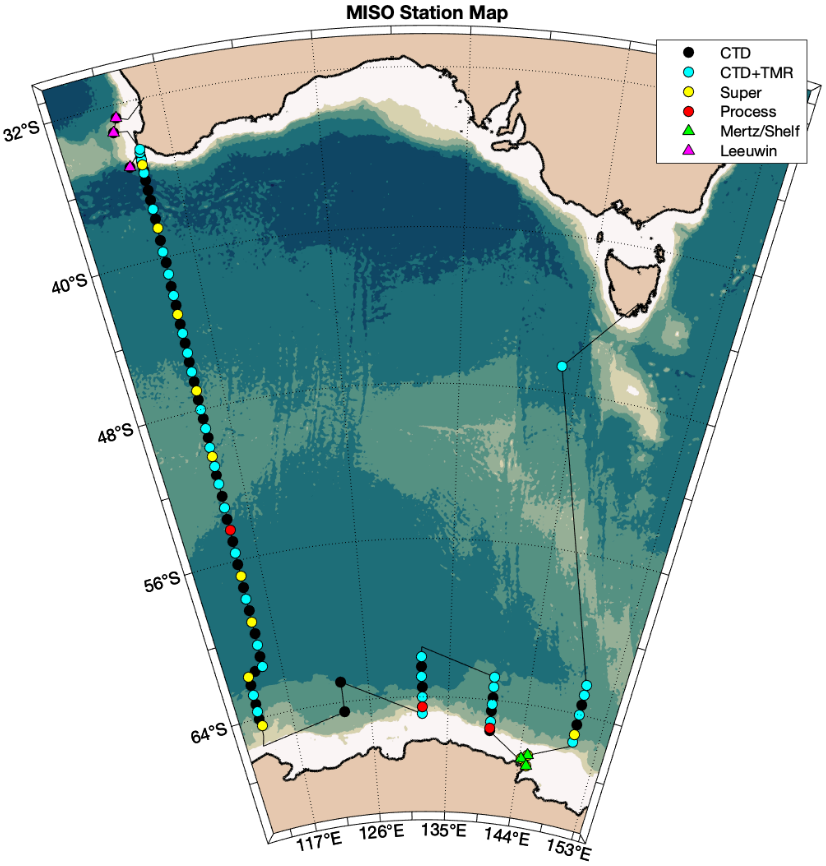
CRUSIE REPORT: I09S 2024

(Updated June 2025)



Highlights

Cruise Summary Information

Section Designation	I09S (+ southern end of SR3)
Expedition Designation (ExpoCodes)	096U20240101
Chief Scientists	Steve Rintoul, Annie Foppert
Dates	2024 JAN 01 – 2024 MARCH 05
Ship	*R/V Investigator*
Ports of call	Hobart – Fremantle
Geographic Boundaries	31 55.9'S 113 14.8'E 151 25.1'E 67 00.2'S
Stations	103
Floats and drifters deployed	10 BGC Argo; 12 Deep Argo; 4 drogued surface drifters
Moorings deployed or recovered	0

Contact Information

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Links To Select Topics

Shaded sections are not relevant to this cruise or were not available when this report was compiled.

Cruise Summary Information	**Hydrographic Measurements**
Description of Scientific Program	**CTD Data:**
Geographic Boundaries	Acquisition
Cruise Track (Figure)	Processing
Description of Stations	Calibration
Description of Parameters Sampled	Salinities
Bottle Depth Distributions (Figure)	Oxygens
Floats and Drifters Deployed	**Bottle Data:**
Moorings Deployed or Recovered	Oxygen
	Nutrients
Principal Investigators	Carbon System Parameters
Cruise Participants	CFCs
	Helium/Tritium
Problems and Goals Not Achieved	Radiocarbon
Other Incidents of Note	
Underway Data Information	**References**
Navigation Bathymetry	Hydrochemistry
Acoustic Doppler Current Profiler (ADCP)	CTD Processing
Thermosalinograph	Carbon Processing
XBT and/or XCTD	
Meteorological Observatoins	**Acknowledgements**
Atmospheric Chemistry Data	

MNF Voyage Highlights and Summary

VOYAGE #:	IN2024_V01
Voyage title:	Multidisciplinary Investigations of the Southern Ocean (MISO): Linking Physics, Biochemistry, Plankton, Aerosols, Clouds, And Climate
Mobilisation:	Thursday 28 – Sunday 31 December 2023, CSIRO Wharf PW04, Hobart
Pre-medical clearance period:	Monday 1 January – Thursday 4 January 2024, Hobart
Depart:	Friday 5 January 2024, Selfs Point, Hobart
Return:	Tuesday 5 March 2024, Fremantle
Demobilisation:	Wednesday 6 March 2024, Fremantle
VDC and Voyage Manager:	Margot Hind
Chief Scientist:	Dr Steve Rintoul, CSIRO; steve.rintoul@csiro.au
Co-Chief Scientist & Sailing Chief Scientist	Dr Annie Foppert, UTAS; annie.foppert@utas.edu.au
Principal Investigators:	Alain Protat (Atmosphere); Philip Boyd and Robert Strzepek (BioGeoScapes); Andrew Bowie (GEOTRACES); Elizabeth Shadwick (Carbon Chemistry); Steve Rintoul and Annie Foppert (Oceanography);

Voyage Summary

Executive summary

The Southern Ocean and overlying atmosphere have a profound influence on regional and global climate, sea level, biogeochemical cycles, and marine biological productivity. However, present-day models used for forecasts and projections have large and persistent biases in the region. MISO aims to enhance our understanding of how the Southern Ocean region influences the Earth system and use this knowledge to improve models.

Data collected during MISO will characterise the properties of aerosols, clouds, radiation, and precipitation over the Southern Ocean south of Australia and investigate how they are shaped by interactions between the ocean, atmosphere and biosphere. Repeat hydrographic observations will be used to discover how and why the region is changing, and the consequences of Southern Ocean change for climate, biogeochemical cycles, biological productivity, and the future of the Antarctic Ice Sheet. Data collected will provide new insights into the processes controlling the availability of iron and other trace elements and their role in regulating productivity in the Southern Ocean and the production of marine organic aerosols that can drive cloud nucleation.

The observations and insights gained from the voyage will be used to develop, test, and implement new parameterisations for models used for weather forecasts and climate projections. Better climate projections will underpin a more effective national response to the challenges of a changing climate.

Scientific objectives

The **overall objectives** of the project are:

1. To collect integrated physical, biogeochemical, and biological observations of the coupled Southern Ocean – atmosphere system needed to address gaps in scientific understanding of key processes and to understand reasons for biases in Earth System Models (ESMs).
2. To use enhanced process-level understanding and observations to test and improve earth system models and for calibration/validation of satellite measurements.

The specific research questions to be addressed are:

1. What processes and interactions account for the unique aerosol-cloud-precipitation-radiation interactions over the Southern Ocean and how can they be better represented in ESMs to reduce the large and persistent biases in clouds and absorbed solar radiation at the ocean surface?
2. How do biogenic ocean sources influence the aerosol, cloud, precipitation, and radiative properties of the Southern Ocean atmosphere and how can they be better parameterised in models?
3. How and why is the Southern Ocean inventory of heat and carbon south of Australia evolving in time and what are the impacts on sea level rise and ocean acidification?
4. What physical and biogeochemical processes control primary productivity, community composition, and production of biogenic aerosols?

5. How is the Southern Ocean changing near Antarctica and what are the implications for the stability of the Antarctic Ice Sheet and the formation of Antarctic Bottom Water?
6. How well are cloud, aerosol and precipitation properties over the Southern Ocean represented in satellite products and how can they be used to inform data assimilation?

Voyage objectives

Atmosphere: We will use shipboard and satellite instruments to investigate the latitudinal variability of cloud, aerosol, and radiative properties.

Air-sea interface: Ocean-atmosphere interactions will be measured with underway instruments. Air-sea fluxes of CO_2 and sea spray will be measured continuously along the ship track.

Ocean physics: We will re-occupy the I9S repeat hydrographic section at 115°E to assess changes in ocean properties and circulation. We will also track the ongoing and rapid change in Antarctic Bottom Water (AABW) by completing short sections across the AABW export pathway at 132°E, 140°E and 150°E. Deep Argo floats and Biogeochemical Argo floats will be deployed.

Ocean biogeochemistry: Carbon chemistry will be measured throughout the water column. Iron and other trace elements and isotopes (TEIs) will be measured using clean techniques. We will occupy 4 stations for ~3 days to track the evolution of iron biogeochemistry, measuring fluxes of particulate and dissolved iron pools, to investigate processes controlling strong opposing fluxes of iron regeneration and scavenging, organic ligand release, authigenic iron production, and biological uptake and recycling in the upper and mesopelagic ocean.

Ocean biology: Underway measurements will be used to map zonal and meridional distributions of phytoplankton stocks, community structure, physiological status, and biogenic gas concentrations (e.g. DMS). Process studies will focus on the marginal ice zone where phytoplankton blooms are anticipated to supply biogenic precursors to aerosol, cloud condensation nuclei (CCN), and Ice Nucleating Particles (INPs). During process stations, incubation experiments will be conducted on board to quantify the biological production of organic compounds and how they act as precursors for new formation of aerosols.

Satellite calibration/validation: Opportunistic observations collected during satellite overpasses will be used to evaluate and refine satellite aerosol, cloud, and precipitation products from the Himawari-8, A-Train, GPM and PACE missions.

Voyage narrative

The voyage was a great success. We were able to achieve all the voyage goals – with only 7 planned stations that were not occupied, and 6 of those 7 not occupied because they were inaccessible due to sea-ice cover. We were able to add additional opportunistic stations in the Adelie Depression near the Mertz Glacier region on the Antarctic shelf and in the Leeuwin Undercurrent-Current System off the southwest corner of Western Australia. All 22 float deployments were successful. The final station plan that was completed can be found in the Voyage Track (Figures 1 and 2). Radiosondes were deployed regularly; the DALEC was deployed when weather permitted for PACE satellite validation.

Pre-voyage medical clearance days:

All personnel were pleased with the opportunities to do the test dips (CTD, TMR and ISPs) without any time pressure sometimes associated with “official” voyage activities (i.e. once sea-time starts ticking). Risks were identified, procedures were ironed out, erroneous calibration numbers were found, sampling techniques were practiced, etc. It was a great use of this time.

