to summer and autumn; note that very limited range of NO_x concentrations in summer and autumn likely reflects the analytical detection limit. Seasonal depletion of silica is observed at both sites, with concentrations changing over a broadly similar range. Of particular note is that the silica depletion at Yarrowonga is much less than that observed at Heywoods (see above), likely due to the contributions of both the Kiewa and Ovens rivers; these rivers having higher

silica concentrations and providing a high proportion of River Murray discharge during autumn and winter. Maximum (mean daily) discharge ratio for the Goulburn-Murray confluence occurs during autumn-winter, similar to both the Kiewa-Murray and Ovens-Murray confluences, but with much reduced annual variation.

River Murray at Merbein-Darling confluence

Water quality parameters for the Darling-Murray confluence were investigated using long-term data from the Darling River at Burtundy ('Darling River') and River Murray at Merbein ('Merbein') sites (Figure 36).

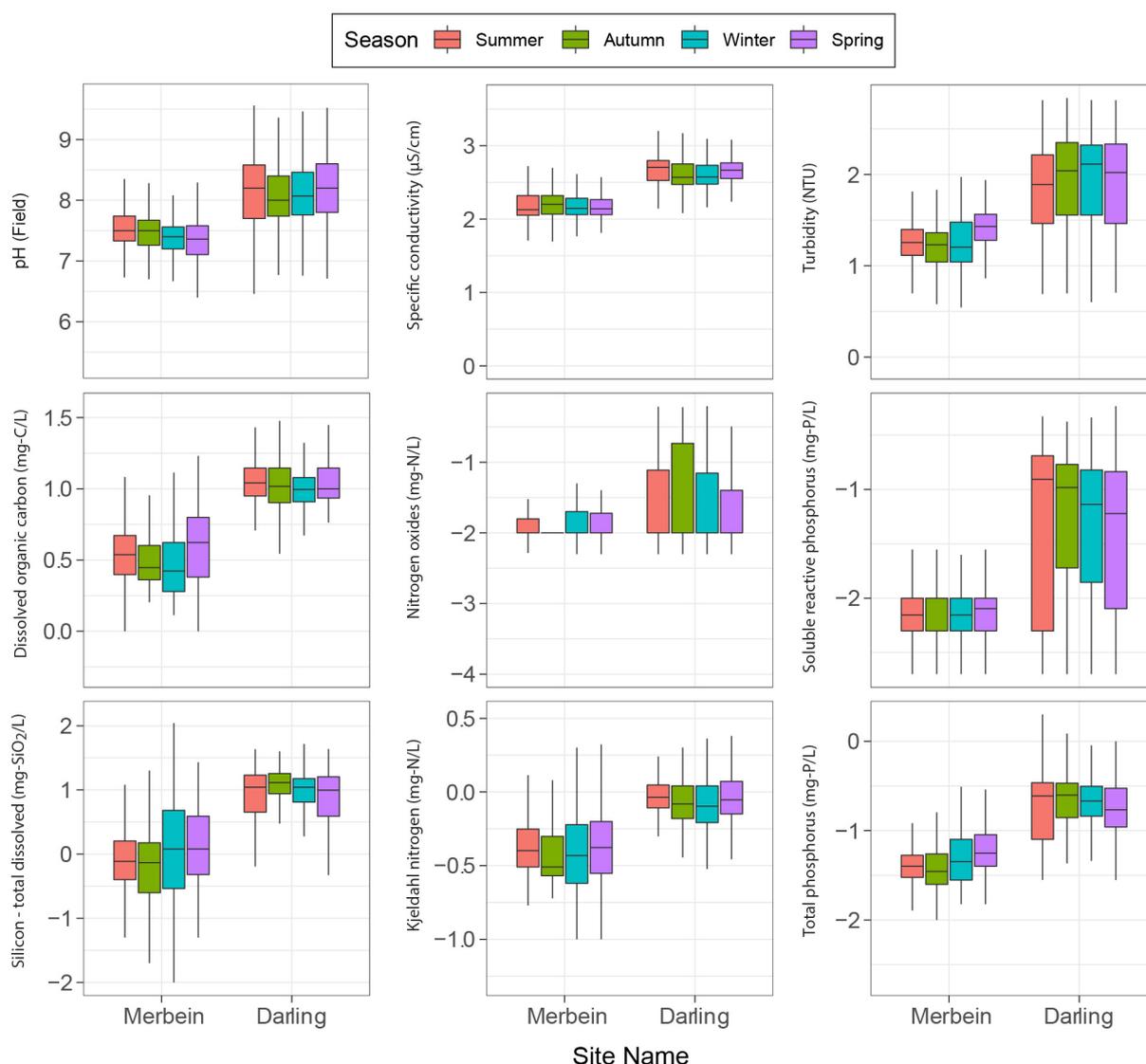


Figure 36. Boxplot of seasonal patterns in water quality variables in the River Murray at Merbein and the Darling River at Burtundy (Murray-Darling confluence). All data (except pH) plotted as logarithm (base-10). Dataset includes all water quality measurements available for the 1978-2021 period and does not show trends in these parameters over this period; outliers removed.

Seasonal water quality patterns at the Merbein and Darling River sites differ strongly for nearly all water quality parameters and with higher concentrations at the Darling River site. Neither site shows strong seasonality for any of the water quality parameters investigated here. Substantial differences are observed for a number of parameters: turbidity, SRP and silica are all approximately 10-fold higher in the Darling River compared to Merbein; conductivity, DOC and TKN are all approximately 3-fold higher in the Darling River compared to Merbein. Discharge ratios for the Darling-Murray confluence indicate that the Darling has a greater influence during spring-summer,

but with very weak annual variation. The significantly higher levels of most water quality parameters in the Darling River are likely the origin of the step change increase in these parameters in the River Murray downstream of Merbein (Figure 36).

Role of tributaries in controlling River Murray water quality

The analysis of the four (4) tributary junctions in the River Murray show that there are some key differences in water quality between main channel and tributary, particularly with respect to seasonal influences. For the upper Murray tributary junctions (Murray-Kiewa and Murray-Ovens) there are distinct differences in the availability of nutrients (NO_x and SiO_2), with strong depletion of these nutrients from the main channel from autumn into winter. The tributaries do provide these nutrients to the main channel, however the strongest tributary influence (Q_T/Q_R) occurs during winter into spring. For the tributary junctions further downstream (Murray-Goulburn and Murray-Darling) there is much less seasonal variation, but with both tributaries providing elevated levels of organic carbon and nutrients relative to the main channel at all times of year.

The parameters recorded by the RMWQMP go some way towards understanding the role of tributaries in regulating water quality in the River Murray, but do not have the capacity to detect more subtle differences in water quality components. Included amongst these are differences in characteristics of both dissolved and particulate organic carbon (POC), reflecting different catchment sources (i.e., allochthonous vs autochthonous) that may be critical to regulating downstream productivity. While such measurements are unsuited to long-term monitoring programs, focused studies around tributary junctions would likely provide greater insight into overall river function and the importance of these tributary inflows in restoring river function.

The influence of tributary inflows on a regulated river are likely to be more pronounced during pulse events due to the delivery of high loads of dissolved and particulate materials. The RMWQMP spot data is not sensitive to pulse processes due to the relatively low frequency of sampling and the low likelihood of capturing high flow events. A focused study on key tributaries around the influence of high flow events on main channel WQ would be extremely useful in understanding the broader influence of tributary systems in the River Murray.

Question 1: How does the tributary-main channel mixing ratio (Q_T/Q_R) change seasonally at key tributary junctions in the River Murray? Do these tributary systems provide water quality components that are depleted in the regulated channel flow?

Response: The two tributaries in the upper Murray considered here (Kiewa River and Ovens River) make a stronger contribution to main channel flow in winter and spring, consistent with (near) natural flow regimes in these rivers; this seasonality in flow contribution is less for the Goulburn River and reversed (i.e., higher in summer) for the Darling River.

Water discharged from Hume reservoir (and Lake Mulwala) is seasonally depleted in some key nutrients (NO_x and SiO_2) that may have impacts on algal community structure in the River Murray; the tributaries in the upper Murray likely have an important role in restoring the water quality of the River Murray downstream of reservoirs.

Tributary inflows may also provide important sources of organic carbon and nutrients to drive the productivity in the River Murray; focused investigations on the influence of these tributary inflows (seasonal and event-based) on in-stream productivity are highly recommended.

Recommendation: Focused studies (separate to the RMWQMP) be conducted into the role of upper Murray tributaries in maintaining WQ in the River Murray, particularly with respect to algal community dynamics and productivity.

BLACKWATER

The mobilisation of organic carbon from floodplains and transfer of this carbon to the main channel can lead to depletion of dissolved oxygen in the water column. The extent of this depletion will depend upon the temperature of the water, the oxygen demand placed by the organic carbon and the rate of oxygen re-supply from the atmosphere (i.e., oxygen transfer rates and mixing effects). Here we consider the impact of a previous low-oxygen (blackwater) event in the River Murray in the context of the long-term patterns in DO saturation, with the impact of the blackwater event considered in terms of the deviation from saturation.

