Cockburn Sound benthic biogeochemistry - Final Report

Theme: Water and Sediment Quality

WAMSI Westport Marine Science Program

WESTERN AUSTRALIAN MARINE SCIENCE INSTITUTION

WESTPORT

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WAMSI WESTPORT MARINE SCIENCE PROGRAM

ABOUT THE MARINE SCIENCE PROGRAM

The WAMSI Westport Marine Science Program (WWMSP) is a $13.5 million body of marine research funded by the WA Government. The aims of the WWMSP are to increase knowledge of Cockburn Sound in areas that will inform the environmental impact assessment of the proposed Westport development and help to manage this important and heavily used marine area into the future. Westport is the State Government's program to move container trade from Fremantle to Kwinana, and includes a new container port and associated freight, road and rail, and logistics. The WWMSP comprises more than 30 research projects in the biological, physical and social sciences that are focused on the Cockburn Sound area. They are being delivered by more than 100 scientists from the WAMSI partnership and other organisations.

FUNDING SOURCES

The $13.5 million WAMSI Westport Marine Science Program was funded by the Western Australian Government, Department of Transport. WAMSI partners provided significant in-kind funding to the program to increase the value to >$22 million.

DATA

Finalised datasets will be released as open data, and data and/or metadata will be discoverable through Data WA and the Shared Land Information Platform (SLIP).

YEAR OF PUBLICATION

September 2025

This report is part of the project: Cockburn Sound benthic nutrient flux dynamics.

CITATION

Eyre, B., van Haastregt, B., Eyre, J., Yeo, J. (2025). Cockburn Sound Benthic Biogeochemistry Final Report. Prepared for the WAMSI Westport Marine Science Program. Western Australian Marine Science Institution, Perth, Western Australia. 38 pp.

FRONT COVER IMAGE

Theme: Water and Sediment Quality

Front cover image: Drone image of Cockburn Sound coastline. Photo courtesy of Michael Cuttler (The University of Western Australia).

Contents

The WAMSI Westport Marine Science Program is a $13.5 million body of research that is designed to fill knowledge gaps relating to the Cockburn Sound region. It was developed with the objectives of improving the capacity to avoid, mitigate and offset environmental impacts of the proposed Westport container port development and increase the WA Government's ability to manage other pressures acting on Cockburn Sound into the future. Funding for the program has been provided by Westport (through the Department of Transport) and the science projects are being delivered by the Western Australian Marine Science Institution.

1 Cockburn Sound Benthic Biogeochemistry Final Report

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Project

3.5.1 Cockburn Sound Benthic Nutrient Flux Dynamics

Executive Summary

The Centre for Coastal Biogeochemistry was commissioned by the Western Australian Marine Science Institution (WAMSI) to undertake a sediment biogeochemistry study of Cockburn Sound. Twelve sites, representing the major benthic habitat types in Cockburn Sound, were sampled in triplicate in April to May 2024.

Respiration rates at deep sites in the middle of Cockburn Sound were relatively low and reflect the decomposition of fresh to slightly degraded phyto-detritus. These sites were classified mostly as oligotrophic, with one site classified as slightly mesotrophic. The highest respiration rates were in the shallow sites due to the decomposition of organic matter produced in situ by benthic microalgae and epiphytes, and some seagrass detritus.

The four deep sites, and two shallow sites without seagrass (sites 7 and 8) showed net oxygen consumption with O_2 gross primary productivity/respiration ratios (P/R) below one. However, sediment oxygen demand (SOD) was well below the mean global SOD for shallow (0 to 10 m) marine shelf sediments. All the remaining shallow seagrass sites had O_2 P/R above one, reflecting net oxygen production. This highlights the important role of the shallow shelf sediments, and associated autotrophic communities, in maintaining oxygen concentrations in Cockburn Sound.

Across the Sound there was a net efflux of dissolved inorganic nitrogen (DIN) when the sediment O_2 P/R was <1, reflecting net heterotrophic sediments releasing nitrogen via respiration. In contrast, there was a net uptake of DIN when the sediment O_2 P/R was >1 reflecting net autotrophic sediments assimilating DIN to support gross primary productivity. The deep sites recycled DIN to water as expected for the amount of decomposition of phyto-detritus. In contrast, the shallow sites released little DIN, or took up both DIN and dissolved organic nitrogen (DON), due to nitrogen limitation in the sediments.

Total phosphorus concentrations in the bottom sediments range from 0.031 to 0.080%, which is similar to the range seen across Australian coastal systems (0.021 to 0.093%). Dissolved inorganic phosphorus (DIP) fluxes were all very small (<2 $\mu mol\ m^{-1}\ h^{-1}$), probably due to trapping of phosphorus in the oxidised upper sediment layers by iron oxy-hydroxides, possibly enhanced through the injection of oxygen by benthic productivity. The combined uptake of DIP + dissolved organic phosphorus (DOP) in the light was insufficient to support gross primary productivity, particularly at the shallow sites, and gross primary productivity was most likely supplied by the sediment pool of phosphorus. This pool of phosphorus in the sediments may drive the nitrogen limitation of benthic communities in Cockburn Sound.

Denitrification is coupled to nitrification in the sediments, and eight of the 12 sites showed a decrease in denitrification rates from the dark to light, most likely due to competition for NH_4^+ and NO_3^- by benthic primary producers. An increase in denitrification in the light (i.e. sites 7, 8, 11, 12) suggests they did not have resource limitation and the associated increase in oxygen penetration from benthic production would enhance coupled nitrification–denitrification and/or an increase in the supply of labile carbon for denitrification. The large NO_3^- fluxes at the deep sites suggests there may have been organic matter limitation of denitrification.

Eight of the 12 sites in Cockburn Sound were consistent with the denitrification efficiency (DE) versus carbon decomposition relationship that has been developed for the deposition mud basins of Australian estuaries. The low DE at deep sites 2 to 4 in the mud basin reflect organic matter limitation of denitrification. All four sites in the central mud basin had DE that would be classified as oligotrophic. Site 7 near the proposed Westport footprint and site 8 on the Southern Flats had DE that would be classified as mesotrophic and site 5 in the restored seagrass had DE that would be classified as eutrophic. Four sites did not fit the DE versus carbon decomposition relationship, mostly due to the dark assimilation of DIN by heterotrophic bacteria in the high C:N seagrass sites.

The DE optimum in Cockburn Sound occurs around dissolved inorganic carbon (DIC) flux of about 1,500 µmol m^{-2} h^{-1}, which is consistent with other coastal systems. The low concentrations of water column chlorophyll-a in Cockburn Sound are consistent with organic matter decomposition rates below 1200 µmol DIC m^{-2} h^{-1} in most of the central mud basin. Site 1 at the northern end has a higher organic matter deposition rate reflecting an input of other organic matter (e.g. seagrass). However, any increase above 2200 µmol DIC m^{-2} h^{-1} due to increased organic matter loading is likely to result in a drop in the DE in the central mud basin.

Plain English Summary

Sediment biogeochemical processes play a central role in maintaining the ecological health of Cockburn Sound by cleansing the system of nitrogen via denitrification. The shallow sediments also add oxygen to the water column. The sediment biogeochemical processes were functioning as expected for a healthy to slightly degraded ecosystem. The sediments had modest sediment oxygen consumption. However, any additional organic matter loading to the sediments, and further loss of seagrasses, would reduce the capacity of the system to remove nitrogen, and to add oxygen to the water column. The sampling for this project was only undertaken once in Autumn. Further work should be undertaken during periods of maximum bottom water temperature and low dissolved oxygen, and experimental work is required to better understand how the sediments will be impacted by future stressors such a low dissolved oxygen, warming and acidification.

2 Introduction

The Western Australian State Government plans to build a new container port at Outer Harbour in Cockburn Sound. Westport is a long-term program to investigate, plan and build the container port. To inform the planning of the container port, Westport, in partnership with the Western Australian Marine Science Institution (WAMSI), is undertaking a major marine science study (WAMSI Westport Marine Science Program) to independently and transparently address knowledge gaps and to research and trial restoration initiatives that will maintain ecosystem integrity within Cockburn Sound into the future. This project (3.5) *Cockburn Sound Benthic Nutrient Flux Dynamics* is part of Theme 3 on Water and Sediment Quality. Theme 3 will "deliver baseline monitoring and knowledge to address recognized knowledge gaps (e.g. a nutrient budget for Cockburn Sound) to adequately inform a cumulative environmental impact assessment and the effective ongoing environmental management of Cockburn Sound" (WAMSI Westport Marine Science Program 2022).

The aim of this project was to measure benthic metabolism and nutrient flux rates in the 12 major benthic habitat types in Cockburn Sound. These measured fluxes will be used to calibrate a fine-scale sediment biogeochemistry model of oxygen metabolism and nutrient cycling. In addition, this project assesses the overall "ecological health" of Cockburn Sound through several benthic indicators such as benthic respiration, gross primary productivity/respiration ratios (P/R), and denitrification efficiency.

3 Materials and Methods

Twelve major benthic habitats were identified in Cockburn Sound (Figure 1). These 12 major benthic habitats are mostly the habitats with the largest surface area, but also include habitats of particular interest (e.g. seagrass communities, dredge spoil restoration). These have been identified based on synthesis of past sediment type and benthic substrate data. The sites were split into three groups (A) deeper sites (i.e. sites 1 to 4), (B) the shallower sites in the southern Cockburn Sound (i.e. 5 to 8) and (C) shallower sites in the northern Cockburn Sound (i.e. 9 to 12), for the incubations (Figure 1; Table 1).

Table 1. Sample sites.