Transit south:

Favourable weather for most of the transit south allowed for an early arrival at our first southern waypoint, nearly one day ahead of schedule. In addition to regular radiosonde and XBT deployments, we took advantage of the transit south for three other activities, all of which highlight the opportunities for cross-voyage and/or cross-project collaboration.

1. We towed the Continuous Plankton Recorder from Tasmania to the SOTS mooring site, adding to the long-term plankton records in the Southern Ocean.
2. We deployed a full-depth CTD and shallow TMR (1500 m) at the SOTS mooring site, which will help to underpin and constrain seasonal variability observed in the long-term mooring timeseries.
3. We mapped the seafloor in a region important for Antarctic Circumpolar Current dynamics, where the strong currents interact with bathymetry to allow for transport of heat toward the Antarctic. This will complement and enhance the data collected from the previous voyage (IN2023_V07).

150°E (Leg 1):

Operations along 150E went smoothly, and the teams all found their grooves. Details on timing to between CTD recovery and TMR deployment were ironed out to maximise efficiency and minimize time on deck for the TMR.

Sea-ice coverage on the southern end of 150E made the southernmost station inaccessible, so the superstation on 140E was swapped with the process station on 150E and moved north to allow all superstation activities to be completed away from any sea ice.

2 Deep Arvor floats and 1 SOCCOM float were successfully deployed along this transect.

Adelie Depression / Mertz Glacier region:

Real-time monitoring of satellite ice imagery showed an opening to the Mertz Glacier region and Adelie Depression. An agreed alteration to the voyage plan allowed the ship to divert to the Mertz Glacier region and carry out three opportunistic CTD, TMR, and ISP deployments, and two bongo net tows in the Adelie Depression. We also increased the deployment frequency of XBTs and rapid-cast CTDs in the region. This is the first time the Dense Shelf Water formed in the Mertz Polynya has been sampled since 2017. These data are extremely valuable and will be very useful for interpreting the changes in Antarctic Bottom Water observed in the deep ocean, understanding trace metal input from glacial melt, and informing how continental airflow from Antarctica influences the atmospheric properties above the Southern Ocean – all key scientific objectives of the MISO voyage. All three Mertz stations were superstations, i.e. all included ISPs and the first two included bongos.

The lead we entered through had closed while we were inside the Mertz region occupying stations. We cruised along the ice edge looking for an opening but could not find one. Satellite ice imagery showed that the potential southern route along the Antarctic coast also appeared to be a dead end. As L’Astrolabe had only just left Dumont d’Urville station earlier that morning, we called for their assistance in escorting us out through the ice. This was (1) to ensure a safe exit and (2) to continue the planned science program as soon as possible.

140°E (Leg 2):

Successful repeat of the southern section of SR3. Lost ~1.5 days due to weather on this line.

Process Station #1 was not completed in full, as the second Triaxus tow and shallow TMR were cut from the plan due to bad weather. The deckboard incubation experiments were successful, however, the mesocosms were unfortunately unsuccessful. The tanks had acid remaining in them, as seen by very low pH of seawater and very high CO2 in the headspace of the tanks. The tanks were emptied before the weather arrived.

One Deep Arvor, one Deep SOLO, and one SOCCOM float were deployed successfully on this transect.

132°E (Leg 3):
Successful repeat of stations along 132E, previously occupied in 2018. Note that the northernmost station on 132E was dropped to gain back some contingency time used due to bad weather and at the additional sites in the Mertz Glacier region.

Process Station #2 occurred just south of a 'blob' of very high chlorophyll seen in the satellite data. The Triaxus was towed from the 'blob' station to the process station to resolve the gradient between inside and outside, or on the edge of, the bloom. After the mesocosm tanks were filled, weather again deteriorated, and operations ceased for about 19 hours. Some process station activities – bongos and the second Triaxus tow – were not fulfilled due to the weather deteriorating again towards end of station activities, but the process station was considered a success overall.

One Deep Arvor float, two Deep SOLO floats, and one SOCCOM float were all successfully deployed along this transect.

123°E (Leg 4):
Two CTD-only stations on 123E and associated Deep SOLO float deployments were successful.

115°E (I9S):
The southernmost five stations on I9S were inaccessible due to sea-ice cover. A station was added nearly due east of station 33 when we were unsure whether we would be able to access 33, which we eventually did. While operations were also delayed along I9S due to both weather and mechanical issues with the ship, we were able to keep on or ahead of schedule, given the contingency days in place, and the line was successfully completed.

A low-pressure system delayed operations at one of the superstations (station 51), causing an overall loss of about 2 days and limiting the amount of superstation activities we could complete. In the end, we were able to complete the full-depth CTD, full-depth TMR – which was prioritized over the shallow TMR in a weather window, with bottle depths chosen with the expectation that we may not be able to do the shallow TMR – and ISPs. Thus, we fulfilled nearly all the superstation activities.

Mechanical issues with the ship were encountered on southern part of I9S, causing a delay in operations due to slow transit times. While transit times between stations were extended, the ship's officers and crew were comfortable with operations continuing. The issue was quickly resolved by the ship's crew (~48 hours after major fault was identified).

We undertook two process stations and seven superstations on I9S. The first process station (PS3) did not include filling the mesocosm tank, to let the experiment from the prior process station continue to play out. There were issues with the first Triaxus tow at PS3 – including the Triaxus flying in such a way that there was a significant increase of tension on the wire – that resulted in the tow being aborted and the Triaxus requiring re-termination. All activities were successfully completed at the final process station (PS4).

3 Deep SOLO and 7 SOCCOM floats were all successfully deployed.

Transit to Fremantle:
With ~36 hours of remaining time in the science budget, we undertook an opportunistic survey of Leeuwin Current System, where we completed three SADCP and rapid-cast CTD transects across the shelf break. Over 6 hours was lost due to having to repeat the first transect because the SADCP was turned off and not recording currents. Full-depth CTDs were deployed on the offshore end of all three transects, as was a full-depth TMR at Leeuwin-1 and Leeuwin-3. Reduced resolution of hydrochemistry samples were collected (12 depths) and no carbon samples or biology samples were collected during this short survey.

We arrived off Fremantle in time to meet the pilot on the morning of 5 March 2024.

Summary

The MISO voyage plan was very ambitious, and we were able to accomplish the vast majority of planned activities – and in some cases even add activities. All voyage objectives were achieved. We arrived in Fremantle to conclude the 65-day voyage having successfully completed many activities, including (but not limited to):

- 103 CTD casts
- 72 TMR casts
- 16 ISP deployments
- 14 bongo net tows
- 5 Triaxus tows
- 22 profiling float deployments (12 Deep Argo and 10 SOCCOM BGC-Argo)
- 4 surface drifter deployments
- 109 XBT deployments
- 27 rapid-cast CTD deployments
- 160 radiosonde deployments
- 2 mesocosm incubation experiments
- 26 deckboard incubation experiments
- 1 continuous plankton recorder (CPR) tow

We gratefully acknowledge the support and hard work of the crew and the MNF support staff on board, and all those who supported these efforts from shore. We would also like to acknowledge the Australian Antarctic Program Partnership (AAPP) for its support for this voyage. Note that all ship data, including primary and secondary CTD data, hydrochemistry, underway data, bathymetry, etc. is available online through the MNF Data Trawler.

Voyage Track

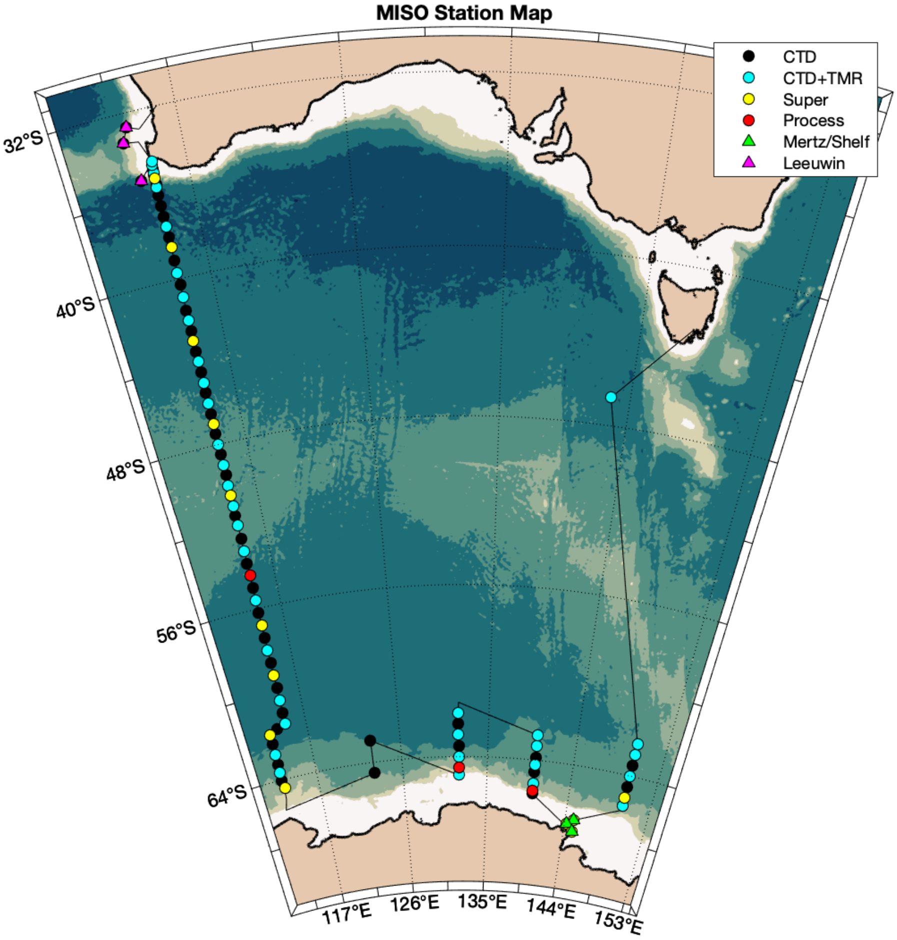

MISO Station Map

Figure 1. Map of MISO (IN2024_V01) station occupations. Note that the black line is only a graphical representation of the actual ship track.