Seasonal patterns: Water temperature, DO, DO-% (Murray main channel sites)

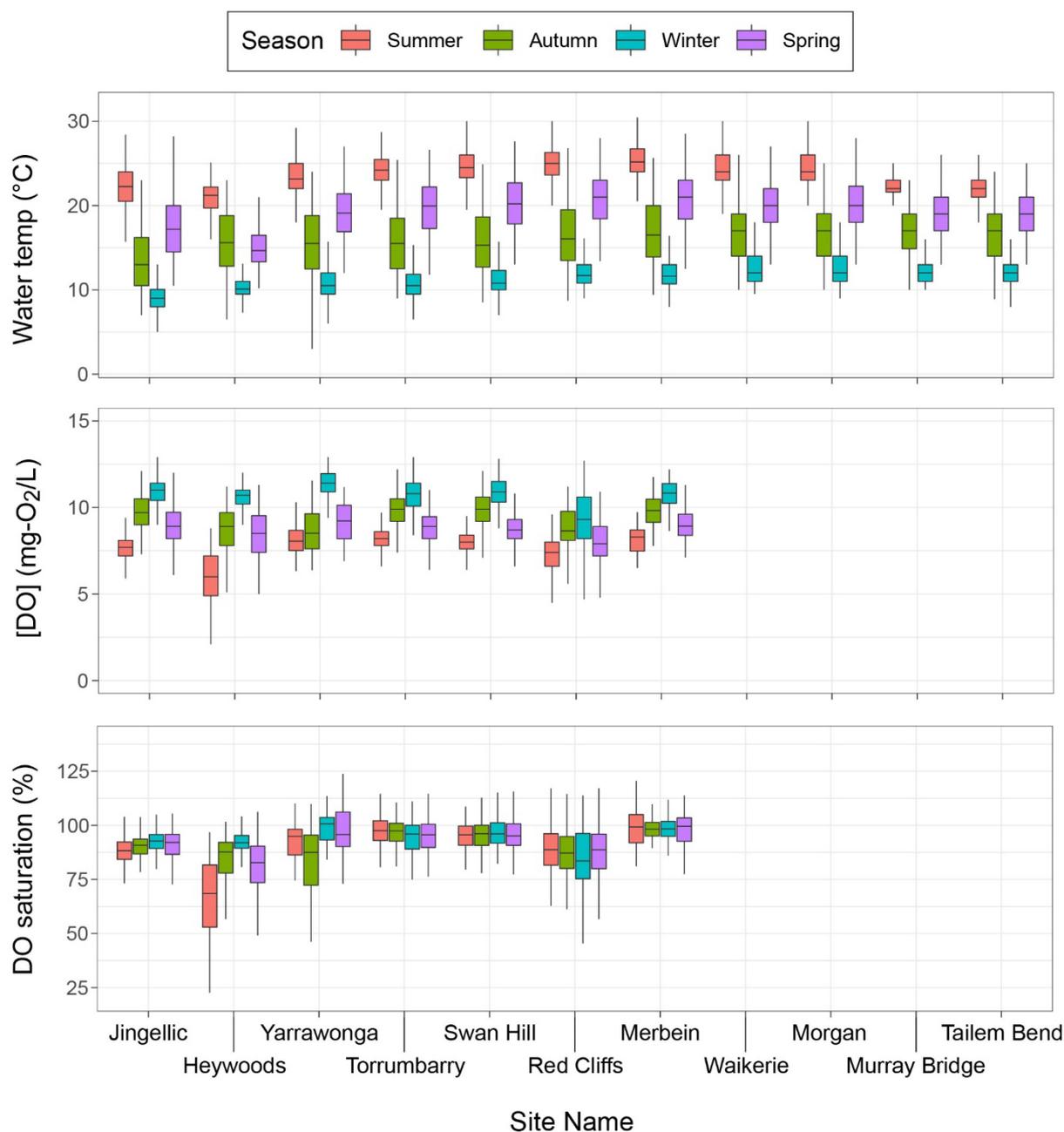


Figure 37. Boxplot of seasonal patterns in: (a) water temperature, (b) dissolved oxygen concentration (mg-O₂/L) and (c) dissolved oxygen saturation (%) for River Murray sites (main channel only). Dataset includes all water quality measurements available for the 1978-2021 period and does not show trends in these parameters over this period.

Analysis of seasonal variations in water temperature, DO concentration and DO saturation over the entire available data record for River Murray Sites generally shows patterns consistent with that expected for surface water in contact with the atmosphere (Figure 37). Water temperatures are higher in summer compared to winter, with higher ranges observed at upper River Murray sites (keeping in mind that water quality measurements will likely be recorded during day-time periods). DO concentrations show the reverse pattern (higher in winter and lower in summer), consistent with the approximate inverse relationship between temperature and levels of dissolved oxygen from atmospheric equilibration (note: no data available downstream of Merbein). DO saturation values are generally in the range 90-100 % at all sites, with the exception of River Murray at Heywoods and River Murray d/s Yarrowonga weir where lower values do occur in the spring-autumn period. This is likely due to reservoir stratification during these periods and the development of anoxic bottom water. Overall, the saturation levels indicate that DO concentrations are largely controlled by atmospheric equilibration and not highly influenced by shorter time scale physical or ecological processes that may shift the DO concentration from this equilibrium.

Detection of Floodplain return water

Short-term excursions of DO concentrations (and saturation) are expected to occur in response to a range of natural and managed events (floodplain inundation, catchment wildfire, reservoir & pool stratification). An example of this type of event are the floods which occurred in the River Murray in the summers of 2010-11 and 2011-12 (Figure 38). These floods resulted in high concentrations of dissolved organic carbon (DOC) transferred from floodplains to the main channel and the depletion of oxygen from the water column due to microbial respiration; as noted elsewhere, the detrimental effects of oxygen drawdown were exacerbated by the summer timing of these events when the levels of DO are at an annual minimum (Whitworth et al., 2012).

The RMWQMP spot measurements captured the key features of the blackwater event, including the elevated levels of DOC at all sites downstream of Yarrowonga weir, with DOC concentrations increasing from approx. 5 mg-O₂/L prior to the flood event to as high as 25 mg-C/L during the high flow period (Figure 38(a)). Associated with this DOC pulse is a strong depletion of the DO concentrations at all sites, apart from downstream of Yarrowonga weir (Figure 38(b)). This depletion is most easily visualised as a deviation from atmospheric equilibration, where the atmospheric equilibration value is calculated from the water temperature and assuming a typical saturation level of 90% (Figure 38(c)). The very close correspondence between calculated and measured DO concentrations at all times prior to the two flood events, as well as after these events, strongly supports the contention that DO concentrations are normally controlled by atmospheric exchange and therefore highly predictable. The data also shows that deviations from atmospheric equilibration will be relatively short in duration compared to the 40+ year data record (but may have significant ecological consequences), with DO returning to equilibration levels through atmospheric exchange. An important point is that spot measurements are unlikely to capture extreme levels (high or low) of DO given the frequency of measurements, but do provide insight into the length of time that non-equilibrated DO conditions persist. Spot measurements are also unlikely to provide capacity for real-time management and intervention given the delay between measurement and reporting. The absence of DO spot measurement data for any River Murray site down stream of Merbein prevents any analysis or understanding of the propagation distance of the low DO conditions; specifically, the return to atmospheric oxygen saturation is not captured.