Site	Incubation	Location		Depth (m)	Description
1	A	-32.1444845	115.7039690	20.35	125-250 µm grainsize, central mud basin
2	A	-32.1806548	115.7148546	20.57	63-125 µm grainsize, central mud basin
3	A	-32.2166028	115.7230148	20.72	31-63 µm grainsize, central mud basin
4	A	-32.2506462	115.7346295	18.94	31-63 µm grainsize, central mud basin
5	B	-32.19066	115.746122	7.20	Seagrass dredge spoil restoration area I; decomposing seagrass in core
6	B	-32.19289	115.743299	7.48	Seagrass dredge spoil restoration area II; seagrass shoots in core
7	B	-32.21288	115.752896	7.95	125-250 µm grainsize area near to proposed Westport footprint
8	B	-32.26900	115.714560	5.58	350-500 µm grainsize area, Southern Flats
9	C	-32.1085176	115.7452494	8.60	Seagrass area; decomposing seagrass in sand
10	C	-32.1379079	115.7309483	8.75	Seagrass area, Parmelia Bank; seagrass shoots in sand
11	C	-32.1536793	115.7507840	9.81	500-1000 µm grainsize area, Jervoise Bank; seagrass shoots in sand
12	C	-32.1282670	115.6854408	5.74	Seagrass area off Garden Island; most dense seagrass in cores

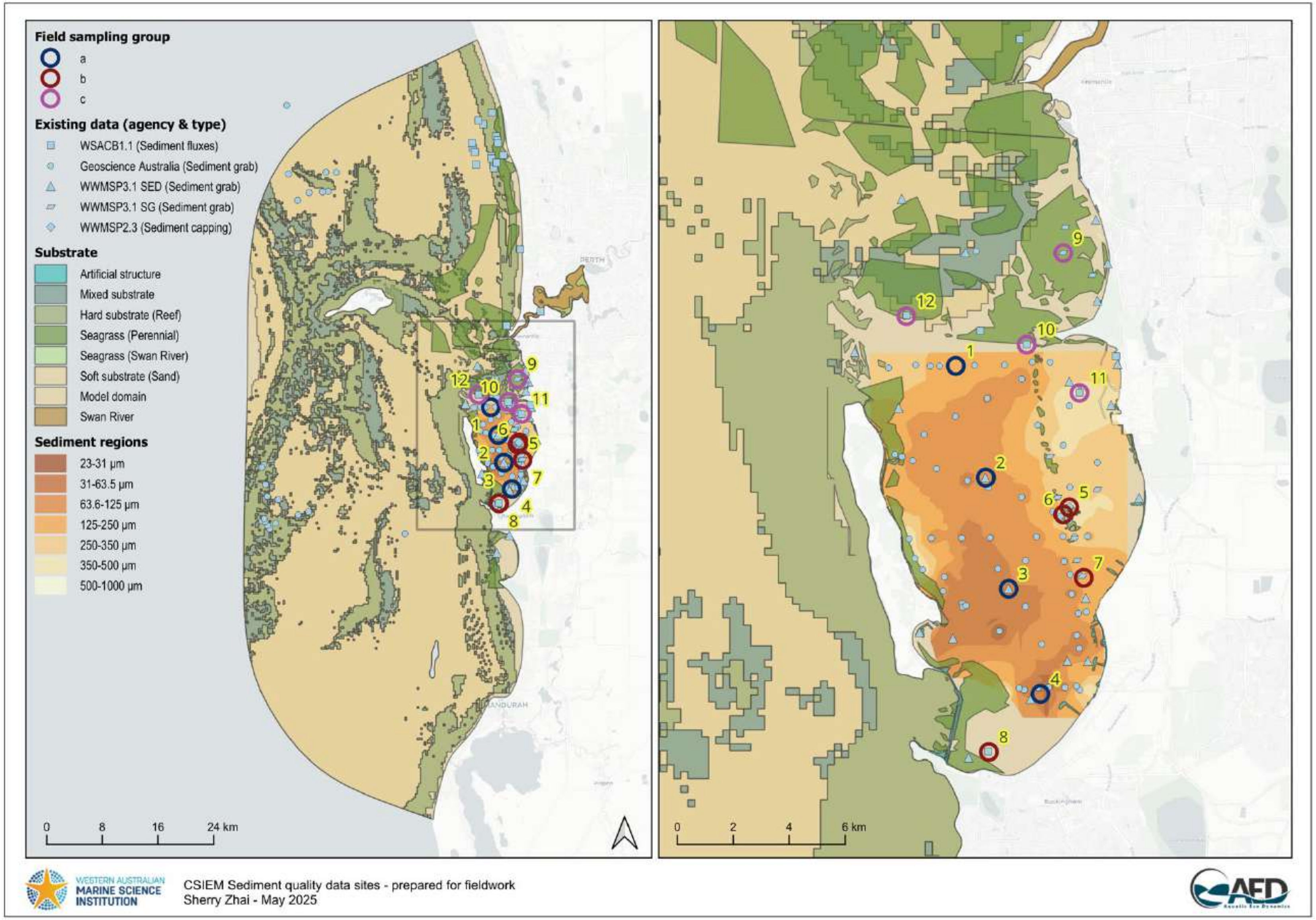

Figure 1. Map of the 12 sample sites where triplicate cores were collected.

Triplicate sediment cores were collected by divers at each of the 12 sites (Figure 1) (36 cores in total; see photos in Appendix 1) by divers in 95 mm internal diameter x 500 mm long clear Plexiglas tubes, retaining approximately 200 mm sediment and 300 mm (2.5 L) overlying water (Figures 2 and 3). Only cores with an undisturbed sediment surface were retained (Figure 3). Cores could only be collected in areas of sparse seagrass. Sampling was undertaken between 29 April and 3 May 2024. The wind was between 10 to 15 knots during sampling, which would result in no resuspension at the deep sites and some resuspension at the shallower sites. Vegetation would reduce resuspension at the shallower sites.

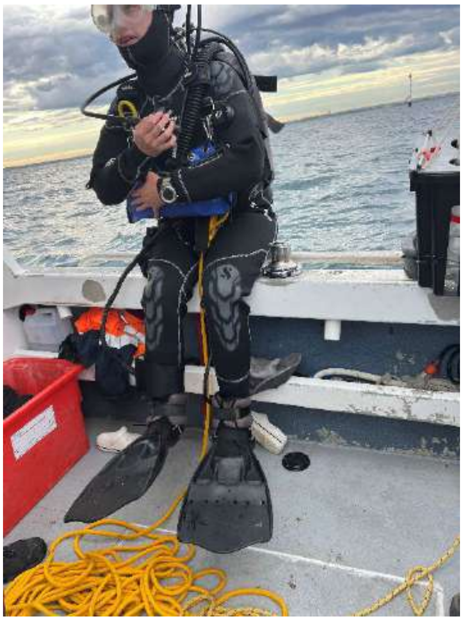

Figure 2. Diver about to collect undisturbed cores.

Figure 3. Undisturbed sediment core from a seagrass site.

Cores were transported to an on-shore laboratory within six hours of collection, where they were placed uncapped into an incubator with 150 L of recirculated and aerated site water at collection temperature. The site water was collected from just above the sediment surface in the middle of the four sites for each group (i.e. three incubations, one for each group A, B, C; Table 1). In situ diurnal light - dark climate was maintained throughout the incubation, and photosynthetically active radiation

(PAR) irradiance was set at the daily mean at the sediment surface at an average for the sites of collection, at the time of year the cores were collected; Group A 99 µE s^{-1}, Group B 10 µE s^{-1}, and Group C 99 µE s^{-1} PAR. Cores were equipped with self-stirrers set at 10 cm above the sediment surface and stirring rates set to just below resuspension. A 24-hour equilibration period was observed, and flux incubations started approximately at dawn the following evening.

Cores were capped and samples for the analysis of total alkalinity (TA), di-nitrogen gas (N_2), argon (Ar), ammonium (NH_4^+), nitrate (NO_3^-), dissolved organic nitrogen (DON), dissolved inorganic phosphorus (DIP), and dissolved organic phosphorus (DOP) were taken every six hours using three 50 mL plastic syringes (Figure 4). The replacement water was withdrawn from a sealed collapsible reservoir bag of site water, also equilibrated at in-situ temperature. TA samples were collected in 12 ml glass exetainers. Nutrient samples were passed through 0.45 µm filters and transferred to two 10 ml sample-rinsed polyethylene vials. N_2:Ar samples were collected in triplicate into 7 ml gas-tight glass-stoppered glass vials filled to overflowing. TA samples were stored refrigerated at 4°C. All nutrient samples were immediately frozen at -20 °C. N_2:Ar samples were poisoned with 20 µl of 5% $HgCl_2$ and stored submerged 1 to 2 °C below the incubation temperature. Dissolved oxygen concentrations (±0.01 mg L^{-1}) and pH (±0.001) were measured in the cores electro-chemically using a Metrohm Electrode Plus pH and dissolved oxygen probe. At the end of the incubation one core from each site was extruded and the top 2 mm of sediment collected for chlorophyll-a, and the top 2 cm of sediment was collected for organic carbon, nitrogen and phosphorus concentrations. Chlorophyll-a samples were placed immediately in 90% acetone in 15 mL centrifuge tubes and stored at 4 °C. Sediment samples were frozen at -20°C (Table 2).

Figure 4. Collecting samples during a core incubation at the on-site laboratory.

Table 2. Total numbers of cores collected, measurements made and samples collected. Dissolved oxygen (DO).

Cores	DO	pH	Temperature	Total Alkalinity	N_2: Ar	Inorganic Nutrients	Total Dissolved Nutrients	Sediment samples	Chlorophyll-a
36	180	180	180	180	540	180	180	12	12

3.1 Laboratory Analysis

TA samples were analysed immediately at the on-shore laboratory (Figure 5). N_2:Ar, nutrient, chlorophyll-a and sediment samples were transported back to Southern Cross University for analysis. TA was determined by Gran titration using a Metrohm Titrando. Precision and accuracy of the TA was determined using Dickson CRM and was ~2 µmol kg^{-1}. DIC was calculated from pH (NBS) measured in the core and TA using CO2SYS (Pierrot et al. 2006) with constants set to (Mehrbach et al. 1973) refit by (Dickson & Millero, 1987). All nutrient analyses were carried out colourmetrically using Lachat™ Flow Injection Analysis (Eyre & Ferguson, 2005). Dinitrogen gas (N_2) was determined from N_2:Ar ratios measured using membrane inlet mass spectrometry with O_2 removal (0.01%) (Eyre et al., 2002). Total sediment organic carbon and nitrogen were determined by a Thermo FlashEA 1112 analyser, with carbonates removed using 2M HCl prior to analysis. Total sediment phosphorus was extracted in a nitric acid and HCl digest and analysed by ICP-OES (Eyre et al., 2008).