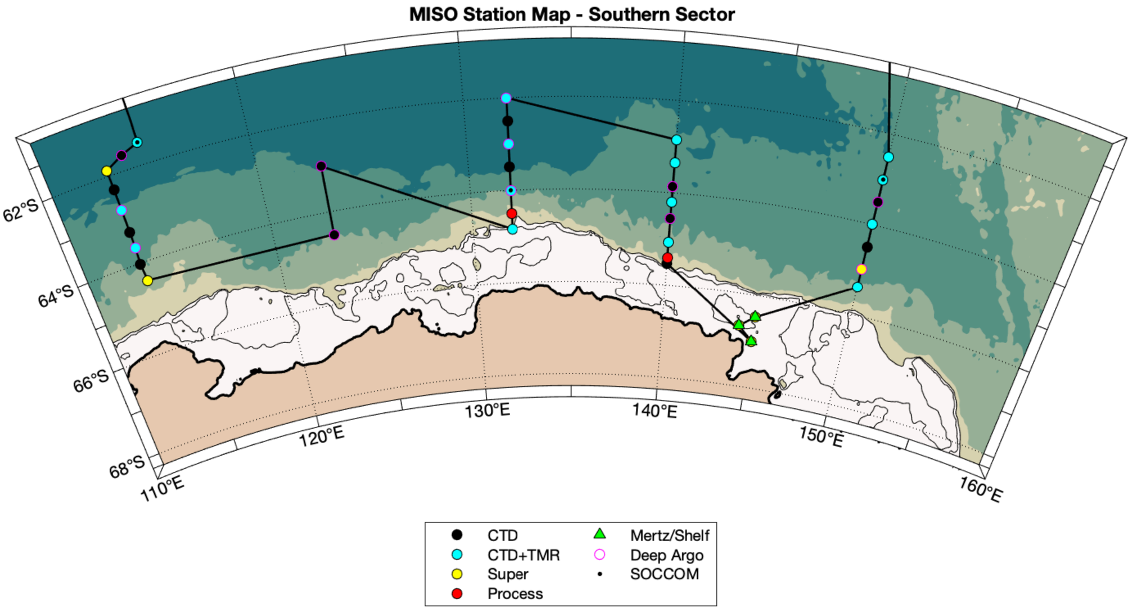

MISO Station Map - Southern Sector

Figure 2. Map of the southern sector of the station plan, showing float deployment locations.

List of All Stations

Station	Start Time	Bottom Time	End Time	Longitude	Latitude	Depth	Notes
1	2/1/2024 08:21	2/1/2024 08:51	2/1/2024 09:31	148.117	-43.551	1252	test cast
2	6/1/2024 06:43	6/1/2024 07:59	6/1/2024 09:49	142.666	-46.665	4171	SOTS mooring site
3	10/1/2024 14:28	10/1/2024 15:40	10/1/2024 17:41	149.994	-62.503	3894	
4	11/1/2024 01:27	11/1/2024 02:33	11/1/2024 04:23	150.002	-63.001	3820	SOCCOM
5	11/1/2024 11:25	11/1/2024 12:33	11/1/2024 14:22	150.01	-63.494	3705	Deep Arvor
6	11/1/2024 18:46	11/1/2024 19:50	11/1/2024 21:38	150.003	-64	3621	
7	12/1/2024 04:00	12/1/2024 05:04	12/1/2024 06:34	150	-64.5	3473	
8	12/1/2024 13:15	12/1/2024 14:15	12/1/2024 15:49	149.997	-65.011	3261	Deep Arvor
9	13/1/2024 04:57	13/1/2024 05:54	13/1/2024 07:28	150.003	-65.342	2928	
10	14/1/2024 11:43	14/1/2024 11:53	14/1/2024 12:32	144.948	-66.476	426	Mertz-1
11	15/1/2024 08:29	15/1/2024 08:48	15/1/2024 09:38	144.192	-66.7	857	Mertz-2
12	15/1/2024 21:07	15/1/2024 21:31	15/1/2024 22:23	145.002	-67.002	1139	Mertz-3
13	17/1/2024 21:12	17/1/2024 21:45	17/1/2024 23:00	139.996	-65.531	1775	
14	18/1/2024 02:20	18/1/2024 02:31	18/1/2024 03:09	139.999	-65.4	2418	
15	19/1/2024 05:14	19/1/2024 05:22	19/1/2024 05:45	140.001	-65.386	2476	
16	20/1/2024 19:59	20/1/2024 20:43	20/1/2024 22:08	139.995	-65.4	2421	
17	21/1/2024 04:58	21/1/2024 05:47	21/1/2024 07:15	140.005	-65	2665	
18	21/1/2024 15:04	21/1/2024 15:58	21/1/2024 17:38	140.006	-64.548	3070	Deep Arvor & SOCCOM
19	21/1/2024 21:39	21/1/2024 22:43	22/1/2024 00:28	140.003	-64.213	3535	
20	22/1/2024 05:55	22/1/2024 07:01	22/1/2024 08:51	140.003	-63.872	3681	Deep SOLO
21	22/1/2024 13:24	22/1/2024 14:33	22/1/2024 16:24	140.004	-63.351	3779	
22	23/1/2024 00:18	23/1/2024 01:16	23/1/2024 02:51	139.999	-62.853	3213	
23	24/1/2024 06:05	24/1/2024 07:25	24/1/2024 09:17	132.002	-62	4480	Deep SOLO

24	24/1/2024 19:15	24/1/2024 20:36	24/1/2024 22:40	132.003	-62.5	4447	
25	25/1/2024 03:21	25/1/2024 04:37	25/1/2024 06:28	132.001	-63.002	4300	Deep SOLO
26	25/1/2024 14:17	25/1/2024 15:28	25/1/2024 17:27	132.001	-63.501	4011	
27	25/1/2024 21:49	25/1/2024 22:47	26/1/2024 00:27	131.998	-64.001	3220	Deep Arvor & SOCCOM
28	26/1/2024 21:52	26/1/2024 22:27	26/1/2024 23:48	132.051	-64.521	1517	
29	28/1/2024 03:37	28/1/2024 04:07	28/1/2024 05:17	132.125	-64.524	1324	
30	28/1/2024 15:29	28/1/2024 15:51	28/1/2024 16:34	131.994	-64.84	978	
31	29/1/2024 23:34	30/1/2024 00:52	30/1/2024 02:49	122.999	-63.001	4017	Deep SOLO
32	30/1/2024 11:56	30/1/2024 12:51	30/1/2024 14:22	122.995	-64.482	3017	Deep SOLO
33	31/1/2024 23:32	1/2/2024 00:20	1/2/2024 01:52	113.877	-64.443	2558	
34	1/2/2024 09:46	1/2/2024 10:33	1/2/2024 11:59	113.37	-64.341	2469	
35	1/2/2024 23:28	2/2/2024 00:22	2/2/2024 02:10	113.299	-64.02	2986	
36	2/2/2024 06:36	2/2/2024 07:41	2/2/2024 09:16	113.325	-63.639	3270	Deep SOLO
37	2/2/2024 19:46	2/2/2024 20:49	2/2/2024 22:40	113.333	-63.28	3508	
38	3/2/2024 05:04	3/2/2024 06:13	3/2/2024 07:57	113.3	-62.784	3829	Deep SOLO
39	3/2/2024 15:03	3/2/2024 16:15	3/2/2024 18:12	113.297	-62.307	4070	
40	3/2/2024 22:17	3/2/2024 23:30	4/2/2024 01:27	113.28	-61.88	4189	
41	4/2/2024 05:41	4/2/2024 05:50	4/2/2024 06:09	113.364	-61.898	4180	
42	5/2/2024 04:15	5/2/2024 04:25	5/2/2024 04:47	113.589	-61.966	4197	
43	5/2/2024 08:03	5/2/2024 09:23	5/2/2024 11:33	114.156	-61.661	4291	Deep SOLO
44	5/2/2024 16:13	5/2/2024 17:35	5/2/2024 19:38	115.012	-61.51	4340	SOCCOM
45	6/2/2024 00:56	6/2/2024 02:14	6/2/2024 04:22	115.021	-61.01	4395	
46	6/2/2024 07:54	6/2/2024 09:13	6/2/2024 11:22	115.003	-60.399	4461	
47	6/2/2024 19:17	6/2/2024 20:37	6/2/2024 22:47	115.033	-59.812	4497	
48	7/2/2024 04:42	7/2/2024 06:03	7/2/2024 07:57	115.002	-59.203	4526	

49	7/2/2024 21:58	7/2/2024 23:18	8/2/2024 01:22	114.992	-58.599	4537	SOCCOM
50	8/2/2024 07:43	8/2/2024 09:10	8/2/2024 11:21	114.998	-57.997	4575	
51	8/2/2024 17:54	8/2/2024 19:14	8/2/2024 21:38	115.002	-57.403	4566	
52	9/2/2024 12:44	9/2/2024 14:47	9/2/2024 17:18	114.991	-56.806	4532	
53	11/2/2024 22:07	12/2/2024 00:18	12/2/2024 03:14	114.977	-56.185	4496	
54	12/2/2024 10:09	12/2/2024 12:07	12/2/2024 14:41	115.004	-55.599	4600	
55	13/2/2024 02:02	13/2/2024 03:31	13/2/2024 05:53	115.002	-54.998	4423	
56	14/2/2024 04:11	14/2/2024 05:30	14/2/2024 07:26	115.017	-54.386	4129	SOCCOM
57	15/2/2024 04:25	15/2/2024 04:34	15/2/2024 05:00	114.991	-54.369	4200	
58	15/2/2024 09:45	15/2/2024 11:03	15/2/2024 13:03	115.013	-53.81	4036	
59	15/2/2024 16:47	15/2/2024 18:00	15/2/2024 20:09	115.013	-53.21	3983	
60	16/2/2024 01:07	16/2/2024 02:13	16/2/2024 04:16	115.001	-52.61	3779	
61	16/2/2024 08:04	16/2/2024 09:12	16/2/2024 11:06	115.001	-51.98	3660	
62	16/2/2024 18:04	16/2/2024 19:06	16/2/2024 20:55	115.013	-51.47	3528	
63	17/2/2024 01:44	17/2/2024 03:06	17/2/2024 05:28	115	-51.001	3941	SOCCOM
64	17/2/2024 14:26	17/2/2024 15:31	17/2/2024 17:14	115.001	-50.492	3159	
65	18/2/2024 07:17	18/2/2024 08:25	18/2/2024 10:17	115.004	-49.99	3893	
66	18/2/2024 17:21	18/2/2024 18:31	18/2/2024 20:29	115.013	-49.501	3437	
67	19/2/2024 01:32	19/2/2024 02:41	19/2/2024 04:45	115.021	-48.99	3918	
68	19/2/2024 14:08	19/2/2024 15:29	19/2/2024 17:22	115	-48.471	3877	
69	19/2/2024 21:15	19/2/2024 22:20	20/2/2024 00:17	115	-48.002	3649	
70	20/2/2024 05:55	20/2/2024 07:02	20/2/2024 08:53	115.001	-47.502	3736	
71	20/2/2024 13:03	20/2/2024 14:15	20/2/2024 15:56	115.027	-47.013	3907	
72	21/2/2024 05:35	21/2/2024 06:49	21/2/2024 08:50	115.015	-46.512	4016	
73	21/2/2024 12:51	21/2/2024 14:03	21/2/2024 15:58	114.998	-46.019	4122	SOCCOM