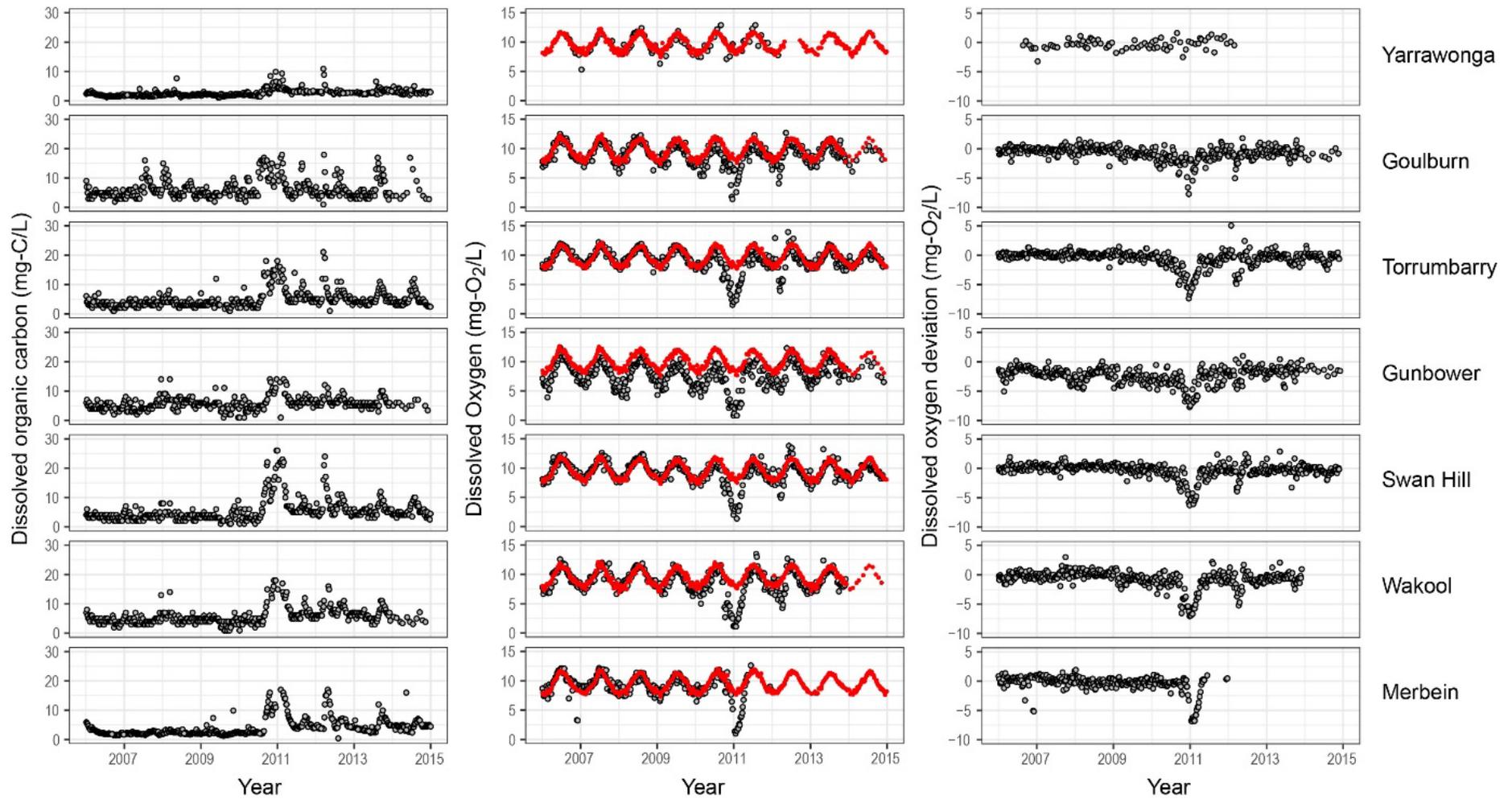


Figure 38. Response of dissolved oxygen (DO) to dissolved organic carbon (DOC) pulse over the time period 2006 – 2015 for River Murray main channel and tributary sites between Yarrawonga and Merbein. Shown are: (a) DOC concentration time series, (b) measured (black) and calculated (red) DO concentrations, based on 90% atmospheric saturation, and (c) DO deviation from 90% saturation.

Question 2: Does the RMWQMP capture the spatial and temporal extent of blackwater events, including the downstream return to atmospheric oxygen saturation?

Response: The RMWQMP spot measurement program captures the temporal extent and downstream movement of low DO conditions for the sites where this parameter is reported; below Merbein the absence of available spot measurement data prevents the ultimate fate of the low conditions (i.e., export to estuary/ocean or atmospheric re-equilibration) from being observed. The severity of oxygen depletion is partially captured by the spot measurement program, recognising that low frequency sampling is unlikely to detect more extreme conditions that may occur.

Recommendation: It is recommended that spot measurements of dissolved oxygen are included data reported for RMWQMP sites downstream of Merbein.

Wildfire

Wildfire frequency and intensity is predicted to increase in the coming decades due to climate change effects (Abram et al., 2021). As discussed above (Section: review of processes that impact WQ), wildfire is expected to have impacts on both the composition and loads of materials mobilised from catchments, with strong effects in the weeks and months following fire and closely coupled with catchment run-off. The upper Murray experienced widespread and high intensity fires during the 2019 - 2020 summer, with likely impacts on the water quality at the River Murray at Jingellic site ('Jingellic'). This site represents the most upstream of the RMWQMP sites and therefore likely to be the most affected by wildfire effects on water quality; the catchment area is however large (6527 sq. km) and contains a number of sub-catchments with different river distances from this monitoring site as well as a range of fire impacts. The Jingellic site had existing telemetry (EC and Temperature) prior to the 2019 - 20 wildfire, with additional sensors (turbidity, DO, pH) added 2 months after fire impacts (March 2020). It is likely that the telemetry data collected at the Jingellic site represents one of the first post-fire responses captured on the WQ telemetry network in the River Murray. The Jingellic site (Class 2) also has weekly sampling for spot data, providing an opportunity to compare physical data collected by the two parallel systems.

Comparison of spot and telemetry data for the Jingellic site prior to, and post-fire, shows generally good agreement between the data sets (Figure 39), but critically, none of the post-fire events associated with catchment run-off were captured by the spot measurement system. Spot measurements were also suspended for several weeks after the fire, likely due to safety and access difficulties. Electrical conductivity (EC) telemetry shows several high EC periods (events) post fire, likely attributable to wash-out processes in fire affected catchments, the magnitude of which attenuated over several months post-fire likely due to removal of these easily transported components from the catchment. Comparison with discharge data shows that these high EC events do not directly correlate with high discharge periods, probably reflecting the large catchment size and variable contributions from fire affected and non-fire affected sub-catchments.

Following the implementation of telemetry sensors for turbidity, DO and pH, several events were captured that likely represent post-fire effects. The attributes of these events are: elevated turbidity (due to increased particle erosion and mobilisation), elevated EC (due to solubilisation of salts from ash and burnt soils), depleted DO (due to oxygen demand associated with mobilised organic matter) and decreased pH (mechanism likely complex, but possibly related to the partitioning of alkalinity components to soil in burnt catchments).

Closer inspection of the first event captured by the complete telemetry system (03 – 11 Mar; 2020; Figure 40) reveals the inherent complexity of pulse events at this catchment scale, with multiple pulses evident, possibly originating from separate sub-catchments with differing travel distances and/or multiple spates in these sub-catchments. Two separate spates that occurred later in this event (labelled **I** and **II**) have been further investigated through their concentration-discharge (C-Q) relationships; C-Q plots allow some assessment of the origin and relative mobility of water quality constituents. In the case of spate **I**, water quality effects (increased turbidity and EC; decreased DO and pH) occur late in the ascending limb suggesting either that the sources were more distal in

the affected sub-catchment, or that the constituents were slow to mobilise (less likely). It is notable that elevated turbidity occurred later in the cycle, probably due to the slower movement of particulate matter compared to dissolved components. Spate II shows the mobilisation of water quality constituents even later in the storm cycle, with elevated turbidity and EC (and decreased DO and pH) occurring late in the descending limb. Again, the most likely explanation for this behaviour is the movement of post-fire materials from smaller and more distal locations (but highly fire affected) in the particular sub-catchment.

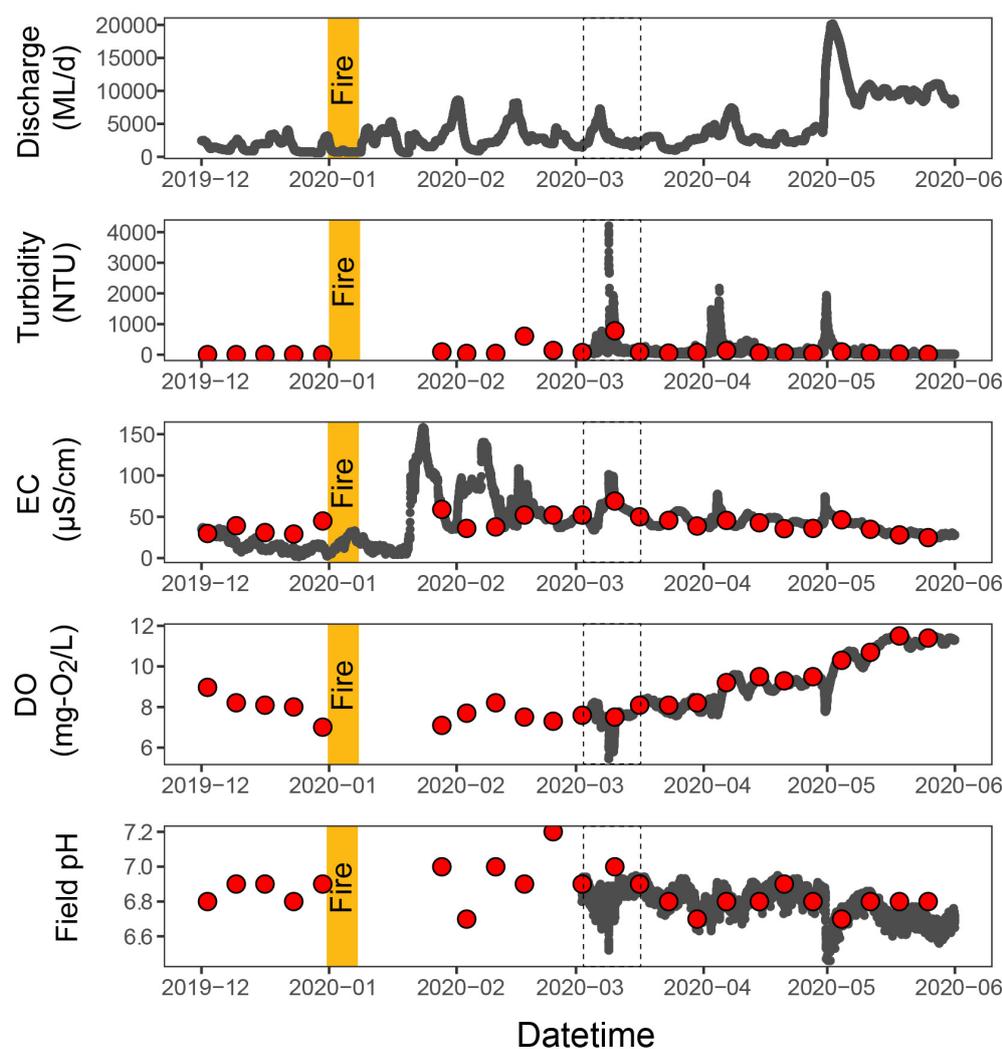


Figure 39. Post-fire water quality response at the River Murray at Jingellic site. Shown are: (a) discharge (ML/d), (b) turbidity (NTU), (c) electrical conductivity (EC; $\mu\text{S}/\text{cm}$), (d) dissolved oxygen (DO; $\text{mg-O}_2/\text{L}$) and (e) field pH; grey points correspond to telemetry data (15 minute) and red markers to spot measurements. Also shown are the approximate period of fire activity in January 2020) and the first post-fire event at which all telemetry variables were available (see Figure 40).