Figure 5. Alkalinity measurements at the on-site laboratory.

3.2 Data Analysis

Fluxes across the sediment-water interface were calculated by linear regression of the concentration data, corrected for the addition of replacement water as a function of incubation time, core water volume and surface area. Dark flux rates were calculated using concentration data from the dark hours of the incubation and light flux rates were calculated using concentration data from the light hours of the incubation. Net flux rates are calculated from the dark flux*dark hours plus the light flux*light hours divided by 24 hours (Eyre et al., 2011).

Benthic respiration rate (R) = change in DIC/ O_2 dusk to dawn

Benthic net productivity (NPP) = change in DIC/ O_2 dawn to dusk

Benthic gross productivity (GPP) = respiration plus net production

Benthic P/R = Gross primary productivity x daylight hours/ respiration by 24 hours

Respiratory quotient (RQ) = dark DIC efflux/ dark O_2 uptake

N-remineralisation ratio = dark DIC flux/dark total dissolved inorganic N efflux (NO_3-+NH_4^++N_2-N)

P-remineralization ratio = dark DIC flux/ dark total dissolved inorganic phosphorus (DIP) efflux

Denitrification efficiency (DE) = (((dark N_2-N/(NH_4^++NO_3^-+N_2-N)) x 100%) (uptakes are not included)

4 Key Observations and Discussion

4.1 Organic Matter Decomposition, Sediment Oxygen Demand and Benthic Production

4.1.1 Organic Matter Decomposition

The dark dissolved inorganic carbon (DIC) efflux is a measure of the amount of organic matter being decomposed in the sediments (respiration; R), although it may also include some carbonate sediment dissolution. The deep sites in the middle of Cockburn Sound had the lowest respiration rates (Table 3), and the low in-situ production shows this material would have been mostly sourced from the water column. Molar C:N ratios in the top 2 cm of sediment at deep sites 2 to 4 were between 6.4 and 6.7 (Table 4) suggesting it was mostly freshly decomposed Redfield (molar C:N ratio = 6.6) phyto-detritus. The higher C:N ratios at the other sites, including deep site 1, would be due to the decomposition of more degraded phyto-detritus and/or the input of material like seagrass detritus that has a higher C:N ratio (20:1) (Duarte, 1990; Eyre et al., 2013). The correlation between chlorophyll-a in the top 2 mm of the sediment, a good measure of the phyto-detritus (i.e. phytoplankton, benthic microalgae and epiphytes), and DIC respiration at most sites ($r^2 = 0.80$, $p < 0.01$, $n = 9$; Figure 6), suggests that most of the respiration was from phyto-detritus with some decomposition of other organic matter like seagrass material. Chlorophyll-a concentrations decreased exponentially with depth ($r^2=0.76$; $p<0.05$; $n=12$).

Table 3. Benthic dissolved inorganic carbon (DIC) fluxes (µmol m^{-2} h^{-1}).

Site	Dark (respiration; R)	± SD	Gross Primary Production (GPP)	± SD	GPP/R	± SD
1	2833	1016	3742	-	0.96	-
2	1140	-	2382	-	1.13	-
3	990	18	540	3087	0.28	1.68
4	815	353	1591	409	1.30	0.92
5	3739	1935	6225	231	1.03	0.49
6	4530	1323	7312	2180	0.87	0.01
7	2352	475	3338	72	0.73	0.14
8	2313	561	3096	397	0.75	0.16
9	4168	457	9798	978	1.28	0.15
10	1451	1369	4474	641	2.81	2.41
11	4732	1201	8743	1054	1.02	0.13
12	3923	487	8546	1032	1.18	0.10

Table 4. Sediment solid-phase.

Site	Organic Carbon (%)	Organic Nitrogen (%)	Total Phosphorus (%)	Molar C:N Ratios	Chlorophyll-a (mg m^{-2})
1	0.49	0.05	0.047	8.3	14.7
2	0.84	0.11	0.056	6.7	-
3	1.41	0.19	0.065	6.4	8.0
4	1.85	0.24	0.080	6.5	6.7
5	0.69	0.07	0.036	8.5	97.5
6	0.57	0.07	0.031	7.0	129.5
7	0.41	0.05	0.029	7.4	58.7
8	0.70	0.08	0.050	8.0	152.2
9	0.40	0.04	0.018	7.9	58.7
10	0.30	0.03	0.043	9.0	33.4
11	0.77	0.08	0.035	8.1	44.1
12	0.23	0.02	0.044	11.6	86.8

Respiration rates of < 2,000 µmol DIC m^{-2} h^{-1} would just classify deep sites 2 to 4 as oligotrophic (Eyre & Ferguson, 2009). Deep site 1 was just above 2,000 µmol DIC m^{-2} h^{-1} and would be classified as mesotrophic.

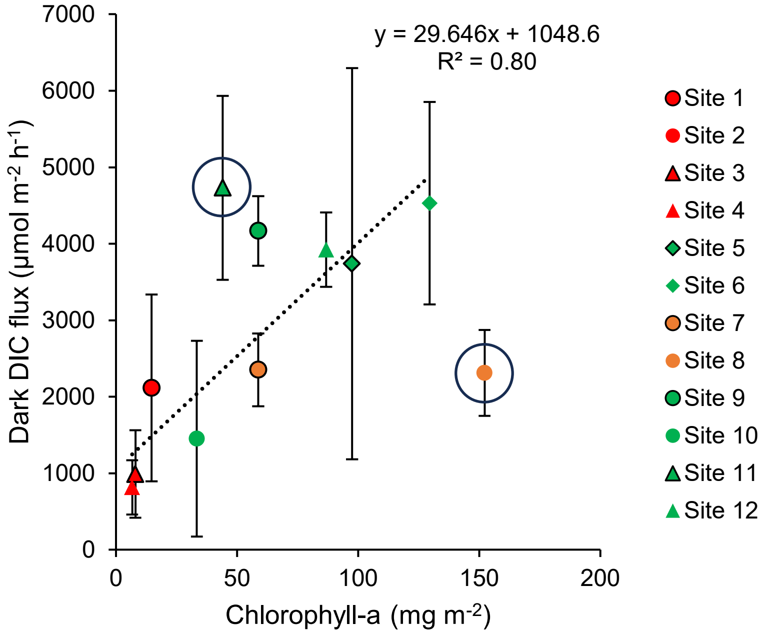

Figure 6. Sediment chlorophyll-a versus dark DIC fluxes (respiration). Circled outliers were excluded from the regression. Red symbols are the deep sites, orange symbols are the shallow sites, and green symbols are the seagrass sites.

The highest respiration rates were in the shallow sites, and in particular sites 5, 6 9, 11 and 12 which had seagrass community including epiphytes and benthic microalgae (Table 3). The shallow sites also had high rates of gross primary production (GPP), and respiration and GPP were correlated (r^2=0.82, p<0.001, n=12). As such, the high respiration rates at the shallow sites reflect the decomposition of organic matter produced in situ by benthic microalgae and epiphytes, and some seagrass detritus.

4.1.2 Sediment Oxygen Demand

Sediment oxygen demand (SOD) is measure of the oxygen consumed when organic matter decomposes (respiration), although it may also include some iron, sulphide and ammonia oxidation. Dark O_2 uptakes (SOD) (Table 5) and dark DIC effluxes were correlated for most sites (r^2=0.89, p<0.001, n=10) and the SOD shows the same pattern as described above for dark DIC effluxes. SOD and chlorophyll-a in the top 2 mm of the sediment were strongly correlated at most sites reflecting the decomposition of phyto-detritus (r^2=0.95, p<0.001, n=9; Figure 7).

A SOD of 30 mmol m^{-2} d^{-1} was calculated from water column dissolved oxygen profiles collected in March 2019 in Cockburn Sound (Dalseno et al., 2024). This was the most severe oxygen depletion event during the sampling campaign and occurred during a period of low wind speed. Site 3 is the closest, and the most similar, to the location where the oxygen profiles were measured. Site 3 had SOD of 27.3 mmol m^{-2} $d^{-1}$and a net oxygen flux 21.2 mmol m^{-2} d^{-1}. The time of year and associated temperature difference (i.e. warmer in March which would increase SOD) could account for the lower SOD in the cores, which were collected on May 1, 2024 compared to the oxygen profiles which were measured on March 11, 2019. In addition, the oxygen profiles also include any oxygen consumption in the water column, although most of it probably occurred in the sediments. All these rates of SOD are lower than the mean global SOD for shallow (0 to 10 m) marine shelf sediments of 45±22 mmol m^{-2} d^{-1} (Jørgensen et al., 2022).

Table 5. Benthic oxygen fluxes (µmol m^{-2} h^{-1}).