74	21/2/2024 23:07	22/2/2024 00:21	22/2/2024 02:25	115	-45.503	4171	
75	22/2/2024 06:32	22/2/2024 07:46	22/2/2024 09:36	115.012	-45.001	4236	
76	22/2/2024 16:37	22/2/2024 17:53	22/2/2024 20:23	115.001	-44.489	4371	
77	23/2/2024 00:31	23/2/2024 01:46	23/2/2024 04:03	115.001	-43.989	4344	
78	23/2/2024 09:16	23/2/2024 10:35	23/2/2024 12:38	115.002	-43.5	4446	
79	23/2/2024 18:15	23/2/2024 19:31	23/2/2024 21:27	114.989	-42.997	4310	SOCCOM
80	24/2/2024 09:24	24/2/2024 10:41	24/2/2024 12:42	115.001	-42.501	4335	
81	24/2/2024 16:33	24/2/2024 17:51	24/2/2024 20:06	115.002	-42	4526	
82	25/2/2024 01:10	25/2/2024 02:30	25/2/2024 04:59	115	-41.508	4627	
83	25/2/2024 09:07	25/2/2024 10:28	25/2/2024 12:37	115.001	-40.87	4652	
84	25/2/2024 19:08	25/2/2024 20:34	25/2/2024 23:07	114.999	-40.289	4856	
85	26/2/2024 02:49	26/2/2024 04:11	26/2/2024 06:28	115	-39.7	4745	
86	26/2/2024 11:04	26/2/2024 12:27	26/2/2024 14:34	115.002	-39.11	4758	
87	26/2/2024 21:38	26/2/2024 23:02	27/2/2024 01:18	115.003	-38.5	4694	
88	27/2/2024 16:28	27/2/2024 17:58	27/2/2024 20:26	115	-37.998	4788	
89	28/2/2024 00:15	28/2/2024 01:46	28/2/2024 04:29	114.998	-37.501	5264	
90	28/2/2024 09:10	28/2/2024 10:50	28/2/2024 13:19	115	-37.04	5713	
91	28/2/2024 17:54	28/2/2024 19:40	28/2/2024 22:24	114.998	-36.53	5398	
92	29/2/2024 14:59	29/2/2024 16:32	29/2/2024 18:48	115.001	-36.012	5252	SOCCOM
93	1/3/2024 00:10	1/3/2024 02:04	1/3/2024 04:29	115.003	-35.648	5033	
94	1/3/2024 05:55	1/3/2024 06:42	1/3/2024 08:04	115	-35.508	2309	
95	1/3/2024 10:25	1/3/2024 10:58	1/3/2024 11:59	114.999	-35.2	1485	
96	1/3/2024 21:22	1/3/2024 21:46	1/3/2024 22:31	115.009	-35.052	763	
97	1/3/2024 23:41	1/3/2024 23:50	2/3/2024 00:22	115.01	-34.95	209	
98	2/3/2024 02:43	2/3/2024 02:51	2/3/2024 03:12	114.999	-34.82	149	

99	2/3/2024 05:10	2/3/2024 05:14	2/3/2024 05:30	115.049	-34.599	101	
100	2/3/2024 07:27	2/3/2024 07:33	2/3/2024 07:45	115.09	-34.459	51	
101	2/3/2024 18:32	2/3/2024 19:47	2/3/2024 22:05	114.216	-35.178	3515	Leeuwin-1
102	3/3/2024 17:04	3/3/2024 17:40	3/3/2024 18:40	113.792	-33.331	1910	Leeuwin-2
103	3/3/2024 22:40	3/3/2024 23:24	4/3/2024 00:38	114.154	-32.657	2531	Leeuwin-3

Float Deployments

Float Type	**Float ID#**	**Float WMO# (if known)**	**Deployment time (UTC)**	**Deployment latitude**	**Deployment longitude**	**CTD on deployment**
SOCCOM	22537		11/01/2024 07:07 UTC	63° 0.75' S	149° 59.52' E	yes, #004
Deep Arvor		6902885	11/01/2024 14:54 UTC	63° 29.64' S	150° 0.36' E	yes, #005
Deep Arvor		6902891	13/01/2024 01:47 UTC	65° 1.44' S	149° 59.64' E	yes, #008
Deep Arvor		1902662	21/01/2024 17:50 UTC	64° 33.38' S	139° 57.40' E	yes, #018
SOCCOM	22751		21/01/2024 18:10 UTC	64° 33.32' S	139° 57.01' E	yes, #018
Deep SOLO	12080	7900952	22/1/2024 09:11 UTC	63° 52.72' S	140° 0.34' E	yes, #020
Deep SOLO	12078	7900953	24/01/2024 13:39 UTC	62° 1.21' S	132° 0.67'E	yes, #023
Deep SOLO	12077	7900954	25/1/2024	63° 0.25' S	131° 58.09' E	yes, #025
Deep Arvor		3902566	26/01/2024 03:12 UTC	64° 0.12' S	131° 58.98' E	yes, #027
SOCCOM	20265		26/1/2024 03:04	64° 0.00' S	131° 58.94' E	yes, #027
Deep SOLO	12073	7900955	30/01/2024 03:11 UTC	62° 59.94' S	122° 59.88' E	yes, #031
Deep SOLO	12074	7900956	30/01/2024 14:42 UTC	64° 28.95' S	122° 59.78' E	yes, #032
Deep SOLO	12075	7900957	2/2/2024 11:10	63° 39.24' S	113° 18.36' E	yes, #036
Deep SOLO	12079	7900958	3/2/2024 11:24	62° 47.02' S	113° 18.99' E	yes, #038
Deep SOLO	12076	7900959	5/2/2024 11:47	61° 39.46' S	114° 9.41' E	yes, #043
SOCCOM	23596		5/2/2024 21:00	61° 30.88' S	115° 0.70' E	yes, #044

SOCCOM	22496		8/2/2024 01:37	58° 36.03' S	114° 59.77' E	yes, #049
SOCCOM	22080		15/2/2024 05:15	54° 22.14' S	114° 59.39' E	yes, #056
SOCCOM	21648		17/2/2024 08:35	51° 0.54' S	114° 59.67' E	yes, #063
SOCCOM	22725		21/2/2024 17:33	46° 1.91' S	114° 59.96' E	yes, #073
SOCCOM	23599		24/2/2024 06:34	43° 0.02'S	114° 59.60'E	yes, #079
SOCCOM	21977		29/2/2024 19:05	36° 00.84' S	115° 00.00' E	yes, #092

Sea-going Personnel List (non-crew)

	Name	Role	Organisation
1.	Annie Foppert	Chief Scientist + CTD	University of Tasmania
2.	Kathy Gunn	CTD	University of Southhampton
3.	Paul Spence	CTD	University of Tasmania
4.	Kaihe Yamazaki	CTD	University of Tasmania
5.	Julia Neme	CTD	University of New South Wales
6.	Sophie Bestley	CTD	University of Tasmania
7.	Abe Passmore	Carbon	CSIRO
8.	John Akl	Carbon	CSIRO
9.	Wayne Dillon	Carbon	CSIRO
10.	Lavy Ratnarajah	Carbon	University of Tasmania
11.	Alain Protat	Atmosphere	Bureau of Meterology
12.	Jay Mace	Atmosphere	University of Utah
13.	Joel Alroe	Atmosphere	Queensland University of Tech
14.	Kelsey Barber	Atmosphere	University of Utah
15.	Marc Mallet	Atmosphere	University of Tasmania
16.	Robert Strzepek	BioGeotraces	University of Tasmania
17.	Pauline Latour	BioGeotraces	University of Tasmania
18.	Anita Butterley	BioGeotraces	University of Tasmania
19.	Brandon McNabb	BioGeotraces	University of British Columbia
20.	Talitha Nelson	BioGeotraces	University of Tasmania
21.	Scott Meyerink	Geotraces	University of Tasmania
22.	Rebecca Zitoun	Geotraces	University of Tasmania
23.	Tom Williams	Geotraces	University of Tasmania
24.	Chris Traill	Geotraces	University of Tasmania
25.	Knut Heintaz	Geotraces	University of Tasmania
26.	McKeira Cumming	Geotraces	University of Tasmania
27.	Margot Hind	Voyage Manager	CSIRO MNF
28.	Hanuman Crawford	SIT Support	CSIRO MNF