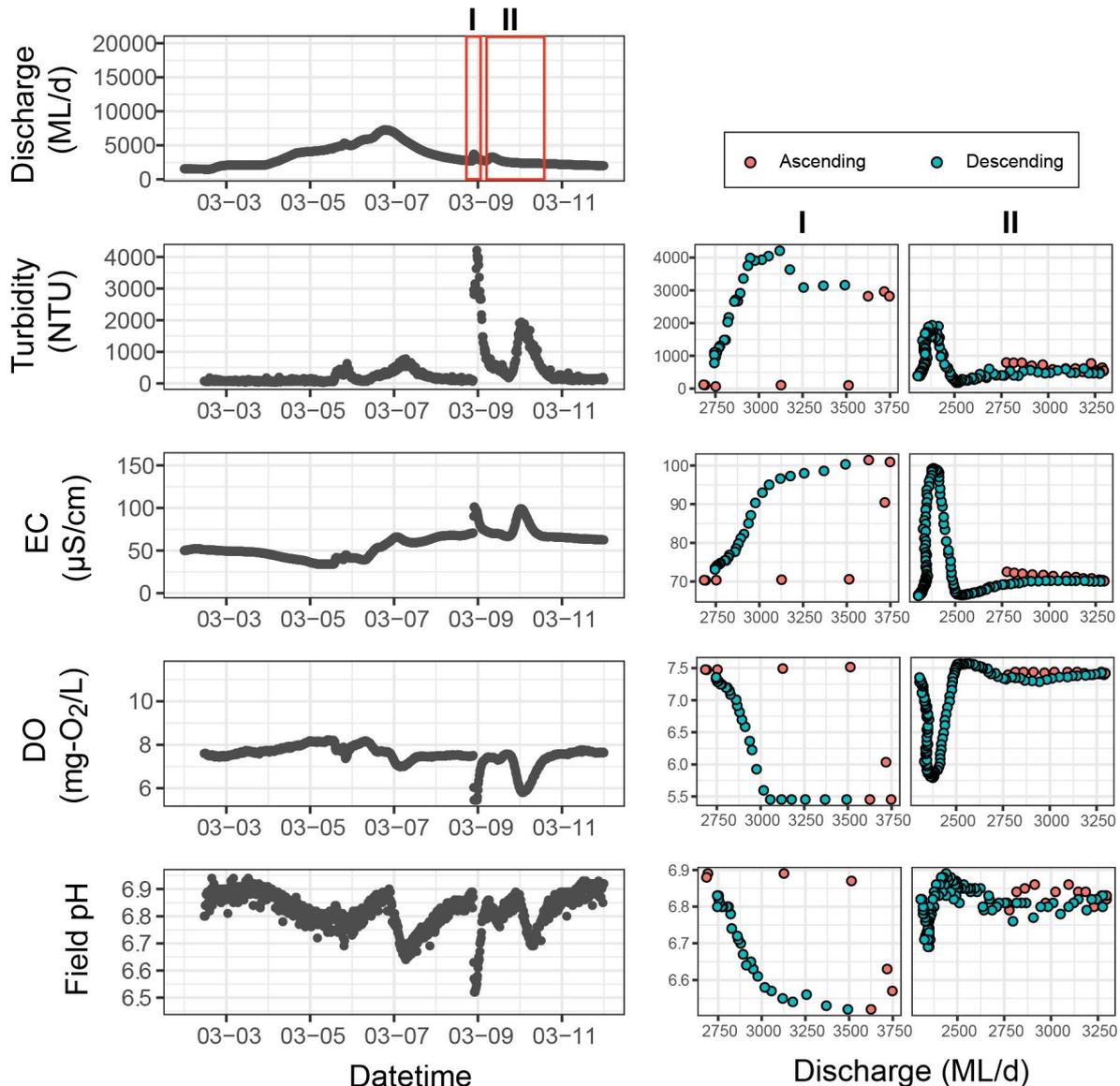


Figure 40. Water quality at the River Murray at Jingellic site in response to a single post-fire event (03-03-2020 to 11-03-2020) (see: Figure 39). Shown are (LHS): (a) discharge (ML/d), (b) turbidity (NTU), (c) electrical conductivity (EC; $\mu\text{S}/\text{cm}$), (d) dissolved oxygen (DO; $\text{mg-O}_2/\text{L}$) and (e) field pH; RHS: concentration-discharge (C-Q) plots for two discrete spates that form part of this post-fire event.

The post-fire water quality effects observed at the Jingellic site are generally consistent with that expected from previous studies, with elevated turbidity and EC, consistent with increased export of particulate matter and ionic materials ('salts') from the fire affected areas. Similarly, decreased DO concentrations can be related to the export of organic carbon (and potentially other reduced materials, e.g., Fe^{II}) that place an oxygen demand on the water column. The decrease in pH observed at Jingellic is not consistent with increased soil alkalinity that is expected as a fire response, however there are a range of processes that can impact pH in aquatic systems and this effect would require further investigation to understand the underlying mechanism(s). The increased export of nutrients that can occur in fire affected catchments was not explored here; nutrient concentrations are measured at the Jingellic site as part of the spot measurement program, and as shown here for physical water quality parameters, the frequency of these measurements is unlikely to capture short time-scale processes.

The analysis of the telemetry data collected from the Jingellic site shows that the range of physical water quality sensors currently installed at this site is well suited to capturing water quality effects from fire-affected catchments. The frequency of data collection by this system allows for rapid response to changes in water quality by downstream users, provided that the data is being monitoring in real time. The high frequency of these data

also allows more detailed analysis of catchment processes (e.g., C-Q analysis) than can be achieved by the spot measurement system.

Question 3: Are wildfire water quality run-off components detected by the RMWQMP and/or the WQ telemetry systems over the day → week timescales?

Response: The WQ effects of wildfire are more likely to be encountered in upper Murray sites due to the proximity of these sites to highly forested land. Hydrological processes at these upper sites occur on relatively fast timescales (hours-days) and the WQ impacts of post-fire run-off are extremely unlikely to be captured by the RMWQMP spot measurement program. The high frequency (15 minute) WQ telemetry network is, however, well-suited to capturing post-fire effects on WQ, particularly at sites where a wide range of sensors are deployed (e.g., T, pH, EC, DO, Turb).

Recommendation: Telemetry WQ sensors (T, pH, EC, DO, Turb) be deployed and maintained at all upper Murray tributaries; note that the majority of these sensors are already in place, with the exception of the Mitta Mitta River where sensor deployment should occur upstream of Lake Dartmouth.

Comments on RMWQMP

The RMWQMP has changed over the years since its inception with respect to: sites that are routinely monitored, the suite of parameters measured, the frequency of measurement and data precision, likely reflecting changes in funding support, management priorities and analytical instrument performance. In this section we consider whether changes should occur to the frequency of measurement, the range of water quality parameters routinely measured or the precision at which analytes are measured and reported.

SAMPLING FREQUENCY

There is a large variability in sampling frequency across the RMWQMP and the additional state programs, ranging from daily – monthly. In this trends analysis we have averaged by month as the analysis methods used requires all data to be of the same frequency, and monthly represents the common frequency that is available for all sites and parameters. There are distinct advantages in measurement at higher frequency than monthly; monthly mean values of several values (measured at weekly or daily frequency) provides a more reliable estimate of water quality conditions for that month while single monthly values are more likely to be influenced by unseasonal events. Monthly frequency also presents a higher risk with respect to sample loss. However, given that future analyses of the RMWQMP dataset are likely to deal with the variable sampling frequency in the same way as done here, there are few advantages in changing the existing arrangements for the key (the 28) River Murray sites. As shown in this report, missing data can in any case be managed through imputation techniques.

While the RMWQMP dataset is well-suited to assessing long-term trends in water quality parameters (and the associated loads), the data is completely unsuited to capturing short timescale events or allowing timely response to adverse changes in water quality. There are two broad contexts in which higher frequency data would be advantageous in management of the River Murray, including: (i) upland rivers where discharge can change rapidly over short timescale, with associated changes in water quality, and (ii) lowland river sites receiving floodplain return water or anoxic reservoir water. For upland rivers the implementation of higher frequency measurement would allow pulse events to be more accurately recorded and loads to be more accurately calculated. It is noted that the telemetry network is more strongly focused at upland sites, consistent with the need for higher frequency data in these locations. The parameter sets recorded in this network are limited to physical variables (pH, EC, T, DO), but do go some way to detecting pulse events at these sites.