Site	Dark (respiration; R) (sediment oxygen demand; SOD)	± SD	Gross Primary Production (GPP)	± SD	GPP/R	± SD	Respiratory Quotient; RQ	± SD
1	1129	8	318	156	0.15	0.07	1.88	-
2	1165	242	538	72	0.26	0.08	1.12	-
3	1140	44	472	75	0.22	0.03	0.85	0.00
4	1009	41	130	110	0.07	0.06	0.80	0.32
5	2064	702	4266	827	1.18	0.31	1.54	0.35
6	2354	431	4812	702	1.11	0.07	1.90	0.25
7	1625	615	2638	900	0.89	0.16	1.60	0.68
8	1882	150	2921	223	0.85	0.07	1.24	0.36
9	3556	706	9503	1189	1.46	0.15	1.19	0.18
10	1303	516	2967	763	1.31	0.32	1.03	0.52
11	1490	163	3757	743	1.36	0.12	3.23	1.01
12	2275	176	6498	669	1.54	0.12	1.72	0.08

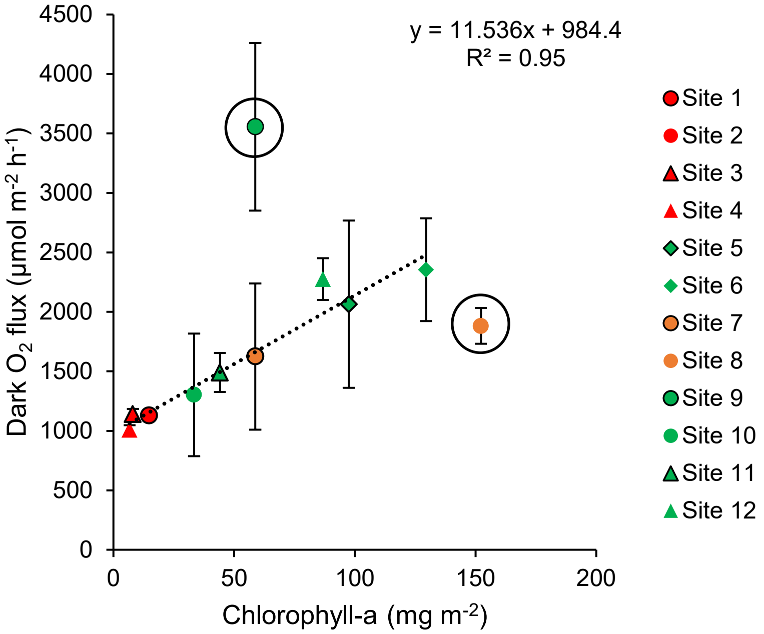

Figure 7. Sediment chlorophyll-a versus dark O_2 fluxes (sediment oxygen demand). Circled outliers were excluded from the regression. Red symbols are the deep sites, orange symbols are the shallow sites, and green symbols are the seagrass sites.

The respiratory quotient (RQ) Table 5) gives some insight into the pathways of benthic organic matter decomposition and oxygen consumption. RQs of around one reflect organic matter decomposed by oxic respiration, RQs greater than one reflect organic matter decomposition by anoxic respiration (mostly sulphate reduction), and RQs below one reflect oxidation of reduced sulphides. Deep sites 3 and 4 had RQs below one suggesting oxidation of reduced sulphides such as iron monosulphides (FeS) and hydrogen sulphide (H_2S). The RQ of 0.7 calculated from the oxygen profiles (Dalseno et al., 2024) also compares well to the RQ of 0.85 measured at site 3. RQs and alkalinity fluxes (Table 6) were correlated with an increasing flux of alkalinity as RQ increased, reflecting an increasing amount of sulphate reduction and associated carbonate dissolution (r^2=0.79; p<0.001, n=12; Figure 8). The alkalinity fluxes at seagrass sites 11 and 12 (Table 6) were nearly equal to the dark DIC efflux minus the dark O_2 uptake (0.86 and 0.94, respectively), suggesting these high respiration sites were dominated by sulphate reduction (i.e. each mole of sulphate reduced produces one mole of alkalinity).

Table 6. Benthic alkalinity fluxes (µmol m^{-2} h^{-1}).

Site	Dark	± SD	Light	± SD	Net	± SD
1	1568	-	-2098	-	-418	-
2	827	-	-1442	-	-402	-
3	0	1026	-2799	1018	-1245	563
4	557	218	-1165	660	-186	97
5	2315	1385	-896	1118	576	1240
6	2978	955	-998	683	824	158
7	1565	421	-603	205	462	321
8	1032	550	-307	192	306	293
9	1476	344	-1743	535	-268	180
10	558	446	-1361	1048	-482	772
11	3432	1365	-1793	725	602	521
12	1954	496	-689	163	522	223

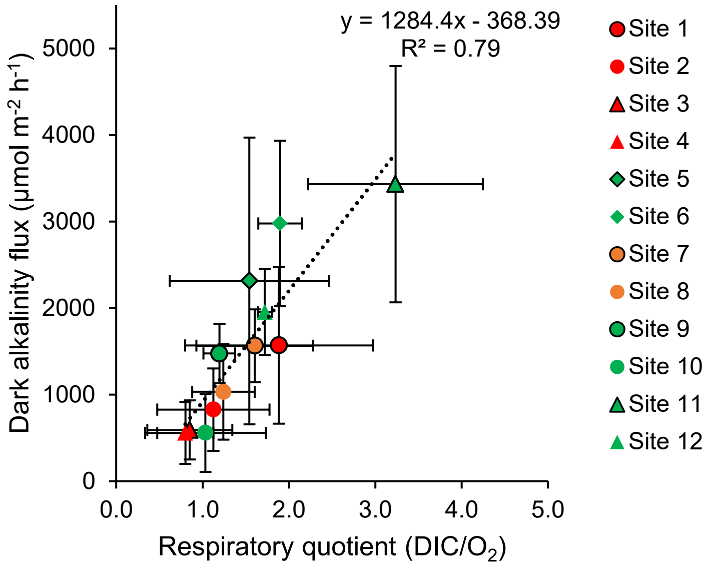

Figure 8. Respiratory quotient versus dark alkalinity fluxes. Red symbols are the deep sites, orange symbols are the shallow sites, and green symbols are the seagrass sites.

4.1.3 Benthic Production and Net Oxygen Demand

Gross benthic O_2 and CO_2 production (GPP) occurred at all sites, but was low at the deep sites and high at the shallow sites (Table 5). The seagrass sites 5, 6 9, 11 and 12 had the highest rate of GPP reflecting a combination of seagrass, epiphyte and benthic microalgae communities and high light.

P/R were well below 1 at the four deep sites (site 1 to 4), and the two shallow sites without seagrass (site 7 and 8) had O_2 P/R just below 1, reflecting net oxygen consumption (Table 5). All the remaining shallow seagrass sites had O_2 P/R above 1 reflecting net oxygen production. This highlights the important role of the shallow shelf sediments, and associated autotrophic communities, in maintaining oxygen concentrations in Cockburn Sound.

4.2 Sediment-water Fluxes of Nitrogen and Phosphorus

4.2.1 Nitrogen Fluxes

The N-remineralisation ratio should have a 1:6.6 stoichiometry (i.e. Redfield) if the organic matter undergoing decomposition is phyto-detritus, and a stoichiometry around 1:20 if the organic matter undergoing decomposition is seagrass (Eyre & Ferguson, 2002). The deep mud basin sites 2 to 4 had N-remineralisation ratios just above 6.6 (9 to 10) suggesting the decomposition of slightly degraded phyto-detritus (Figure 9; Tables 7, 8, 12). All the other sites had N-remineralisation ratios well above Redfield. The N-remineralisation ratios were also correlated with sediment C:N ratios (r^2=0.82, $p<0.001$, n=12; Figure 9) with higher N-remineralisation ratios at higher sediment C:N, suggesting the N-remineralisation ratios increased as the amount of seagrass material being decomposed increased, although the N-remineralisation ratios were mostly well above the C:N of seagrass material (20:1).

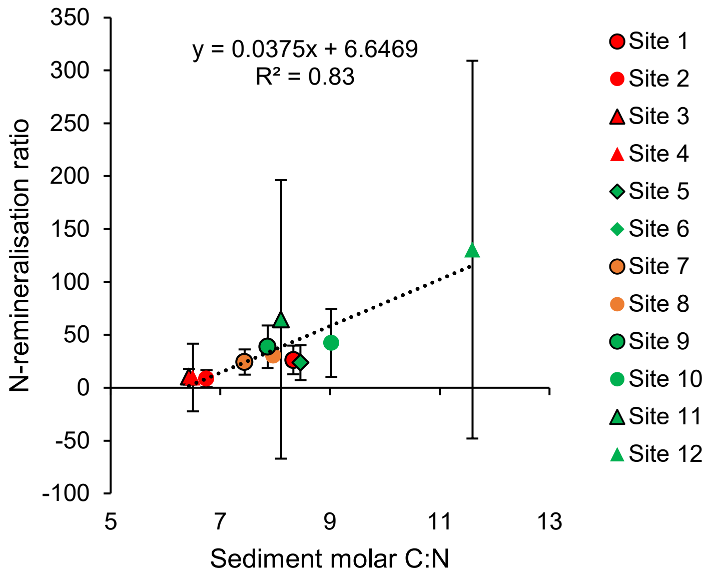

Figure 9. N-remineralisation ratios versus sediment molar C:N ratios. Red symbols are the deep sites, orange symbols are the shallow sites, and green symbols are the seagrass sites.

Table 7. Benthic nitrate (NO_3^-) fluxes (µmol m^{-2} h^{-1}) +ve = efflux, -ve = uptake.

Site	Dark	± SD	Light	± SD	Net	± SD
1	26.1	18.3	16.2	19.2	20.7	16.8
2	13.3	13.5	22.9	25.8	18.5	8.1
3	20.0	3.9	1.6	6.6	10.0	5.4
4	12.4	3.5	16.8	5.7	14.8	3.4
5	3.2	1.4	-0.7	3.2	1.1	2.2
6	-5.4	10.0	4.9	4.2	0.2	3.9
7	-9.2	14.6	3.7	4.8	-2.2	9.1
8	5.5	13.7	0.6	8.4	2.9	2.9
9	-9.9	9.2	1.3	4.0	-3.8	3.9
10	-1.5	1.3	1.9	1.9	0.4	0.6
11	-1.0	1.7	2.5	4.4	0.9	2.9
12	0.1	5.8	-2.1	2.1	-1.1	2.7

Table 8. Benthic ammonium (NH_4^+) (µmol m^{-2} h^{-1}) +ve = efflux, -ve = uptake.