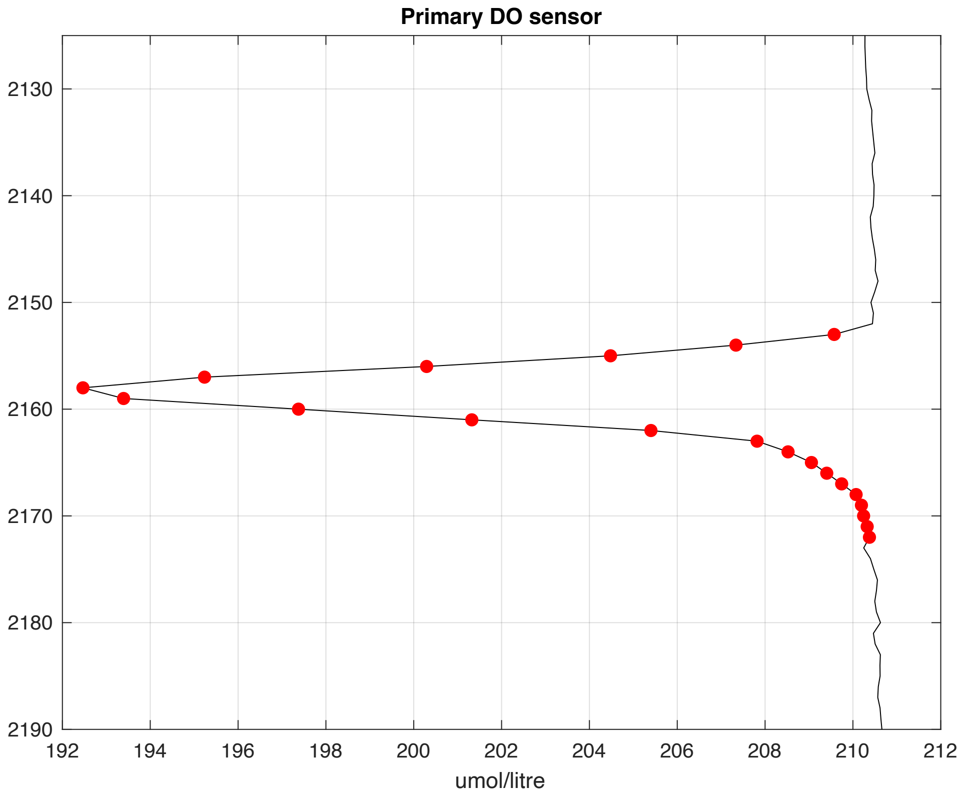
29.	Brendan Coulson	SIT Support	CSIRO MNF
30.	Richard Atkinson	DAP Support	CSIRO MNF
31.	Francis Chui	DAP Support	CSIRO MNF
32.	Nelson Kuna	GSM Support	CSIRO MNF
33.	Augustin Deplante	GSM Support	CSIRO MNF
34.	Merinda McMahon	Hydrochemistry Support	CSIRO MNF
35.	Pavie Nanthasurasak	Hydrochemistry Support	CSIRO MNF
36.	Maddy Lahm	Hydrochemistry Support	CSIRO MNF
37.	Christine Rees	Hydrochemistry Support	CSIRO MNF
38.	Helen Fry	Doctor	ASPEN MEDICAL
39.	Deborah Sier	Registered Nurse	ASPEN MEDICAL

CTD Processing Report

The follow report details the processing and calibration of the CTD data.

Note that the units of dissolved oxygen have since been converted from umol/litre to umol/kg using the seawater density (oxy_umolkg = oxy_uM/((1000+sigma0)/1000), where sigma0 is the potential density anomaly with a reference pressure of 0 dbar) prior to the submission of the data to CCHDO.

Note that the *ctdoxyQC* flags for cast #53 were manually modified. Appendix A3 of the following report shows a large spike in the data in the primary sensor, not seen in the secondary sensor. This was not picked up by the internal QC processing and initial QC did not have these data flagged as bad. DO data from the primary sensor from 2153 to 2172 dbar have since been flagged as bad (red dots is figure below show the data that have flagged as bad).



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Australia’s National Science Agency,
on behalf of the nation

RV *Investigator* CTD Data Processing Report

Voyage ID	**IN2024_V01**
Voyage Title	Multidisciplinary Investigations of the Southern Ocean (MISO): Linking Physics, Biochemistry, Plankton, Aerosols, Clouds, And Climate
Depart	Hobart TAS, Monday 1st January 2024 21:00 UTC
Return	Freemantle WA, Monday 4th March 2024 02:20 UTC
Chief Scientist	Dr Steve Rintoul (CSIRO)
Data Processor	Vito Dirita (CSIRO – E&T Data Acquisition & Processing)

Document History

Date	Version	Author	Comments
6 May 2024	1.0	Vito Dirita	Initial version
15 May 2024	1.1	Vito Dirita	Final version

Contents

1 Summary

The objective of this voyage was to improve the understanding of how the Southern Ocean region influences the Earth system and use this knowledge to improve models. This voyage characterised the properties of aerosols, clouds, radiation, and precipitation over the Southern Ocean south of Australia and investigate how they are shaped by interactions between the ocean, atmosphere, and biosphere. Repeat observations were used to discover how and why the region is changing and the consequences of Southern Ocean change for climate, biogeochemical cycles, biological productivity, and the future of the Antarctic Ice Sheet. The voyage sought new insights into the processes controlling the availability of iron and other trace elements and their role in regulating productivity in the Southern Ocean and the production of marine organic aerosols that can drive cloud nucleation. The observations and insights gained from the voyage will be used to develop, test, and implement new parameterisations for models used for weather forecasts and climate projections This report describes the production of quality controlled, calibrated CTD data from RV *Investigator* voyage IN2024_V01.

Data for 103 CTD deployments were acquired using the Sea-Bird SBE9+V2 CTD unit #25 (S/N 1354), fitted with 36 twelve-litre bottles on the rosette sampler. Sea-Bird-supplied calibration factors were used to compute the pressures and preliminary conductivity values. CSIRO-supplied calibrations were applied to the temperature data. The data were subjected to automated QC to remove spikes and out-of-range values.

The configuration of the CTD for casts 1-103 is shown in table 1 below.

The final conductivity calibration was based on a single deployment grouping. The final calibration from the primary sensor had a standard deviation (SD) of 0.0012679 PSU, within our target of 'better than 0.002 PSU'. The standard product of 1-decibar binned averages were produced using data from the primary sensors.
The dissolved oxygen data (primary) calibration fit had a SD of 0.94146 (Casts: 1-52) and 0.94773 (Casts: 53-103) µM. The agreement between the CTD and bottle data was good.

Additional sensors include: Altimeter (Tritech PA500), Transmissometer (Wetlabs C-Star), CDOM, Chlorophyll-a, Scattering (Wetlabs ECO FLCDRTD) were installed on the auxiliary A/D channels of the CTD.

To access the full voyage plan and other reports and data associated with this voyage, please see the contact information at the end of this report.

1.1 Voyage Track

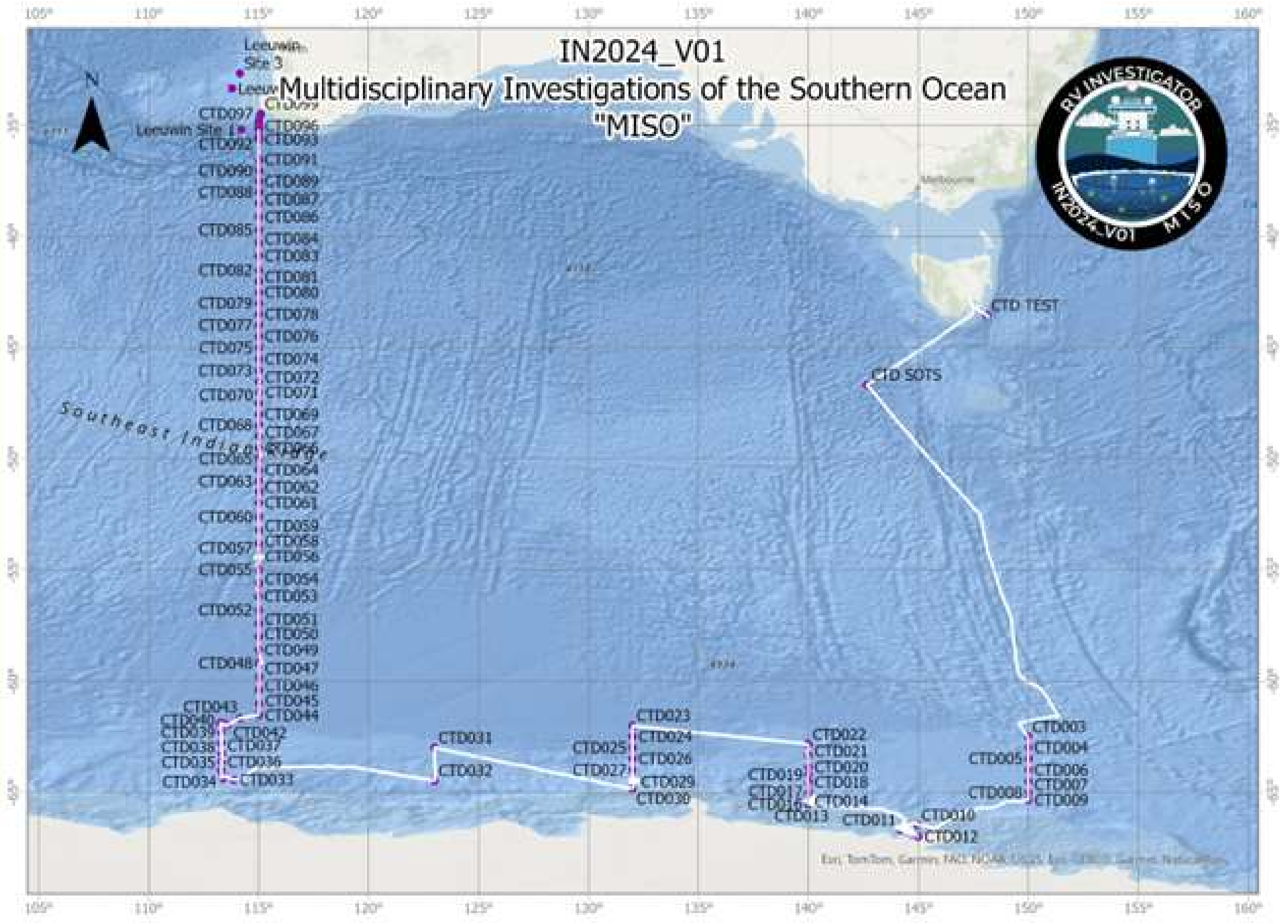


Figure 1: Voyage track

2 Data Processing

2.1 Background Information

103 CTD deployments were conducted on this voyage. The data were acquired with the CSIRO CTD unit #25 (S/N 1354), a Sea-Bird SBE911 with dual conductivity and temperature sensors.

The CTD was additionally fitted with SBE43 dissolved oxygen sensors including Altimeter, PAR, CDOM-Fluorometer, Transmissometer, Chlorophyll-a, and Turbidity. These sensors are described in Table 1 below including instrument serial numbers and calibration dates.

103 CTD casts were performed following the SR-3 southern transit to the ice edge and then the I09S transit north from the ice edge to the Australian continental shelf.

On the first two casts, there was a significant difference between the primary and secondary dissolved oxygen sensor readings. The secondary dissolved oxygen sensor was replaced after cast 2 to a sensor with a more recent membrane service. This configuration was kept till the end of the voyage, refer to Table 1.