For lowland river sites that may receive floodplain return water there is no obvious mechanism for responding to such events through the RMWQMP; spot measurements do not provide capacity for real-time management and intervention given the delay between measurement and reporting. There is a strong argument that DO sensors should be installed into mid-Murray sites (Yarrowonga – Waikerie) as these are the sites likely to receive floodplain return water and experience DO depletion from the water column. Real-time measurements (at 15 – 30 minute frequency) allows for rapid detection of DO changes and the implementation of a management action (e.g. water release from an upstream reservoir) that ameliorate the potential detrimental effects. Similarly, a DO telemetry network will allow real time monitoring of the effects of managed floodplain inundation. This will be critical for the development and validation of hydrodynamic models used to predict the effects of inundation events; such models are likely to feature strongly in future river management (Holland et al., 2020).

WQ PARAMETERS

The range of water quality parameters routinely measured in the RMWQMP is consistent with that expected for inland freshwater systems, allowing assessment of landscape connectivity and (potential) aquatic productivity. In such programs there is always scope to increase the range and complexity of the measured parameters in order to further investigate ecosystem function. Examples include the characterisation of DOC (and DON) to determine bioavailability and source (i.e., allochthonous vs autochthonous) (Holland et al., 2018); while extremely informative, such measurements are likely more appropriately dealt with as part of focused investigations of particular locations and/or events on the River Murray (e.g., tributary junctions, managed floodplain inundation) (Harris et al., 2018).

Of greater concern are periods of missing data for many of the sites, across most of the water quality parameters, likely reflecting funding availability to support the program. Moreover, several of the 28 MDBA sites are currently not recording key water quality parameters, data gaps that may put future trends analyses at a disadvantage. Table 4 lists sites where the twelve (12) water quality parameters analysed in this report are currently not measured.

Table 4. Stations where key water quality parameters are currently not recorded in the RMWQMP dataset.

Water Quality Parameter	Stations where parameter currently <u>not measured</u>
Field pH	Murrumbidgee at Balranald
Water temperature	Murrumbidgee at Balranald
Dissolved Oxygen	Murray River d/s Yarrowonga, Wakool River at Kyalite, Murrumbidgee at Balranald, Darling River at Burtundy, River Murray below Rufus (and all sites downstream)
Electrical conductivity	Murrumbidgee at Balranald
Turbidity	Murrumbidgee at Balranald
Alkalinity	All stations except: Murray River d/s Yarrowonga, Campapse River at Rochester, River Murray at Swan Hill, Wakool River at Kyalite, River Murray at Merbein, Darling River at Burtundy, River Murray at Morgan
Dissolved organic carbon	Murrumbidgee at Balranald, River Murray below Rufus, River Murray at Waikerie
Total Kjeldahl nitrogen	Murray River d/s Yarrowonga, Murrumbidgee at Balranald, River Murray below Rufus, River Murray at Waikerie
Nitrogen oxides	Murray River d/s Yarrowonga, Murrumbidgee at Balranald, River Murray below Rufus, River Murray at Waikerie

Total phosphorus	Murray River d/s Yarrawonga, Wakool River at Kyalite, Murrumbidgee at Balranald, River Murray at Merbein, Darling River at Burtundy, River Murray below Rufus (and all sites downstream)
Soluble reactive phosphorus	Murray River d/s Yarrawonga, Wakool River at Kyalite, Murrumbidgee at Balranald, River Murray at Merbein, Darling River at Burtundy, River Murray below Rufus, River Murray at Waikerie
Dissolved silicon	Murrumbidgee at Balranald, River Murray below Rufus, River Murray at Waikerie

DATA RESOLUTION, DATA PRECISION AND DETECTION LIMITS

The resolution (i.e., significant figures, decimal places) at which data is reported in the RMWQMP has varied over the period of the program, likely due to changing contractual arrangements. By way of context, the data resolution should reflect the typical range over which a parameter varies so as to provide sufficient detail about changes over time and changes in response to events. The data resolution should also reflect the data precision associated with the field or laboratory measurement. Similarly, the detection limits of analytical methods used for sample analysis should match the lower range of concentrations encountered.

The concentrations of many water quality parameters in the River Murray and tributaries are frequently low and require detection limits that are close to currently achievable levels. In many cases the data resolution in the RMWQMP dataset varies between sites and across the analytical range (i.e., there is a step change in quoted analytical resolution at threshold values). Given that this report shows that concentrations of water quality constituents are trending down across the majority of sites, data resolution and detection limits will become more important in future analyses of the RMWQMP dataset. A key recommendation of this report is that minimum standards for data resolution and detection limits be set by the MDBA, commensurate with the composition of the surface sites that form part of the RMWQMP network. By way of a guide, examples of currently achievable instrument precision and detection limits are listed in Table 5. It is further recommended that a standard monitoring protocol be developed that outlines the key variables required to be monitored, standardises methods of collection, measurement, expected analytical precision, reporting units and nomenclature of key parameters.

Table 5. Typical ranges for key water quality parameters in the RMWQMP dataset; recommended recording resolution; achievable analytical precision; achievable detection limits; stations currently recording low precision data.

Water Quality Parameter	Typical range (units)	Recommended reporting resolution	Achievable instrument precision *	Achievable detection limits *	Stations with low resolution data
Field pH	6 - 8	0.01	0.01 †	NA	Murray River d/s Yarrawonga
Water temperature	5 – 35 (°C)	0.1	0.1 †	NA	River Murray at Waikerie (and all stations downstream)
Dissolved Oxygen	0 – 15 (mg-O ₂ /L)	0.01	0.01 †	NA	None
Electrical conductivity	1 – 500 (µS/cm)	0.1 (0 – 100) 1 (>100)	0.001 †	NA	All upper Murray and upper tributary sites

Turbidity	0 – 500 (NTU)	0.1 (0 – 100) 1 (>100)	0.1 †	NA	None
Alkalinity	1 - 100 (mg- CaCO ₃ /L)	0.1	0.5 ‡	0.5 ‡	None
Dissolved organic carbon	0 – 20 (mg-C/L)	0.1	0.22	0.38	Campaspe at Rochester, Wakool at Kyalite, River Murray at Merbein, Darling at Burtundy
Total Kjeldahl nitrogen	0.1 – 1 (mg-N/L)	0.01	0.019	0.014	Broken Creek at Katamatite, Campaspe at Rochester, Wakool at Kyalite, River Murray at Merbein, Darling River at Burtundy
Nitrogen oxides	0.01 – 0.1 (mg-N/L)	0.001	0.003	0.002	Murray River d/s Yarrawonga, Wakool at Kyalite, River Murray at Merbein, Darling River at Burtundy 0.01 resolution (>0.1): River Murray at Jingellic, Murray River at Heywoods, Ovens River at Peechelba
Total phosphorus	0.01 – 0.5 (mg-P/L)	0.001 (0 – 0.1) 0.01 (>0.1)	0.005	0.005	None
Soluble reactive phosphorus	0.01 – 0.05 (mg-P/L)	0.001	0.005	0.005	Murray River d/s Yarrawonga, Wakool at Kyalite, River Murray at Merbein, Darling River at Burtundy
Dissolved silicon	0 – 20 (mg-SiO ₂ /L)	0.1	0.002	0.012	1.0 resolution (>10 mg-SiO ₂ /L): River Murray at Jingellic, Murray River at Heywoods, Mitta Mitta River at Tallandoon, Kiewa River at Bandiana, Ovens River at Peechelba

* Data obtained from commercial NATA accredited laboratories (CSIRO Land and Water; Southern Cross University – Environmental Analysis Laboratory); † Specifications of YSI Pro DSS Multiparameter Water Quality Meter; ‡ alkalinity by titration (Standard Methods for the Examination of Water and Wastewater, 19th ed)

Comments on the WQ telemetry network

The telemetry network represents an important advance in our ability to measure and respond to changes in water quality in the River Murray and tributary rivers. While the early implementation WQ telemetry was strongly focused on EC and Temperature, more recent sensor installations have included turbidity, pH and DO. In general, telemetry measurements of WQ are strongly focused on upper Murray and tributary sites (Table A1).

The WQ telemetry system should not be seen to replace the existing spot measurement program as it is: (i) limited to physical WQ parameters, and (ii) likely to encounter reliability issues. However:

there are several advantages of the WQ telemetry network over spot measurement, including:

- Unattended data acquisition: the ability to acquire WQ information without the attendance of field staff allows data collection to continue through events and conditions where access may be difficult (e.g., post-fire response, high discharge conditions in lowland rivers)
- The high frequency of the WQ telemetry system allows fast processes to be captured, which is particularly advantageous in upper catchments where pulse events are likely to be short in duration
- More frequent measurement makes it more likely to capture excursions outside WQ guidelines
- Telemetric WQ monitoring provides the opportunity for real-time management and response to changes in WQ that are outside guidelines and/or targets.