Site	Dark	± SD	Light	± SD	Net	± SD
1	-23.9	2.9	-5.7	16.2	-14.1	8.1
2	4.1	11.6	20.0	66.8	12.7	41.5
3	11.0	11.7	-9.9	8.4	-0.3	1.0
4	1.2	32.8	11.3	26.6	6.7	28.7
5	125.8	175.7	-88.0	67.6	10.0	44.6
6	-21.0	9.9	-13.2	29.1	-16.8	17.7
7	65.8	5.5	-14.6	64.4	22.3	32.4
8	32.3	27.0	-23.8	5.2	1.9	10.2
9	29.3	17.4	-36.0	29.8	-6.1	8.7
10	-9.8	19.3	0.4	7.7	-4.3	12.0
11	-34.2	9.0	-10.6	3.5	-21.4	5.1
12	-1.7	14.3	-23.9	19.2	-13.7	6.4

The low dissolved inorganic nitrogen efflux for a given respiration rate is most likely due to competition for nitrogen by heterotrophic bacteria (Oakes et al., 2011); N limitation of the microbial decomposition of high C:N organic material results in the uptake and accumulation of nitrogen by heterotrophic bacteria (Lomstein et al., 1998; Tupas & Koike, 1991; van Duyl et al., 1993). Several types of bacteria can assimilate NH_4^+, including sulphate reducers and fermentative bacteria (Koike & Sumi, 1989).

Additionally, sulphate reducers can fix nitrogen (Nielsen et al., 2001). N_2 effluxes are a measure of denitrification minus nitrogen fixation and as such, increased N fixation will result in a reduced N_2 efflux. Furthermore, coupled nitrification-denitrification may be suppressed by H_2S produced during sulphate reduction (Fulweiler et al., 2013; Joye & Hollibaugh, 1995). Consistent with this were the highest N-remineralisation ratios of 65 and 130 that occurred at sites 11 and 12 respectively, where respiration was dominated by sulphate reduction (i.e. alkalinity fluxes were nearly equal to the dark DIC efflux minus the dark O_2 uptake). Nitrogen assimilation and nitrogen fixation by heterotrophic bacteria would be a nitrogen conservation process in high C:N seagrass communities that would otherwise lose large amounts of nitrogen via denitrification due to high rates of benthic respiration (Eyre et al., 2013), i.e., the loss of nitrogen via denitrification per unit of respiration is on average about seven times higher at sites 2 to 4 where respiration from phyto-detritus dominates compared to the seagrass sites (5, 6, 9, 10, 11, 12).

One of the major controls on of the net benthic flux of DIN was the P/R ratio of the sediments. Across Cockburn Sound there was a net efflux of DIN when the sediment O_2 P/R was <1 reflecting net heterotrophic sediment releasing nitrogen via respiration, and there was a net uptake of DIN (except for one site) when the sediment O_2 P/R was >1 reflecting net autotrophic sediments assimilating DIN to support productivity (Figure 10). We have also observed similar relationships between sediment P/R ratios and benthic fluxes in other coastal systems (Eyre & Ferguson, 2002; Eyre & Ferguson, 2005; Eyre et al., 2008). Sediment P/R ratios have important management implications for coastal systems like Cockburn Sound, demonstrating the need to maintain the balance of benthic autotrophy and heterotrophy (Eyre & Ferguson, 2002).

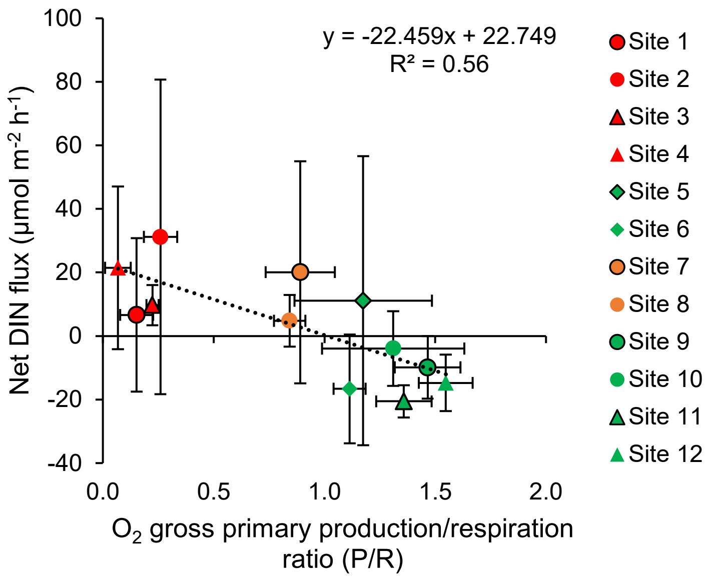

Figure 10. O_2 gross primary production/respiration ratio (P/R) versus net dissolved inorganic nitrogen (DIN) fluxes. Red symbols are the deep sites, orange symbols are the shallow sites, and green symbols are the seagrass sites.

Benthic dissolved organic nitrogen (DON) fluxes were the largest of the benthic nitrogen fluxes across Cockburn Sound (Table 9), and there was mostly an uptake of DON in both the dark and light. Net DON uptake increased with O_2 respiration and O_2 GPP, but there were two different trends, one for the deep sites 1 to 4 and sandy site 8, and one for the shallow sites (Figures 11 and 12). The uptake of DON at the shallow sites was most likely due to assimilation by benthic microalgae (Eyre et al., 2008). Several studies in temperate systems have demonstrated that benthic microalgae use the various components of DON as a N source (Admiraal et al., 1987) (Nilsson & Sundbäck, 1996) (Linares, 2005). Because there is very little freely available DIN in Cockburn Sound, labile DON is probably a major source of nitrogen for benthic microalgae. Assuming a C:N:P stoichiometric ratio of 106:16:1 for benthic microalgae production and 480:27:1 for seagrass production (Eyre and Ferguson 2002), the combined uptake of DIN+DON in the light was insufficient to support O_2GPP at the shallow sites (Figure 13). The shallow benthic communities are probably nitrogen limited, reflecting the low water column nitrogen concentrations, with nitrogen also sourced from the sediment porewaters.

Table 9. Benthic dissolved organic nitrogen (DON) fluxes (µmol m^{-2} h^{-1}) +ve = efflux, -ve = uptake.

Site	Dark	± SD	Light	± SD	Net	± SD
1	-61	11	-33	60	-46	30
2	-103	62	-65	84	-83	47
3	-5	49	-40	37	-24	24
4	-53	26	42	13	-1	7
5	-73	35	-16	16	-42	13
6	-9	61	-67	50	-40	45
7	-38	92	2	21	-16	44
8	-224	155	-26	125	-116	22
9	-160	158	-79	128	-116	137
10	-44	15	18	13	-10	1
11	-17	119	-38	67	-28	53
12	-108	74	-9	75	-54	75

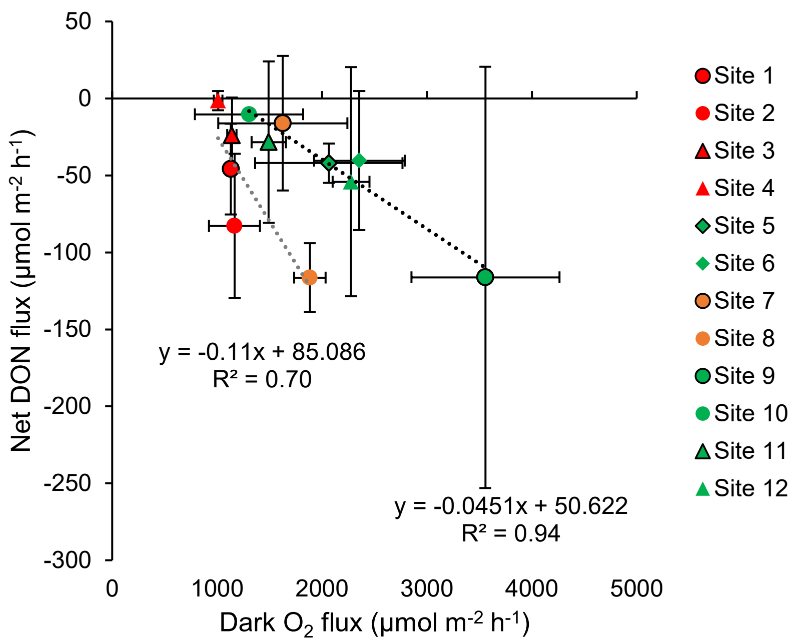

Figure 11. Dark O_2 fluxes (sediment oxygen demand) versus net dissolved organic nitrogen (DON) fluxes. Two trends are shown, one for the deep sites 1 to 4 and sandy site 8, and one for the shallow sites. Red symbols are the deep sites, orange symbols are the shallow sites, and green symbols are the seagrass sites.

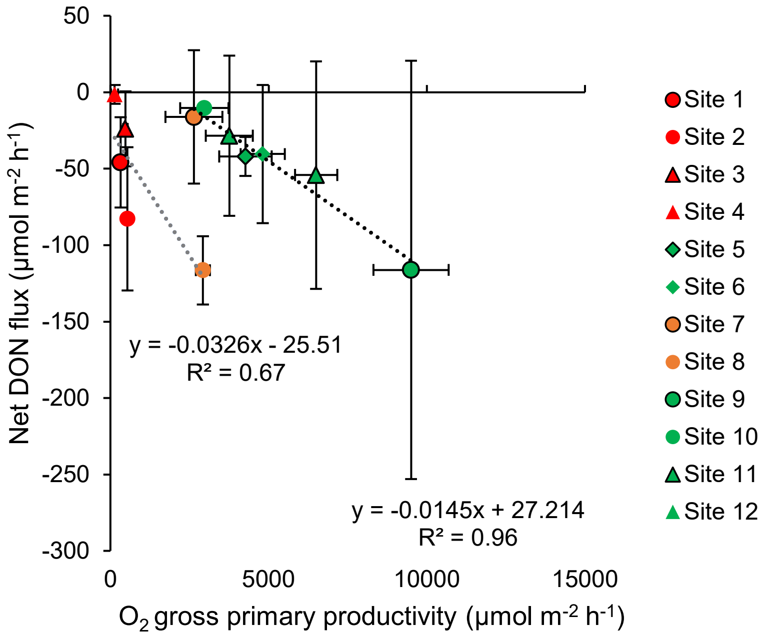

Figure 12. O_2 gross primary productivity versus net dissolved organic nitrogen (DON) fluxes. Two trends are shown, one for the deep sites 1 to 4 and sandy site 8, and one for the shallow sites. Red symbols are the deep sites, orange symbols are the shallow sites, and green symbols are the seagrass sites.