Furthermore, both primary and secondary oxygen sensor calibrations have been divided into two sets: 1-52 and 53-103, to account for gradual sensor drift from by a relatively long voyage.

Sensor Description	Model	Serial No.	A/D Channel	Calibration Date	Calibration Source
Pressure	Digiquartz 410K-134	CTD25#1354	P	25-Jul-2023	Sea-Bird
Primary Temperature	Sea-Bird SBE3*plus*	2751	T0	28-Feb-2023	Sea-Bird
Secondary Temperature	Sea-Bird SBE3*plus*	4682	T1	28-Feb-2023	Sea-Bird
Primary Conductivity	Sea-Bird SBE4C	4774	C0	10-Oct-2023	Sea-Bird
Secondary Conductivity	Sea-Bird SBE4C	4683	C1	2-Oct-2023	Sea-Bird
Primary Oxygen	SBE43	3155	A0	7-Feb-2023	Sea-Bird
Secondary Oxygen (cast #1) **(cast #2)** **(cast#3-103)**	SBE43	3647 3646 3198	A1	10-Aug-2023 10-Aug-2023 10-Aug-2023	Sea-Bird
Altimeter	Tritech PA500	228403	A2	26-May-2022	Tritech
PAR	Biospherical QCP2300HP	70562	A3	13-Jan-2023	
CDOM Fluorometer CDOM	Wetlabs ECO FLBBRTD	7138	A4	1-Feb-2024	Wetlabs
Transmissometer	Wetlabs C-Star (DR)	1421	A5	9-Aug-2022	Wetlabs
Chlorophyll-a	Wetlabs ECO FLBBRTD	6765	A6	10-Apr-2023	Wetlabs/Sea-Bird
Scattering / Turbidity	Wetlabs ECO FLBBRTD	6765	A7	4-Oct-2023	Wetlabs/Sea-Bird
Midas SVX2 sound velocity probe	Valeport	73429			

Table 1: CTD Sensor configuration on IN2024_V01

Water samples were collected using a Sea-Bird SBE32, 12-litre 36-bottle rosette sampler which was fitted to the frame. The raw CTD data were collected in SBE Seasave version 7.26.7.110, converted to scientific units using SBE Data Processing version 7.26.7.129 and written to NetCDF files with CNV_to_Scan (cnv_to_scan_ui2.py, from the CSIRO MNF Data Acquisition and Processing “marinetech” git repository) for processing using the MATLAB-based CapPro software.

The CapPro software version 2.11 was used to apply automated QC and preliminary processing to the data. This included spike removal, identification of water entry and exit times, conductivity sensor lag corrections, conductivity cell thermal inertia corrections, and the determination of the pressure offsets. It also loaded the hydrology data and computed the matching CTD sample burst data (i.e., averaged sensor data) for water-sample-to-sensor data comparisons. The automatically-determined pressure offsets and in-water points were inspected and verified during data processing. The bottle sample data were used to compute final conductivity and dissolved oxygen calibrations. These were applied to the data, after which files of binned 1-decibar averaged data were produced.

2.2 Pressure and Temperature Calibration

The pressure offsets for each deployment are plotted in Figure 2. The blue circles refer to initial out-of-water values (beginning of downcast) and the red circles the final out-of-water values (end of upcast).

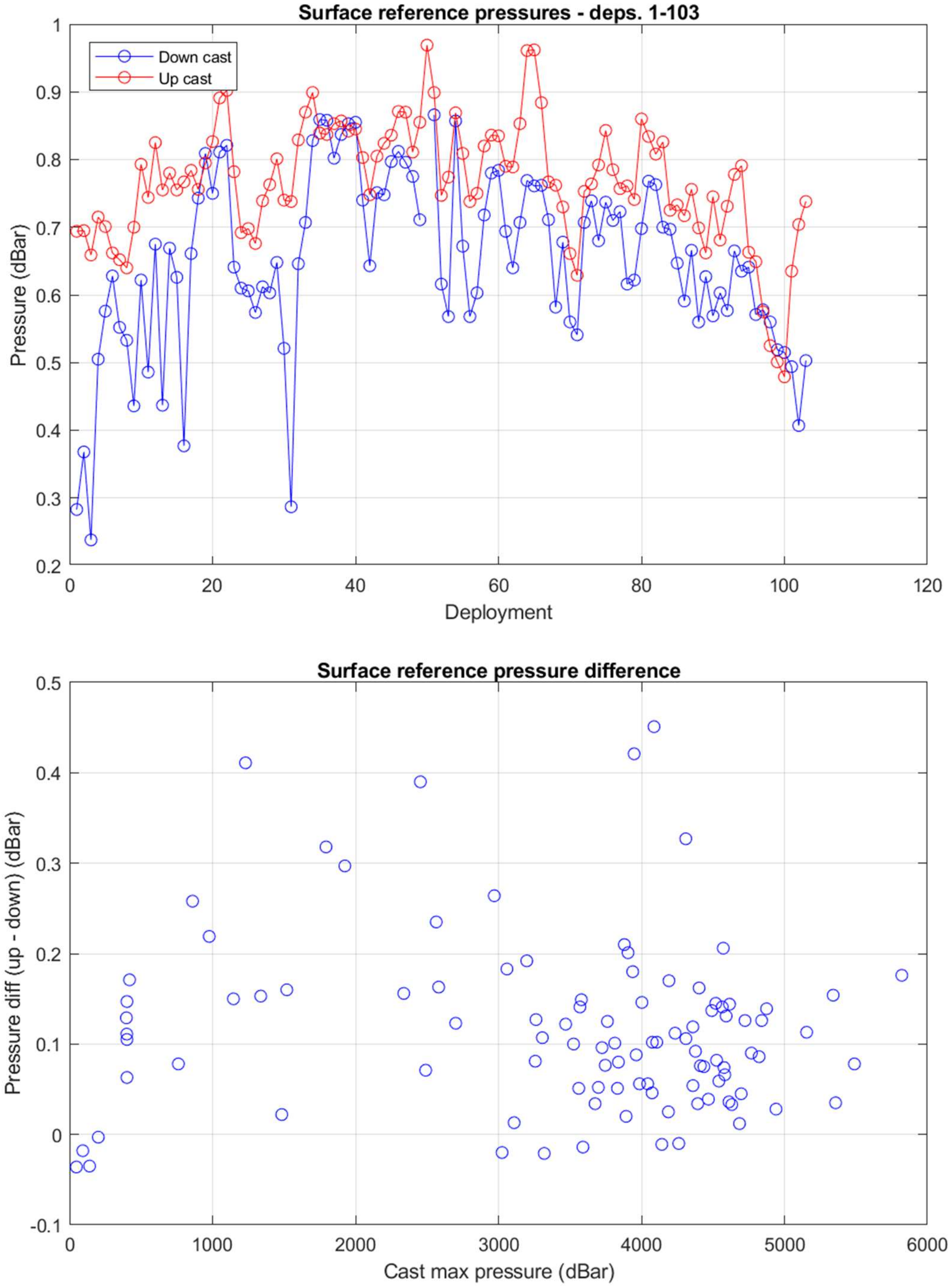


Figure 2: CTD pressure offsets

The difference between the primary and secondary temperature sensors at the bottle sampling depths is plotted in Figure 3. Most deployments plot within ± 0.001 °C of zero – outliers result from sampling in regions of high vertical temperature gradient. The consistent mean difference (red +

markers) between the primary and secondary temperature from deployment to deployment indicates neither sensor has drifted significantly from its calibration. Higher fluctuations in difference presented in the plots represents shallower casts, where the high gradient is present throughout most of the cast.

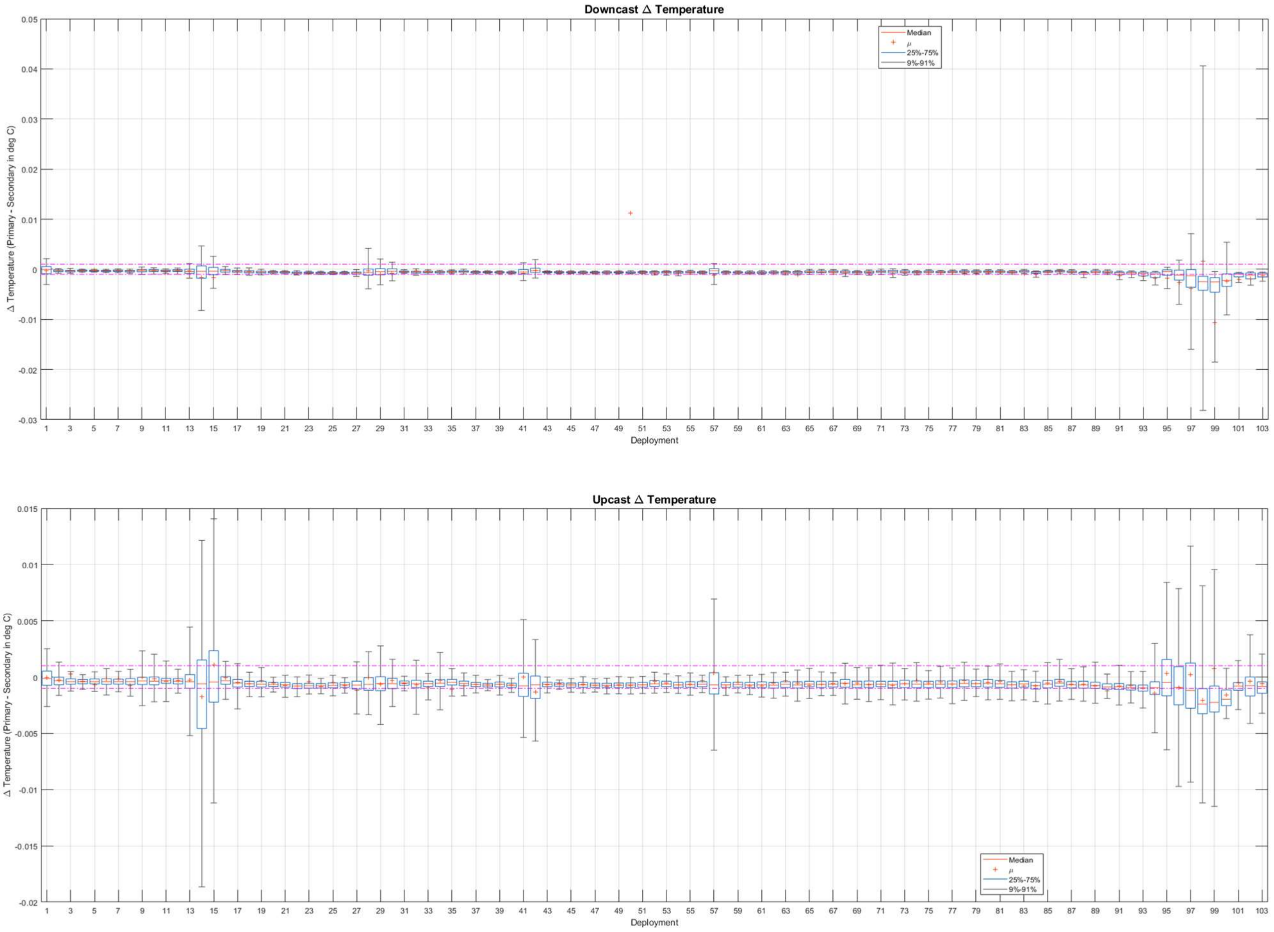


Figure 3: Difference (primary - secondary) between temperature sensor values on downcast (left) and upcast (right)