Two scenarios where telemetry data are highly useful are: (i) wildfire run-off events in upper catchments, and (ii) low DO (blackwater) events in mid to lower Murray locations (see below).

POST-FIRE RESPONSE

As shown for the River Murray at Jingellic site (Scenario: Wildfire) the WQ telemetry system is very effective at capturing post-fire run-off events, with the detection of short timescale changes in turbidity, EC, DO and pH, broadly consistent with that expected from fire affected catchments. High frequency measurement is essential in these settings for capturing high-load pulse events that typically occur over short time scales (hours-days). The suite of physical WQ parameters measured at the Jingellic site should be emulated at other upper tributary sites draining mountainous catchments; in general this has occurred in many of the upper tributaries (Kiewa and Ovens rivers; Table A1). Further, telemetry 'networks' along these tributaries would allow the tracking of fire debris movement in real time. A network of this type would also allow more detailed analysis of sub-catchment processes.

BLACKWATER RESPONSE

As noted above (Scenario: Blackwater) spot measurements are unlikely to provide capacity for real-time management and intervention of blackwater events given the delay between measurement and reporting; telemetry measurement of DO does offer the capacity to respond to the formation of low DO (blackwater) conditions. Real-time measurement of DO through the water quality telemetry system has been implemented at a number of sites in the River Murray and tributaries, although the majority of these sites are in the upper reaches and have been operating over recent years only (2019 onwards) (Table A1). Longer DO telemetry records are available for two sites (Murrumbidgee @ Balranald; Darling @ Burtundy; 2012 - 2022). A number of these sites have a fragmented data record, presumably due to failure of sensors under operating conditions. The most notable feature of the current configuration is the absence of any functioning DO telemetry sites in the main channel of the River Murray downstream of the River Murray @ Heywoods site. These sites are the most likely to receive floodplain return water that could result in DO drawdown events. Without this information there is no capacity to respond to low DO conditions in a timely way. Importantly, DO telemetry does exist for some of the mid-Murray tributaries (Broken, Goulburn, Murrumbidgee and Darling rivers) providing some capacity for anticipating low DO conditions in the River Murray.

A potential improvement in predicting the onset of low DO conditions is through the real-time measurement of dissolved organic carbon (DOC). DOC measurement provides more advanced warning of potential DO drawdown as the leaching of organic carbon from litter precedes oxygen drawdown; DOC concentrations also provide a measure of the potential DO consumption (based on prior knowledge of the biodegradability and oxygen consumption of floodplain derived DOC). DOC sensors are typically optically-based (absorbance @ 250 nm) and are commonly used in 'hostile' water quality environments (e.g., wastewater plants). Optically based sensors can be used as a proxy for DOC concentration, however, are highly dependant on the type of DOC present and turbidity effects. Calibration of sensor measurements against site specific DOC and likely turbidity levels is thus recommended and would also allow carbon loads to be calculated more accurately (Ruhala and Zarnetske, 2017).

Opportunities for new technologies and further investigations

We propose a number of targeted projects and other opportunities to augment the RMWQMP, broadly based on the recommendations contained in this report. These projects and initiatives range from desktop analyses using existing data in the RMWQMP and/or the telemetry data record, to field-based studies and associated laboratory investigations.

Organic carbon characteristics in the River Murray and tributary rivers

The analysis of tributary junctions along the River Murray revealed some differences in water quality between main channel and tributary sites for the upper Murray, particularly with respect to seasonal availability of some nutrients (NO_x and silica; Scenario: Tributary effects). There was, however, very little difference in the DOC concentrations between main channel and tributary sites for these confluences. While there was no substantial difference in the levels of DOC, we could expect a difference in the type of carbon in the main channel and tributary sites. Specifically, higher levels of allochthonous (terrestrial) carbon are expected in unregulated systems due to the strong connectivity with terrestrial landscape. By contrast, DOC from reservoirs is expected to be more autochthonous in character, reflecting the dominance of algal production in reservoirs, and the trapping of particulate organic carbon (POC) through sedimentation. The confluence of a regulated and unregulated river can result in the mixing of these different types of organic carbon. This mixing can give rise to so-called 'priming effects' where carbon assimilation is accelerated and in-stream productivity is enhanced; this productivity can be directly linked to the basal resources available to support food webs. While the analysis of organic carbon characteristics is not necessarily suited to routine monitoring programs, targeted studies around these tributary junctions could characterise the differences in organic carbon (both dissolved and particulate) present in the regulated and unregulated systems. It is likely that the unregulated (or weakly regulated) tributaries along the River Murray are critically important for maintaining productivity in the River Murray.

Silica depletion in the River Murray and the potential link to blue-green algal (BGA) blooms

The seasonal depletion of silica from the regulated flow at the Murray River at Heywoods and Murray River d/s Yarrowonga sites has not been reported in previous trends analyses (to our knowledge). The observed depletion of this nutrient amounts to an order of magnitude (factor 10) decrease in silica availability in summer – autumn, with a strong recovery in winter – spring, likely due to re-supply from upstream (unregulated) rivers. While a general long-term decrease in silica is observed across nearly all of the sites selected for this study, the seasonal aspect of this depletion is not captured by the long-term trends analysis. Seasonal silica-depletion is not observed in the unregulated rivers of the upper Murray and strongly suggests that the associated reservoirs (Lake Hume and Lake Mulwala) are acting as silica-traps (Maavara 2020). The availability of silica in aquatic systems is likely to drive the relative abundance of different algal groups and may be related to the (increasing) occurrence of blue-green algae (BGA) in the River Murray. A current analysis of the long-term algal dataset for the MDBA being conducted by La

Trobre University (MDBA Algal data trend analysis) will further investigate the potential correlation between silica availability and BGA frequency. Depending on the outcome of this current study, the link between silica availability and algal community structure could be further investigated in controlled laboratory studies. These studies could in turn inform potential management options and responses.

Real time analysis of telemetry data

The acquisition of high-frequency real-time data through the water quality telemetry network presents an opportunity to understand river function in ways that were previously unavailable. As noted above (Scenario: wildfire) the WQ telemetry system provides the opportunity to detect short timescale events that would not be detected by the spot measurement system and to respond to these events in a timely way (i.e., advice to downstream users). The high frequency nature of the data also allows more detailed catchment analysis through C-Q response and/or links to sub-catchment run-off data. The addition of new sensors (e.g., DOC, NO_x) at the telemetry sites will increase the power of this network to detect runoff events. The WQ telemetry network also allows excursions in water quality parameters outside of target or trigger values to be more reliably detected.

Loads analysis using high frequency telemetry data

The estimation of loads from spot data measurements has an inherent risk of under-estimating the contributions of high flow events (Baldwin 2013). The availability of high frequency data from the WQ telemetry network allows the direct comparison of load estimates from high frequency and spot measurement data. Given that the accurate calculation of loads is a key justification for the existing sampling frequency in the RMWQMP (Biswas and Lawrence, 2013), the availability of high frequency data provides the opportunity to rigorously assess this need. Specifically, we suggest a targeted project investigating sites with available electrical conductivity (EC) telemetry data, with the load estimates calculated from the high frequency data and compared to load estimates calculated from spot measurement data at different frequencies (i.e., weekly, fortnightly and monthly). Given that monthly frequency is sufficient for the purpose of assessing long-term changes in WQ (i.e., trends), the use of telemetry data for the calculation of loads potentially relaxes the requirement for higher frequency spot sampling. Similar load calculations could also be achieved with TP due to the high correlation with turbidity. The addition of further sensors in the WQ telemetry network (e.g., DOC) would increase the capacity of these data to provide accurate load information.

Potential occurrence of emerging contaminants in the River Murray

While emerging contaminants (e.g., microplastics, PFAS) are not routinely monitored within the MDB, the limited measurements that have been taken suggest that levels of some contaminants can exceed ANZG guidelines (where these are available) or other recommended limits. Given the increase in anthropogenic pressures within the Basin, and elevated risks of emerging contaminants being released to the environment, it is recommended that further investigations be undertaken to determine the spatial distributions and levels of these contaminants. Such investigations are essential to understanding the potential risks to aquatic biota and human health. These investigations should be based around known, or likely, sources of these contaminants and ideally incorporate existing RMWQMP sites.