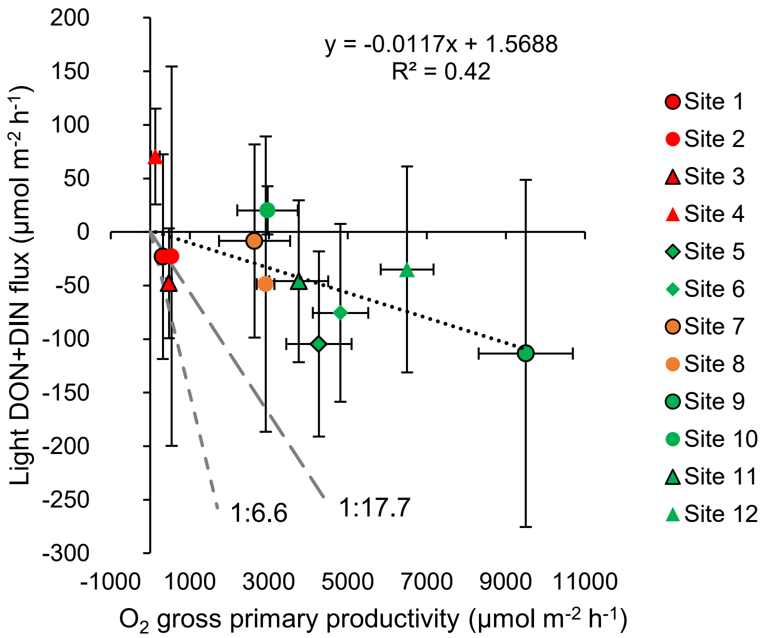

Figure 13. O_2 gross primary productivity versus light dissolved inorganic nitrogen (DIN) + organic nitrogen (DON) fluxes. The 1:6.6 line is the N:C stoichiometric ratio for benthic microalgae production and 1:17.7 is the N:C stoichiometric ratio for seagrass production (Eyre and Ferguson 2002). Red symbols are the deep sites, orange symbols are the shallow sites, and green symbols are the seagrass sites.

Heterotrophic marine bacteria have also been shown to assimilate urea (Jahns, 1992), and marine microbial mats have been shown to assimilate DON (Paerl, 1993; Rondell et al., 2000). This suggests that the DON may be utilized by bacteria under N-limited conditions and the associated DOC may be an additional source of labile C for benthic metabolism (Eyre et al., 2008). This is consistent with an increase in the dark DON uptake with increasing sediment C:N ratios (Figure 14). There are two trends in DON uptake, which most likely reflects two different types of communities, one for the deep sites 1 to 4 and sandy site 8 dominated by bacteria, and one for the shallow sites with seagrass, epiphytes, benthic microalgae and bacteria.

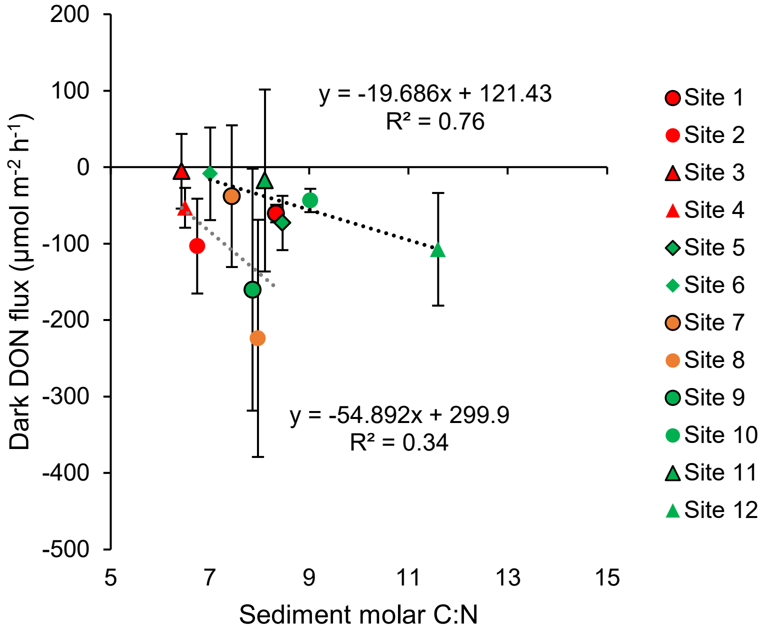

Figure 14. Dark organic nitrogen (DON) fluxes versus sediment molar C:N ratios. Two trends are shown, one for the deep sites 1 to 4 and sandy site 8, and one for the shallow sites. Red symbols are the deep sites, orange symbols are the shallow sites, and green symbols are the seagrass sites.

4.2.2 Benthic Phosphorus Fluxes

The P remineralization ratio should have a 1:106 stoichiometry (i.e. Redfield) if the organic matter undergoing decomposition is phyto-detritus, and a stoichiometry around 1:480 if the organic matter undergoing decomposition is seagrass (Eyre & Ferguson, 2002). Dark, light and net DIP fluxes were all very small (<2 µmol m^{-1} h^{-1}) and P-remineralization ratios were either uptakes or well in excess of 480. This probably reflects the trapping of phosphorus in the oxidised upper sediment layers by iron oxy-hydroxides, possibly enhanced through the injection of oxygen by benthic productivity (Eyre & Ferguson, 2002).

Total phosphorus concentrations in the bottom sediments range from 0.031to 0.080% which is similar to the range seen across Australian coastal systems (0.021 to 0.093%; (Birch et al., 1999). The deeper sites in the mud basin had higher total phosphorus concentrations than the shallow sites, which may reflect the finer grainsize (Table 4). The highest total phosphorus concentrations were at site 4 in the southern mud basin (0.080%), which was similar to disturbed coastal systems like the Hawkesbury and Swan-Canning (Birch et al., 1999). The highest total phosphorus concentrations at the shallow sites were also at the southern end of Cockburn Sound (site 8). The higher total sediment phosphorus concentrations in southern Cockburn Sound may reflect the higher water column nutrient concentrations and poorer flushing (Keesing, 2011; Xiao et al., 2022). Sediment total phosphorus concentrations showed no correlation with DIP fluxes, supporting iron oxy-hydroxide control of DIP fluxes.

Table 10. Benthic dissolved inorganic phosphorus (DIP) fluxes (µmol m^{-2} h^{-1}) +ve = efflux, -ve = uptake.

Site	Dark	± SD	Light	± SD	Net	± SD
1	0.2	1.8	0.3	0.5	0.3	0.6
2	0.7	1.9	1.5	1.9	1.2	1.9
3	-0.8	0.8	1.0	0.1	0.2	0.4
4	0.8	2.2	-0.3	0.5	0.2	1.1
5	-0.2	0.4	0.8	1.4	0.3	0.6
6	-0.3	0.5	1.9	0.7	0.9	0.3
7	1.1	1.6	-0.3	3.5	0.3	1.7
8	-1.3	2.5	-0.2	2.6	-0.7	2.5
9	0.3	0.5	-0.3	1.4	0.0	1.0
10	1.3	2.0	0.8	1.7	1.0	1.4
11	0.4	0.8	-0.4	0.6	0.0	0.0
12	-0.7	3.1	0.0	0.9	-0.3	1.4

Benthic dissolved organic phosphorus (DOP) fluxes were the largest of the benthic phosphorus fluxes across Cockburn Sound (Table 11), and there was mostly an uptake of DOP in both the dark (7 of 12 sites) and light (9 of 12 sites). Benthic net DOP and net DON fluxes were correlated for most sites (r^2=0.88, p<0.001; n=10) and had a ratio of about 1:23. This suggests DOP was involved in similar autotrophic and heterotrophic processes as DON (see above DON discussion). The combined uptake of DIP+DOP in the light was insufficient to support gross primary production, particularly at the shallow sites (Figure 15). Benthic production was most likely supplied by the sediment pool of phosphorus (Eyre et al., 2008). This large pool of phosphorus in the sediments may drive potential nitrogen limitation of benthic communities in Cockburn Sound. The benthic community may ultimately be phosphorus limited on longer timescales because it can replenish nitrogen via nitrogen fixation, but on shorter timescales it is nitrogen limited because of the large pool of phosphorus in the sediments.

Table 11. Benthic dissolved organic phosphorus (DOP) fluxes (µmol m^{-2} h^{-1}) +ve = efflux, -ve = uptake.

Site	Dark	± SD	Light	± SD	Net	± SD
1	-3	0	-1	4	-2	3
2	-1	0	-3	2	-2	1
3	1	4	-3	2	-1	3
4	-3	1	3	2	0	0
5	8	9	-2	1	3	5
6	0	2	-1	2	-1	1
7	0	1	0	4	0	2
8	-36	62	0	5	-17	29
9	0	4	1	1	1	2
10	-2	3	4	2	1	0
11	4	18	-6	6	-2	5
12	-1	2	-5	1	-3	0

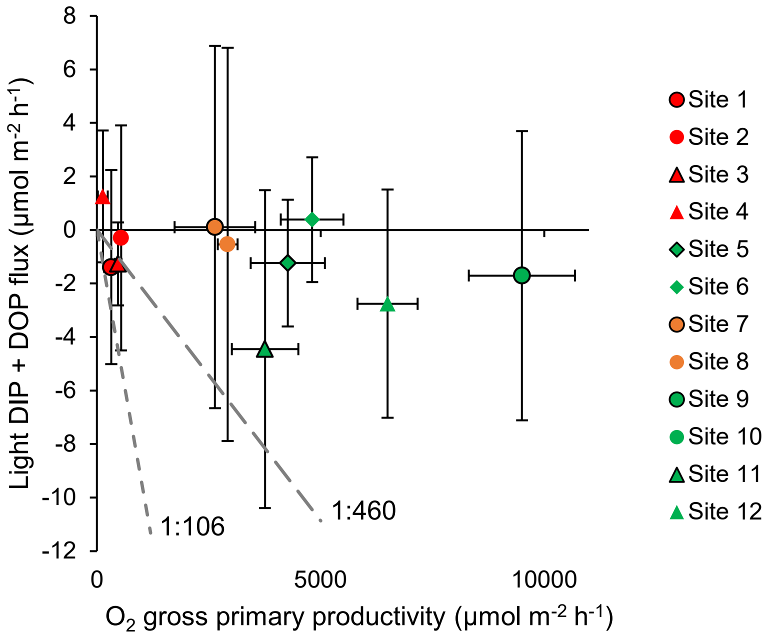

Figure 15. O_2 gross primary production (GPP) versus light dissolved inorganic phosphorus (DIP) + organic phosphorus (DOP) fluxes. The 1:106 line is the P:C stoichiometric ratio for benthic microalgae production and 1:480 is the P:C stoichiometric ratio for seagrass production (Eyre and Ferguson 2002). Red symbols are the deep sites, orange symbols are the shallow sites, and green symbols are the seagrass sites.