2.3 Conductivity Calibration

If any discrepancies or sampling problems occurred during bottle salinity sampling or between primary and secondary CTD conductivity measurements, these would show in the conductivity calibration plots in Figure 4. We observed minor discrepancies based on these calibration results. These discrepancies were due to a large percentage of points being located within the halocline region The profile plots showing the thermocline and halocline ranges are in Figure 5.

The calibrations were based upon the percent of ‘good’ sample data, 1642 of 2227 (73.7%) good samples from the primary unit and 1638 of 2227 (73.5%) good samples from the secondary unit. To perform the calibration with the preferred (default) CapPro calibration settings, a minimum of 70% of the samples need to be in the ‘good’ range. If there is an insufficient number of good samples for a unit, the conductivity difference ‘cutoff’ value must be increased to continue with the calibration process in CapPro. For this set of conductivity calibrations, the cutoff values used were 0.003 (primary) and 0.003 (secondary).

Figure 4 plots CTD - bottle salinity differences for both upcast (Hydro bottle) and downcast (CTD SBE43) data. The ‘bad’ outliers (magenta dots, red dots and red + markers) are excluded from the calibration, the ‘suspect’ outliers (blue dots) are used in the calibration but are weighted based on their distance from the mean. All green dots are considered ‘good’ data points and are not weighted based on distance from the mean.

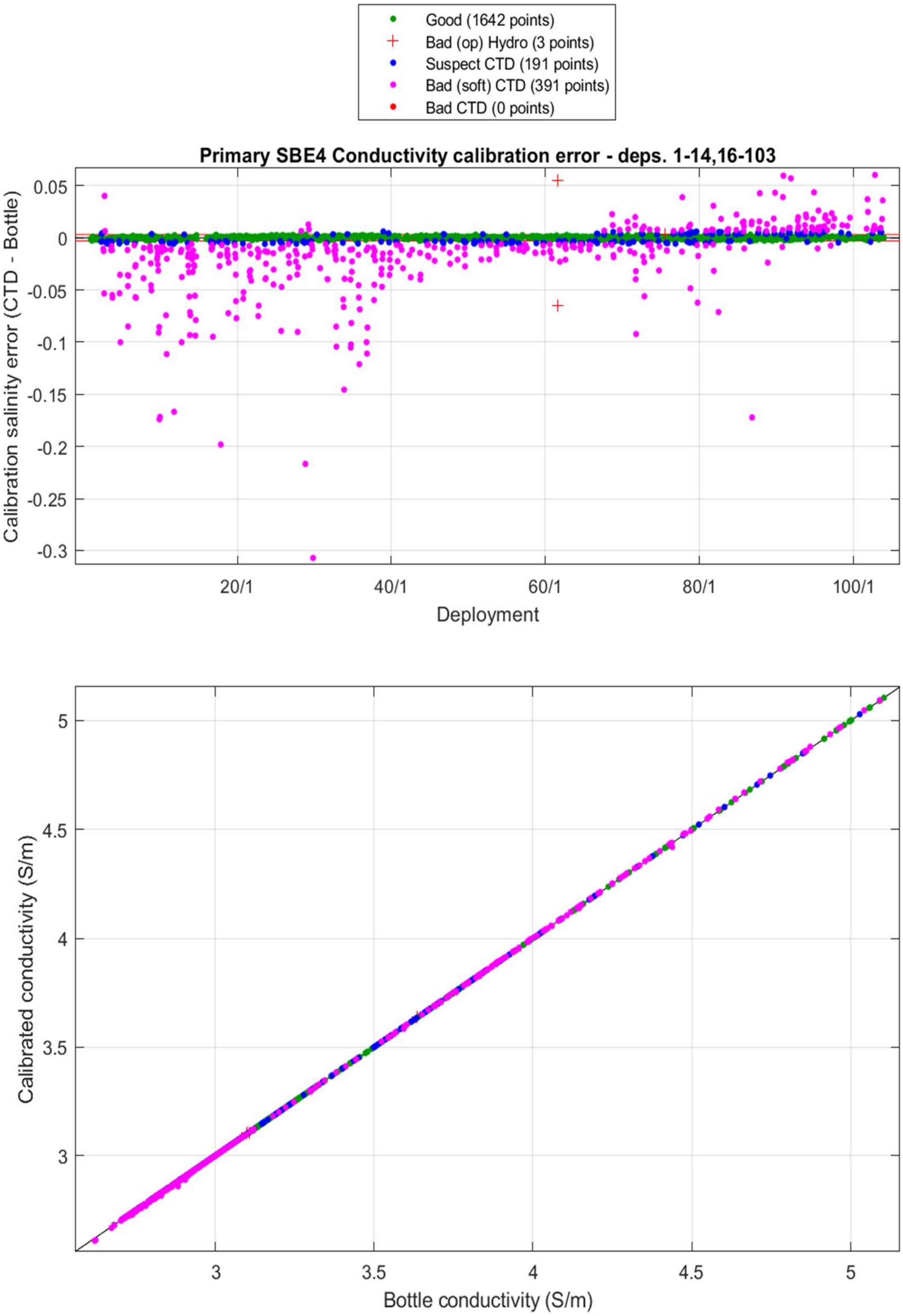


Figure 4a: CTD - bottle conductivity difference and salinity calibration error (primary)

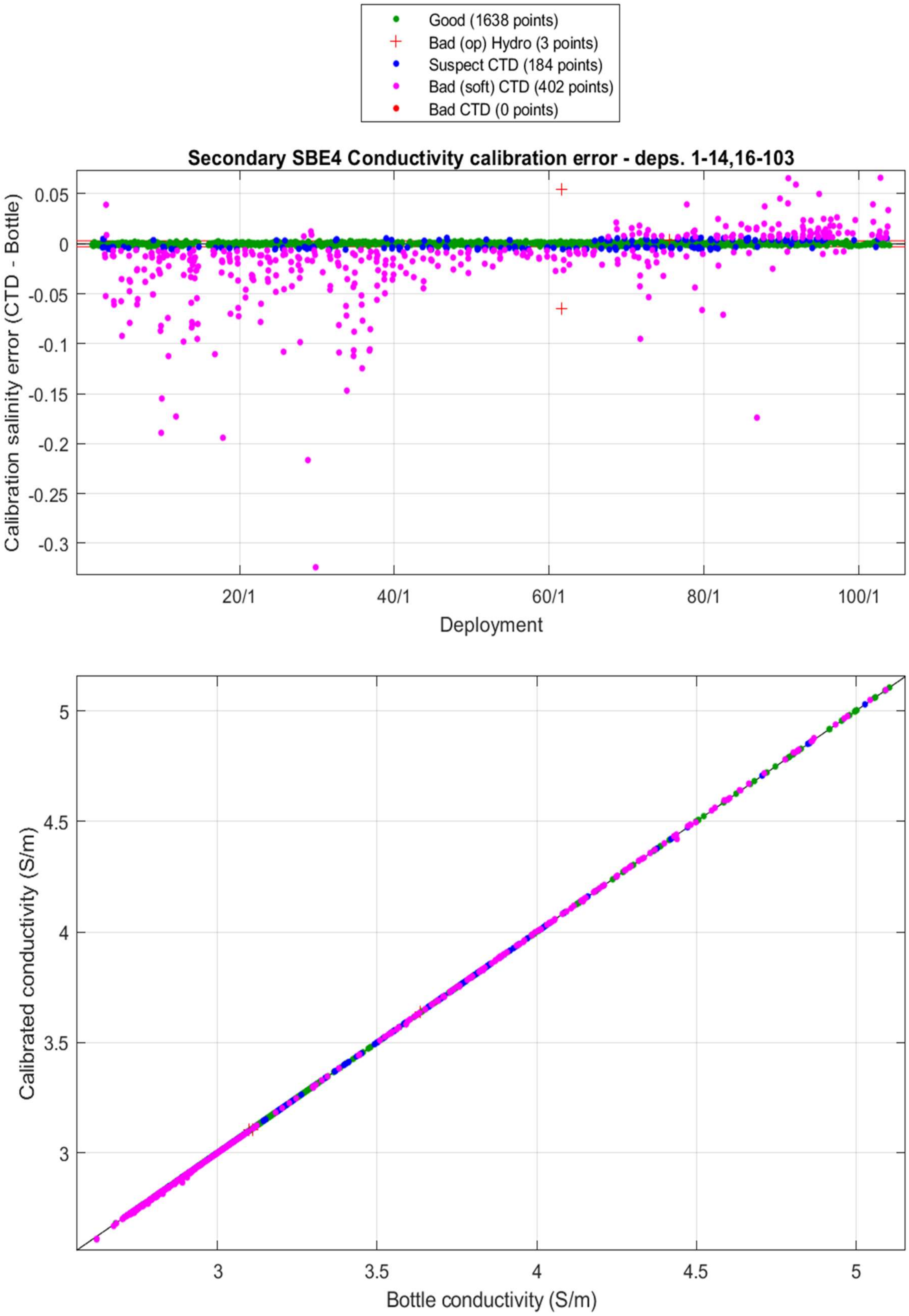


Figure 4b: CTD - bottle conductivity difference and salinity calibration error (secondary)