References

- EPA 2020. PFAS National Environmental Management Plan Version 2.0. In: ZEALAND, E. A. A. N. (ed.).
- ABRAM, N. J., HENLEY, B. J., SEN GUPTA, A., LIPPMANN, T. J. R., CLARKE, H., DOWDY, A. J., SHARPLES, J. J., NOLAN, R. H., ZHANG, T., WOOSTER, M. J., WURTZEL, J. B., MEISSNER, K. J., PITMAN, A. J., UKKOLA, A. M., MURPHY, B. P., TAPPER, N. J. & BOER, M. M. 2021. Connections of climate change and variability to large and extreme forest fires in southeast Australia. *Communications Earth & Environment*, 2, 8.
- ARTS, M. T., ACKMAN, R. G. & HOLUB, B. J. 2001. "Essential fatty acids" in aquatic ecosystems: a crucial link between diet and human health and evolution. *Canadian Journal of Fisheries and Aquatic Sciences*, 58, 122-137.
- AZAML, F., FENCHE, T., FIELD, J., GRA, J., MEYER-REI, L. & THINGSTAD, F. 1983. The ecological role of water-column microbes in the sea. *Marine Ecology - Progress Series*, 10, 257-263.
- BALDWIN, D. S., WHITWORTH, K. & PENGELLY, J. 2013. Investigating the influences of changes in the river murray water quality monitoring program on future capacity to detect trends in water quality. *Internal MDBA report*.
- BERNER, E. K. & BERNER, R. A. 2012. *Global environment: water, air, and geochemical cycles*, Princeton University Press.
- BISWAS, T. & LAWRENCE, B. 2013. Revision of the River Murray Water Quality Monitoring Program. *Internal MDBA report*.
- BISWAS, T. K. & MOSLEY, L. M. 2019. From mountain ranges to sweeping plains, in droughts and flooding rains; River Murray water quality over the last four decades. *Water Resources Management*, 33, 1087-1101.
- BIXBY, R. J., COOPER, S. D., GRESSWELL, R. E., BROWN, L. E., DAHM, C. N. & DWIRE, K. A. 2015. Fire effects on aquatic ecosystems: an assessment of the current state of the science. *Freshwater Science*, 34, 1340-1350.
- BOULTON, A., BROCK, M., ROBSON, B., RYDER, D., CHAMBERS, J. & DAVIS, J. 2014. *Australian freshwater ecology: processes and management*, John Wiley & Sons.
- BRITTON, D. 1990. Fire and the dynamics of allochthonous detritus in a South African mountain stream. *Freshwater Biology*, 24, 347-360.
- BROOKS, M. E., KRISTENSEN, K., VAN BENTHEM, K. J., MAGNUSSON, A., BERG, C. W., NIELSEN, A., SKAUG, H. J., MACHLER, M. & BOLKER, B. M. 2017. glmmTMB balances speed and flexibility among packages for zero-inflated generalized linear mixed modeling. *The R journal*, 9, 378-400.
- BUREAU OF METEOROLOGY 2014. Australian Hydrological Geospatial Fabric (Geofabric) V2.1.1. In: BUREAU OF METEOROLOGY, I. S. A. S. D. (ed.).
- CERTINI, G. 2005. Effects of fire on properties of forest soils: a review. *Oecologia*, 143, 1-10.
- COGGAN, T. L., MOODIE, D., KOLOBARIC, A., SZABO, D., SHIMETA, J., CROSBIE, N. D., LEE, E., FERNANDES, M. & CLARKE, B. O. 2019. An investigation into per- and polyfluoroalkyl substances (PFAS) in nineteen Australian wastewater treatment plants (WWTPs). *Heliyon*, 5, e02316.
- COHN, T. A. 1995. Recent advances in statistical methods for the estimation of sediment and nutrient transport in rivers. *Reviews of Geophysics*, 33, 1117-1123.
- COUSINS, I. T., JOHANSSON, J. H., SALTER, M. E., SHA, B. & SCHERINGER, M. 2022. Outside the Safe Operating Space of a New Planetary Boundary for Per- and Polyfluoroalkyl Substances (PFAS). *Environmental Science & Technology*.
- DAHM, C. N., CANDELARIA-LEY, R. I., REALE, C. S., REALE, J. K. & VAN HORN, D. J. 2015. Extreme water quality degradation following a catastrophic forest fire. *Freshwater Biology*, 60, 2584-2599.
- DIEMER, L. A., MCDOWELL, W. H., WYMORE, A. S. & PROKUSHKIN, A. S. 2015. Nutrient uptake along a fire gradient in boreal streams of Central Siberia. *Freshwater Science*, 34, 1443-1456.
- DUNCAN, J. M., BAND, L. E., GROFFMAN, P. M. & BERNHARDT, E. S. 2015. Mechanisms driving the seasonality of catchment scale nitrate export: Evidence for riparian ecohydrologic controls. *Water Resources Research*, 51, 3982-3997.
- DWYER, G. K., STOFFELS, R. J., REES, G. N., SHACKLETON, M. E. & SILVESTER, E. 2018. A predicted change in the amino acid landscapes available to freshwater carnivores. *Freshwater Science*, 37, 108-120.
- EBELE, A. J., ABDALLAH, M. A.-E. & HARRAD, S. 2017. Pharmaceuticals and personal care products (PPCPs) in the freshwater aquatic environment. *Emerging contaminants*, 3, 1-16.
- EBSARY, E. 2021. another community struggles to come to terms with pfas contamination. *Katherine Times*.
- EMELKO, M. B., STONE, M., SILINS, U., ALLIN, D., COLLINS, A. L., WILLIAMS, C. H., MARTENS, A. M. & BLADON, K. D. 2016. Sediment-phosphorus dynamics can shift aquatic ecology and cause downstream legacy effects after wildfire in large river systems. *Global Change Biology*, 22, 1168-1184.
- FRIEDL, G. & WÜEST, A. J. A. S. 2002. Disrupting biogeochemical cycles - Consequences of damming. *Aquatic Sciences*, 64, 55-65.
- GOLDMAN, J. C. & DENNETT, M. R. 2000. Growth of marine bacteria in batch and continuous culture under carbon and nitrogen limitation. *Limnology and Oceanography*, 45, 789-800.
- GRESSWELL, R. E. 1999. Fire and aquatic ecosystems in forested biomes of North America. *Transactions of the American fisheries society*, 128, 193-221.
- GUNNARSSON, I. & ARNÓRSSON, S. 2000. Amorphous silica solubility and the thermodynamic properties of H₄SiO₄ in the range of 0 to 350 C at Psat. *Geochimica et Cosmochimica Acta*, 64, 2295-2307.

- HARPER, A. R., SANTIN, C., DOERR, S. H., FROYD, C. A., ALBINI, D., OTERO, X. L., VIÑAS, L. & PÉREZ-FERNÁNDEZ, B. 2019. Chemical composition of wildfire ash produced in contrasting ecosystems and its toxicity to *Daphnia magna*. *International Journal of Wildland Fire*, 28, 726-737.
- HARRIS, C. W., REES, G. N., STOFFELS, R. J., PENGELLY, J., BARLOW, K. & SILVESTER, E. 2018. Longitudinal trends in concentration and composition of dissolved organic nitrogen (DON) in a largely unregulated river system. *Biogeochemistry*, 139, 139-153.
- HARRIS, H. E., BAXTER, C. V. & DAVIS, J. M. 2015. Debris flows amplify effects of wildfire on magnitude and composition of tributary subsidies to mainstem habitats. *Freshwater Science*, 34, 1457-1467.
- HENDERSON, B., LIU, Y. & BALDWIN, D. 2013. Trends in physical and chemical aspects of water quality in the Murray-Darling basin 1978-2012. CSIRO Water for a Healthy Country Flagship, Australia.
- HOLLAND, A., MORALES, Y., SILVESTER, E., SIEBERS, A., ROCHELLE, P., S, B., BEN, T. & NICK, B. 2020. Allochthonous carbon loads and modelled dissolved organic carbon concentrations at Lindsay Island, Mulcra Island and Hattah Lakes floodplains during environmental watering. *Centre for Freshwater Ecosystems report*.
- HOLLAND, A., STAUBER, J., WOOD, C. M., TRENFIELD, M. & JOLLEY, D. F. 2018. Dissolved organic matter signatures vary between naturally acidic, circumneutral and groundwater-fed freshwaters in Australia. *Water Research*, 137, 184-192.
- HOLLIBAUGH, J. & AZAM, F. 1983. Microbial degradation of dissolved proteins in seawater 1. *Limnology and Oceanography*, 28, 1104-1116.
- JOHNSON, M. S., COUTO, E. G., ABDO, M. & LEHMANN, J. 2011. Fluorescence index as an indicator of dissolved organic carbon quality in hydrologic flowpaths of forested tropical watersheds. *Biogeochemistry*, 105, 149-157.
- JUNK, W. J., BAYLEY, P. B., SPARKS, R. E. J. C. S. P. O. F. & SCIENCES, A. 1989. The flood pulse concept in river-floodplain systems. 106, 110-127.
- KAINZ, M., ARTS, M. T. & MAZUMDER, A. 2004. Essential fatty acids in the planktonic food web and their ecological role for higher trophic levels. *Limnology and Oceanography*, 49, 1784-1793.
- KENNEDY, R. H. & WALKER, W. W. 1990. Reservoir nutrient dynamics. *Reservoir limnology: ecological perspectives*, 109-131.
- KERR, J. L., BALDWIN, D. S. & WHITWORTH, K. L. 2013. Options for managing hypoxic blackwater events in river systems: a review. *Journal of Environmental Management*, 114, 139-147.
- KIELY, G. 1997. *Environmental Engineering*, London, McGraw-Hill.
- KING, A. D., PITMAN, A. J., HENLEY, B. J., UKKOLA, A. M. & BROWN, J. R. 2020. The role of climate variability in Australian drought. *Nature Climate Change*, 10, 177-179.
- KLEINDL, W., RAINS, M. C., MARSHALL, L. & HAUER, F. 2015. Fire and flood expand the floodplain shifting habitat mosaic concept. *Freshwater Science*, 34, 1366-1382.
- KORTELAINEN, P., MATTSSON, T., FINÉR, L., AHTIAINEN, M., SAUKKONEN, S. & SALLANTAUS, T. 2006. Controls on the export of C, N, P and Fe from undisturbed boreal catchments, Finland. *Aquatic Sciences*, 68, 453-468.
- KOWALCZYK, N., BLAKE, N., CHARKO, F. & QUEK, Y. 2017. Microplastics in the Maribyrnong and Yarra Rivers, Melbourne, Australia. Port Phillip Ecocentre, Victorian Government litter hotspots program.
- KUEHN, K. A., FRANCOEUR, S. N., FINDLAY, R. H. & NEELY, R. K. 2014. Priming in the microbial landscape: periphytic algal stimulation of litter-associated microbial decomposers. *Ecology*, 95, 749-762.
- LEE, C. 1993. Dissolved free amino acids, combined amino acids, and DNA as sources of carbon and nitrogen to marine bacteria. *Marine Ecology Progress Series*, 98, 135-148.1993.
- LI, C., BUSQUETS, R. & CAMPOS, L. C. 2020. Assessment of microplastics in freshwater systems: A review. *Science of the Total Environment*, 707, 135578.
- LIU, H., JEONG, J., GRAY, H., SMITH, S. & SEDLAK, D. L. 2012. Algal uptake of hydrophobic and hydrophilic dissolved organic nitrogen in effluent from biological nutrient removal municipal wastewater treatment systems. *Environmental science & technology*, 46, 713-721.
- LÜDECKE, D. 2018. ggeffects: Tidy data frames of marginal effects from regression models. *Journal of Open Source Software*, 3, 772.
- MAAVARA, T., CHEN, Q., VAN METER, K., BROWN, L. E., ZHANG, J., NI, J. & ZARFL, C. 2020. River dam impacts on biogeochemical cycling. *Nature Reviews Earth & Environment*, 1, 103-116.
- MAAVARA, T., LAUERWALD, R., REGNIER, P. & VAN CAPPELLEN, P. 2017. Global perturbation of organic carbon cycling by river damming. *Nature Communications*, 8, 15347.
- MAAVARA, T., PARSONS, C. T., RIDENOUR, C., STOJANOVIC, S., DÜRR, H. H., POWLEY, H. R. & VAN CAPPELLEN, P. J. P. O. T. N. A. O. S. 2015. Global phosphorus retention by river damming. 112, 15603-15608.
- MATTSSON, T., KORTELAINEN, P., LAUBEL, A., EVANS, D., PUJO-PAY, M., RÄIKE, A. & CONAN, P. 2009. Export of dissolved organic matter in relation to land use along a European climatic gradient. *Science of the Total Environment*, 407, 1967-1976.
- MCKNIGHT, D. M., BOYER, E. W., WESTERHOFF, P. K., DORAN, P. T., KULBE, T. & ANDERSEN, D. T. 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnology and Oceanography*, 46, 38-48.
- MOSLEY, L. M. 2015. Drought impacts on the water quality of freshwater systems; review and integration. *Earth-Science Reviews*, 140, 203-214.