4.3 Denitrification

4.3.1 Denitrification Rates

The highest denitrification rates were in the shallow sandy seagrass site on Jervoise Bank (Site 11), and the lowest denitrification rates were in the two seagrass restoration areas (sites 5 and 6). Only a few sites showed NO_3^- uptakes which is consistent with low water column NO_3^- concentrations (<10 µg L^{-1}). Because NO_3^- uptakes were much less than the N_2 effluxes, most of the denitrification is coupled to nitrification in the sediments.

Eight of the 12 sites showed a decrease in denitrification rates from the dark to light most likely due to competition for NH_4^+ and NO_3^- by benthic primary producers (Risgaard-Petersen et al., 1994) (Sundbäck et al., 2000). An increase in denitrification in the light (i.e. sites 7, 8, 11, 12) suggest they did not have resource limitation and the associated increase oxygen penetration from benthic production would enhance coupled nitrification–denitrification (Risgaard-Petersen et al., 1994), and/or an increase the supply of labile carbon for denitrification.

The large NO_3^- fluxes at the deep sites (1 to 4) suggest there may have been organic matter limitation of denitrification, with the denitrifiers unable to use all the nitrogen released from the decomposition of phyto-detritus.

Table 12. Benthic di-nitrogen gas (N_2) fluxes (µmol N_2 m^{-2} h^{-1}) (denitrification).

Site	Dark	± SD	Light	± SD	Net	± SD
1	39	14	15	8	22	1
2	58	19	17	-	26	-
3	32	21	23	17	27	6
4	36	21	20	6	27	8
5	14	9	4	4	9	7
6	14	13	1	0	8	8
7	20	17	30	1	26	11
8	19	15	56	47	39	32
9	44	18	-	-	-	-
10	23	16	13	8	14	4
11	54	39	63	47	64	47
12	16	12	40	16	26	11

4.3.2 Denitrification Efficiency

It is important to maintain a high denitrification efficiency (DE) because nitrogen that is converted to N_2 via denitrification is permanently lost from the system, whereas nitrogen that effluxes from the sediments as NH_4^+ and NO_3^- can stimulate more algal production in the water column. The stimulation of more water column algal production can in-turn lead to greater organic matter deposition and decomposition (phyto-detritus) and oxygen consumption. Increased sediment oxygen demand inhibits coupled nitrification-denitrification and decreases the denitrification efficiency (Eyre & Ferguson, 2009).

Eight of the 12 sites in Cockburn Sound were consistent with the DE versus carbon decomposition relationship (Figure 16) that has been developed from the deposition mud basins of 17 Australian coastal systems (Eyre & Ferguson, 2009). The relationship between DE and carbon decomposition is due to changes in carbon and NO_3 supply associated with sediment biocomplexity. At the DE optimum there is an overlap of aerobic and anaerobic respiration zones (caused primarily by the existence of anaerobic micro-niches with the oxic zone, and oxidised burrow structures penetrating into the anaerobic zone), which enhances denitrification by improving both the organic carbon and nitrate supply to denitrifiers. Either side of the DE optimum zone there is a reduction in denitrification sites as the sediment loses its 3-dimensional complexity. At low organic carbon loading a thick oxic zone with low macrofauna biomass exists resulting in limited anoxic sites for denitrification, and at high carbon loadings there is a thick anoxic zone and a resultant lack of oxygen for nitrification and associated NO_3^- production. The low DE at deep sites 2 to 4 in the mud basin reflect organic matter limitation of denitrification, which is consistent with the efflux of NO_3^-.

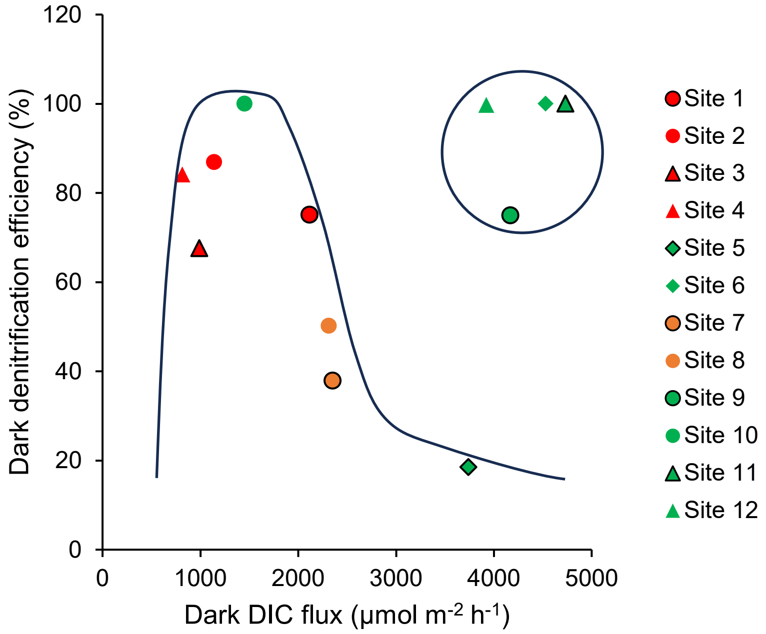

Figure 16. Denitrification efficiency versus dark dissolved inorganic carbon (DIC) fluxes. Red symbols are the deep sites, orange symbols are the shallow sites, and green symbols are the seagrass sites.

The four sites that do not fit the DE versus carbon decomposition relationship were seagrass sites (6, 9, 11, 12). This is consistent with previous work that also showed seagrass sites with high rates of respiration were able to maintain high DE (Eyre & Ferguson, 2009). Seagrass communities are able to maintain moderate rates of coupled nitrification-denitrification by transporting oxygen down to the rhizosphere (Frederiksen & Glud, 2006), although the denitrification rates per unit of respiration at the seagrass sites were seven times lower than the deep sites. Much of the high DE at the four sites is due to the dark assimilation of DIN by heterotrophic bacteria in the high C:N seagrass sites, resulting in all the inorganic nitrogen being released as N_2 .

All four sites in the central mud basin had DE that would be classified as oligotrophic (Table 13). Site 7 near the proposed Westport footprint and site 8 on the Southern Flats had DE that would be classified as mesotrophic and site 5 in the restored seagrass had DE that would be classified as eutrophic. The low DE was due to low denitrification rates and high NH_4^+ fluxes, although the high NH_4^+ flux was only for one of the triplicate cores, and most likely reflects the degraded seagrass biomass at this site.

Table 13. Dark DIC effluxes and denitrification efficiencies for unvegetated sediments in shallow coastal systems of different trophic status (Eyre & Ferguson, 2009).

System Type	Dark DIC flux (µmol m^{-2} h^{-1})	Median Denitrification Efficiency (%
Optimum	500 - 1000	75
Oligotrophic	<2000	68
Mesotrophic	2000 - 4000	40
Eutrophic	4000 - 6000	18
Hypertrophic	>6000	8

The DE optimum in Cockburn Sound occurs around a DIC efflux of about 1,500 µmol m^{-2} h^{-1} (Figure 16), which is consistent with other coastal systems (Table 13). Studies in the sub-tropical Brunswick Estuary have shown that water column chlorophyll-a concentrations (proxy for pelagic productivity) would need to be below about 5 µg L^{-1} to maintain benthic carbon decomposition rates below 2,000 µmol m^{-2} h^{-1} (Eyre & Ferguson, 2005). Chlorophyll-a concentrations in Cockburn Sound are mostly below 1.5 µg L^{-1}, although concentrations above 2 µg L^{-1} have been measured at Southern Flats, and above 5 µg L^{-1} in the Northern Harbour (Keesing, 2011). These low concentrations of chlorophyll-a are consistent with organic matter decomposition rates below 1,200 µmol DIC m^{-2} h^{-1} in most of the central mud basin of Cockburn Sound. Site 1 at the northern end has a higher organic matter deposition rates reflecting an input of other organic matter (e.g. seagrass). However, any increase above 2200 µmol DIC m^{-2} h^{-1} due to increased organic matter loading is likely to result in a drop in the DE (Figure 16) in the central mud basin.

5 Conclusions

Cockburn Sound benthic biogeochemical processes can be divided into three similar groups (1) deep sediments with little, or no light (i.e. central mud basin), (2) shallow sediments that receive light, and have benthic microalgae communities and (3) shallow sediments that receive light, and have seagrass communities. These three groups also form the basis of the Cockburn Sound biogeochemistry model of oxygen metabolism and nutrient cycling (although the seagrass restoration sites are excluded from the seagrass group for the modelling).

Respiration rates at the deep sites in the central mud basin were relatively low and reflect the decomposition of fresh to slightly degraded phyto-detritus. These sites were classified mostly as oligotrophic, with one site classified as slightly mesotrophic. Sediment oxygen demand (SOD) at the deep sites was consistent with SOD estimated previously from water column oxygen profiles, and the rates of SOD at the deep sites are lower than the mean global SOD for shallow (0 to 10 m) marine shelf sediments.