- OHTE, N., TOKUCHI, N. & FUJIMOTO, M. 2010. Seasonal patterns of nitrate discharge from forested catchments: information derived from Japanese case studies. *Geography compass*, 4, 1358-1376.
- PEBESMA, E. 2018. Simple Features for R: Standardized Support for Spatial Vector Data. *The R Journal*, 10, 8.
- PEÑA-GUERRERO, M. D., NAUDITT, A., MUÑOZ-ROBLES, C., RIBBE, L. & MEZA, F. 2020. Drought impacts on water quality and potential implications for agricultural production in the Maipo River Basin, Central Chile. *Hydrological Sciences Journal*, 65, 1005-1021.
- PINHEIRO, J. P. S., WINDSOR, F. M., WILSON, R. W. & TYLER, C. R. 2021. Global variation in freshwater physico-chemistry and its influence on chemical toxicity in aquatic wildlife. *Biological Reviews*, 96, 1528-1546.
- PLANAS, D., DESROSIERS, M., GROULX, S.-R., PAQUET, S. & CARIGNAN, R. 2000. Pelagic and benthic algal responses in eastern Canadian Boreal Shield lakes following harvesting and wildfires. *Canadian Journal of Fisheries and Aquatic Sciences*, 57, 136-145.
- QGIS DEVELOPMENT TEAM 2021. QGIS Geographic Information System,. Open Source Geospatial Foundation.
- REALE, J. K., VAN HORN, D. J., CONDON, K. E. & DAHM, C. N. 2015. The effects of catastrophic wildfire on water quality along a river continuum. *Freshwater Science*, 34, 1426-1442.
- RICHMOND, E. K., ROSI, E. J., WALTERS, D. M., FICK, J., HAMILTON, S. K., BRODIN, T., SUNDELIN, A. & GRACE, M. R. 2018. A diverse suite of pharmaceuticals contaminates stream and riparian food webs. *Nature Communications*, 9, 1-9.
- ROBERTS, J., KUMAR, A., DU, J., HEPPLWHITE, C., ELLIS, D. J., CHRISTY, A. G. & BEAVIS, S. G. 2016. Pharmaceuticals and personal care products (PPCPs) in Australia's largest inland sewage treatment plant, and its contribution to a major Australian river during high and low flow. *Science of the total environment*, 541, 1625-1637.
- RUHALA, S. S. & ZARNETSKE, J. P. 2017. Using in-situ optical sensors to study dissolved organic carbon dynamics of streams and watersheds: A review. *Science of the Total Environment*, 575, 713-723.
- SCHINDLER, D., NEWBURY, R., BEATY, K., PROKOPOWICH, J., RUSZCZYNSKI, T. & DALTON, J. 1980. Effects of a windstorm and forest fire on chemical losses from forested watersheds and on the quality of receiving streams. *Canadian Journal of Fisheries and Aquatic Sciences*, 37, 328-334.
- SCOTT, P. D., BARTKOW, M., BLOCKWELL, S. J., COLEMAN, H. M., KHAN, S. J., LIM, R., MCDONALD, J. A., NICE, H., NUGEGODA, D. & PETTIGROVE, V. 2014. A national survey of trace organic contaminants in Australian rivers. *Journal of environmental quality*, 43, 1702-1712.
- SIMPSON, G. L. 2018. Modelling Palaeoecological Time Series Using Generalised Additive Models. *Frontiers in Ecology and Evolution*, 6.
- SPENCER, C. N. & HAUER, F. R. 1991. Phosphorus and nitrogen dynamics in streams during a wildfire. *Journal of the North American Benthological Society*, 10, 24-30.
- STUMM, W. 1987. *Aquatic surface chemistry: Chemical processes at the particle-water interface*, John Wiley & Sons.
- STUMM, W. & MORGAN, J. J. 1981. *Aquatic Chemistry*, New York, John Wiley & Sons.
- SZABO, D., MOODIE, D., GREEN, M. P., MULDER, R. A. & CLARKE, B. O. 2022. Field-Based Distribution and Bioaccumulation Factors for Cyclic and Aliphatic Per- and Polyfluoroalkyl Substances (PFASs) in an Urban Sedentary Waterbird Population. *Environmental Science & Technology*.
- TANG, F. H., LENZEN, M., MCBRATNEY, A. & MAGGI, F. 2021. Risk of pesticide pollution at the global scale. *Nature Geoscience*, 14, 206-210.
- TUPAS, L. & KOIKE, I. 1990. Amino acid and ammonium utilization by heterotrophic marine bacteria grown in enriched seawater. *Limnology and Oceanography*, 35, 1145-1155.
- VERKAIK, I., RIERADEVALL, M., COOPER, S. D., MELACK, J. M., DUDLEY, T. L. & PRAT, N. 2013. Fire as a disturbance in Mediterranean climate streams. *Hydrobiologia*, 719, 353-382.
- VICENTE-SERRANO, S. M., BEGUERÍA, S. & LÓPEZ-MORENO, J. I. 2010. A multiscalar drought index sensitive to global warming: the standardized precipitation evapotranspiration index. *Journal of climate*, 23, 1696-1718.
- VINSON, M. R. 2001. Long-term dynamics of an invertebrate assemblage downstream from a large dam. *Ecological Applications*, 11, 711-730.
- WALKER, K. F. A review of the ecological effects of river regulation in Australia. 1985 Dordrecht. Springer Netherlands, 111-129.
- WARD, J. V. & STANFORD, J. A. 1995. The serial discontinuity concept: Extending the model to floodplain rivers. 10, 159-168.
- WETZEL, R. G. 2001. *Limnology: lake and river ecosystems*, gulf professional publishing.
- WHITWORTH, K. L. & BALDWIN, D. S. 2016. Improving our capacity to manage hypoxic blackwater events in lowland rivers: the blackwater risk assessment tool. *Ecological Modelling*, 320, 292-298.
- WHITWORTH, K. L., BALDWIN, D. S. & KERR, J. L. 2012. Drought, floods and water quality: drivers of a severe hypoxic blackwater event in a major river system (the southern Murray–Darling Basin, Australia). *Journal of Hydrology*, 450, 190-198.