The four deep sites, and two shallow sites without seagrass (sites 7 and 8) showed net oxygen consumption with O_2 gross primary productivity/respiration ratios (P/R) below one. All the remaining shallow seagrass sites had O_2 P/R above one, reflecting net oxygen production. This highlights the important role of the shallow shelf sediments, and associated autotrophic communities, in maintaining oxygen concentrations in Cockburn Sound. As such, any future loss of autotrophic communities, including seagrass, would enhance deoxygenation of Cockburn Sound.

Across the Sound the sediments acted as a source of dissolved inorganic nitrogen (DIN) under conditions where the O_2 P/R was <1, reflecting net heterotrophic sediments and nitrogen release through benthic respiration. In contrast, there was a net uptake of DIN when the sediment O_2 P/R was >1 reflecting net autotrophic sediments assimilating DIN to support gross primary productivity. The deep sites recycled DIN to water and the shallow sites released little DIN, or took up both DIN and dissolved organic nitrogen, due to nitrogen limitation in the sediments. As such, any future increase in respiration due to organic matter enrichment, or reduction in light and associated autotrophic communities, including seagrasses, would result in more dissolved inorganic nitrogen being recycled to the water column. This in-turn would stimulate more algal production in the water column and lead to greater organic matter deposition and decomposition.

There was little release of dissolved inorganic phosphorus from the sediments, probably due to trapping of phosphorus in the oxidised upper sediment layers by iron oxy-hydroxides. A future increase in deoxygenation would reduce the iron in the upper sediment layers releasing phosphorus to the water column. On long-time scales this may reduce nutrient limitation, as nitrogen can be fixed from the atmosphere, which in-turn may increase algal production in Cockburn Sound.

Denitrification efficiency in the central mud basin was classified as oligotrophic and these sites could tolerate a small increase in organic carbon loading before being pushed past the optimum denitrification efficiency. In contrast, the shallow sites without natural seagrass communities had a denitrification efficiency that would be classified as mesotrophic and eutrophic suggesting some organic matter enrichment at these sites. The sites with seagrass communities maintained high denitrification efficiency. As such, any further organic matter enrichment of the shallow areas without seagrass, and any future loss of seagrass communities, would likely to reduce the loss of nitrogen via denitrification and enhance the recycling of nitrogen from the sediments into the water column. This in-turn would stimulate more algal production in the water column and lead to greater organic matter deposition and decomposition, further reducing the denitrification efficiency. These bottom-up changes have flow-on effects, which alter the structure of higher trophic levels such as fish and macrofauna communities.

6 Further Work and Likely Future Changes in Benthic Biogeochemistry

The sampling for this project was only undertaken once in Autumn. As such, it missed, for example, the periods of maximum water temperature in summer and minimum water temperatures in winter, and periodic hypoxic events (Dalseno et al. 2024), all of which would influence the benthic biogeochemical processes. As such, we recommend additional seasonal sampling should be undertaken, particularly during periods of maximum bottom water temperature and hypoxia. Because the cores could only be collected in areas of sparse seagrass, we also recommend using benthic flume chambers in the seagrass areas (see (Camillini et al., 2021). Also, some experimental work could be undertaken looking at the effects of future stressors such as deoxygenation, acidification (both ocean acidification and linked to hypoxia and eutrophication) and warming on benthic biogeochemical processes.

A short time-period of hypoxia may increase denitrification because denitrifying bacteria require oxygen to be very low or absent. However, a lack of oxygen for a longer time period reduces denitrification overall, because of the exhaustion of the oxidised nitrogen species required for denitrification (NO_3^-, NO_2^- and N_2O). Studies suggest that for an environment like Cockburn Sound, this would be a period of longer than approximately two days (Banks et al. 2012), however, the exact time period where low oxygen reduces denitrification is not known. Additional seasonal measurements and experimental work with future stressors would help us to determine the hypoxia-denitrification time periods. With increasing deoxygenation in the long-term, we would expect denitrification to decrease and more NH_4^+ to be recycled to the water column, because most of the denitrification in Cockburn Sound is coupled to nitrification. Warming would most likely decrease coupled nitrification-denitrification and increase N_2O production in Cockburn Sound (Simon et al. 2024), resulting in more greenhouse gas emissions. However, acidification may offset the warming effect on N_2O production (Simone, 2024}.

7 References

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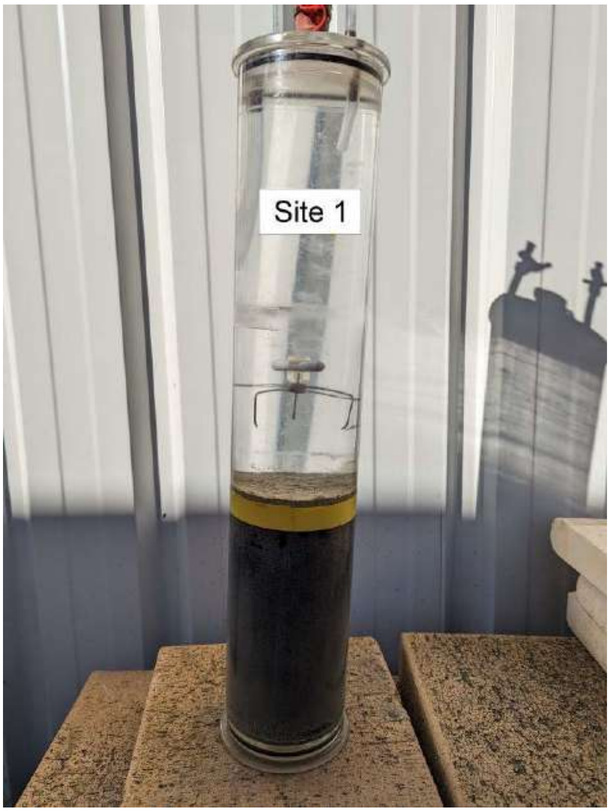
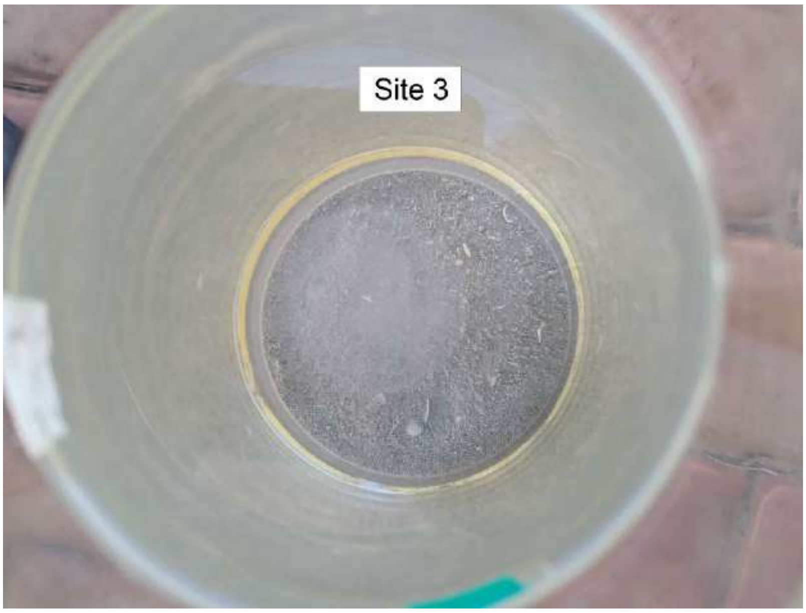
8 Appendices



Supplementary Figure 1. Sediment core from site 1.

Supplementary Figure 2. Sediment core from site 2.



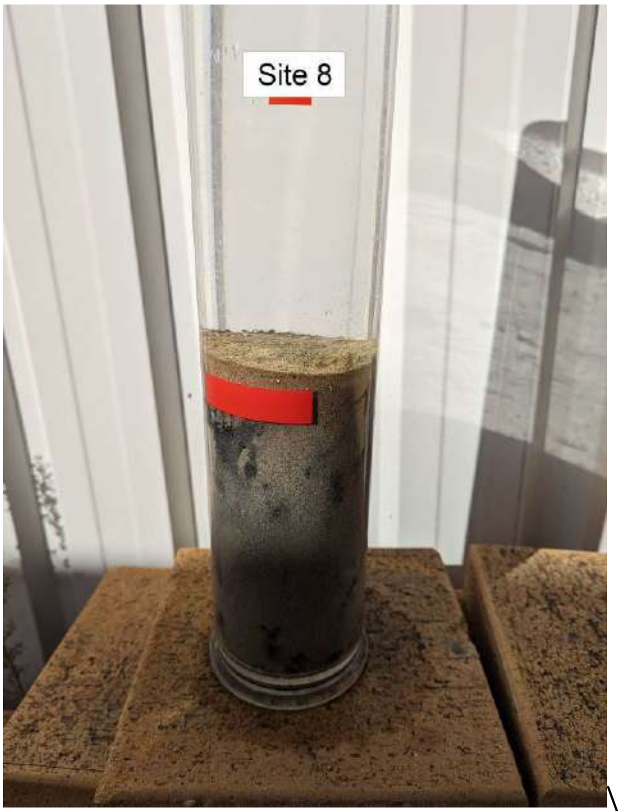
Supplementary Figure 3. Sediment core from site 3.

Supplementary Figure 4. Sediment core from site 4.

Supplementary Figure 5. Sediment core from site 5.

Supplementary Figure 6. Sediment core from site 6.

Supplementary Figure 7. Sediment core from site 7.



Supplementary Figure 8. Sediment core from site 8.

Supplementary Figure 9. Sediment core from site 9.

Supplementary Figure 10. Sediment core from site 10.

Supplementary Figure 11. Sediment core from site 11.

Supplementary Figure 12. Sediment core from site 12.

Submitted as draft	03/03/2025
Review completed	13/05/2025
Submitted as revised draft	08/08/2025
Approved by Science Program Leadership team	02/09/2025
Approved by WAMSI CEO	23/09/2025
Final Report	30/09/2025

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