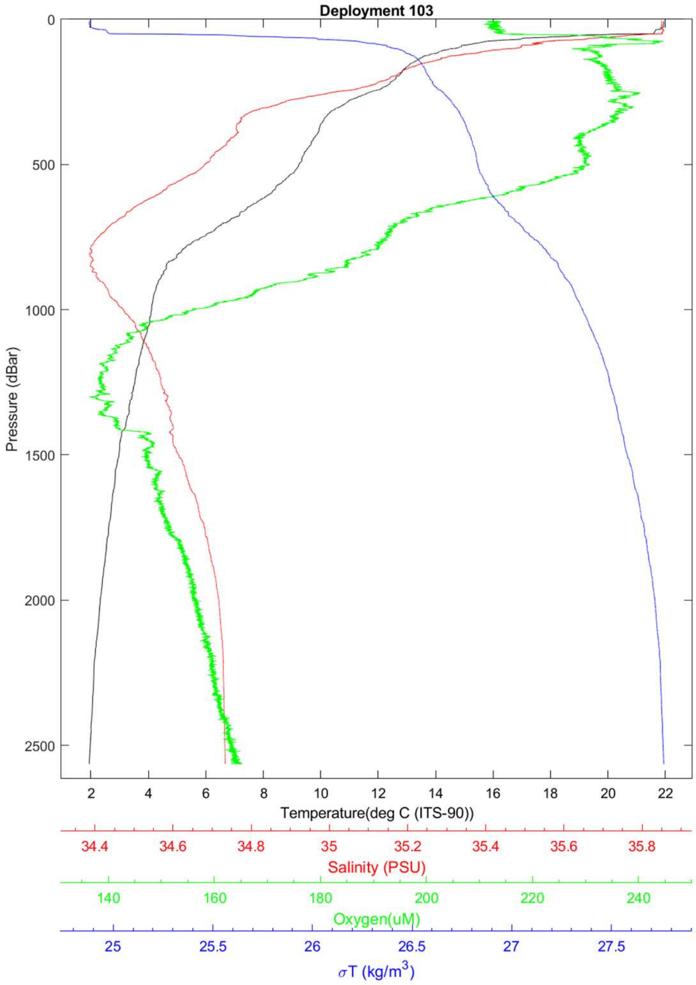


Figure 5: Temperature, salinity, dissolved oxygen and σT profiles

The box plot (Figure 6) of calibrated downcast conductivities (primary - secondary) at the bottle sampling depths for all deployments shows that the calibrated primary and secondary conductivity cell responses corresponded well to each other.

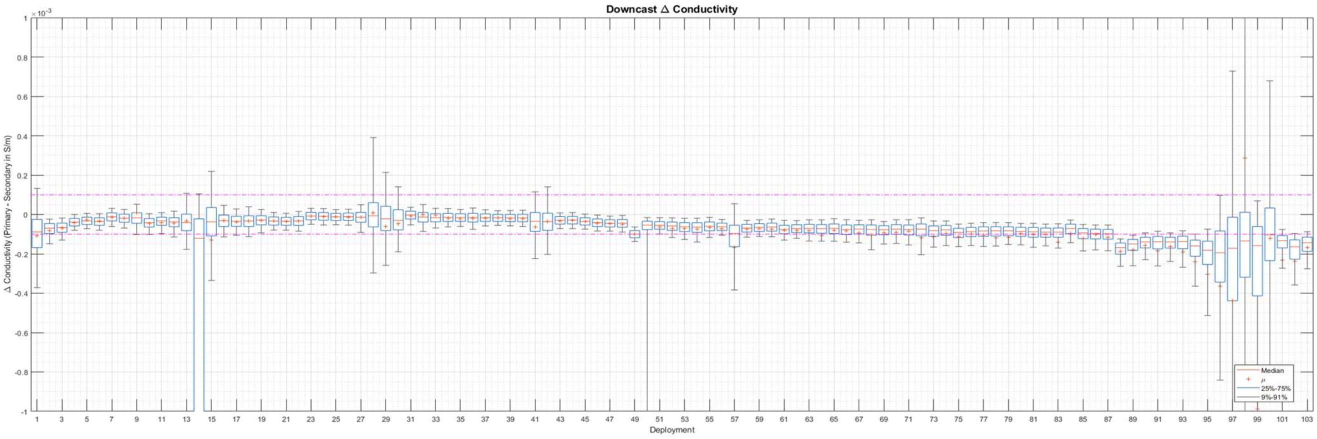


Figure 6: Difference (primary - secondary) between conductivity sensor values on downcast

The final results for the primary and secondary conductivity sensors with respect to their original calibrations are shown in Table 2 and Table 3.

Sensor Group	Deployments	Scale Factor		Offset		Salinity (PSU)	
		a1	±	a0	±	Residual SD	M.A.D.
Primary	1-103	0.99964	0.00015681	0.00073884	0.00052973	0.0012679	0.00088842
Secondary	1-103	0.99967	0.00015132	0.00074918	0.00050985	0.0012645	0.00080845

Table 2: Conductivity calibration with respect to manufacturer's calibration coefficients and post-calibration results

Conductivity Sensor	Deployments	CPcor	±
Primary	1-103	-8.2025e-08	1.4091e-08
Secondary	1-103	-7.6901e-08	1.339e-08

Table 3: Calculated CPcor (the correction for pressure effects on the conductivity cell) for primary and secondary conductivity units compared to the manufacturer's nominal value of -9.5700e-08 (for pressure in decibars) (Sea-Bird, 2017)

This is a good calibration. We normally aim for a SD of 0.002 PSU for 'typical' oceanographic voyages. The above calibration factors were applied to the indicated deployments. Full plots of residuals before and after calibration are available in A.1.

Data from the secondary conductivity and temperature sensors were used to produce the averaged salinities (these data variables have no suffix) with primary sensors included with a suffix '_2'.

2.4 Dissolved Oxygen Sensor Calibration

2.4.1 SBE Calibration Procedure

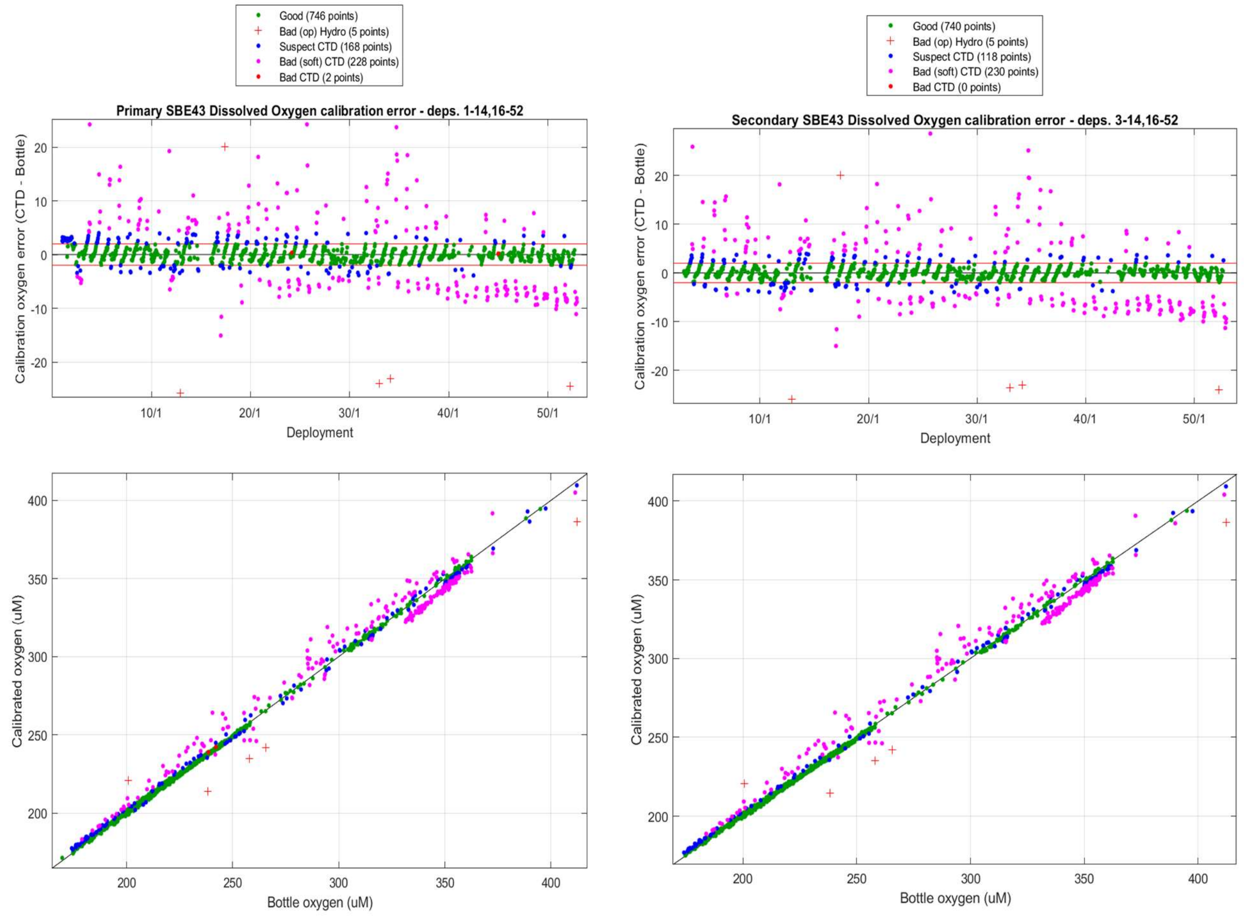
AN64: SBE 43 Dissolved Oxygen Sensor - Background Information, Deployment Recommendations, and Cleaning and Storage (Sea-Bird, 2013) describes the SBE43 dissolved oxygen sensor as "a polarographic membrane oxygen sensor having a single output signal of 0 to +5 volts, which is proportional to the temperature-compensated current flow occurring when oxygen is reacted inside the membrane.
A Sea-Bird CTD that is equipped with an SBE43 oxygen sensor records this voltage for later conversion to oxygen concentration, using a modified version of the algorithm by Owens and Millard (1985)."

Calibration involves performing a linear regression, as per (Sea-Bird, 2012) to produce new estimates of the calibration coefficients Soc and $Voffset$. These new coefficients are used, along with the other, manufacturer-supplied coefficients, to derive oxygen concentrations from the sensor voltages.

2.4.2 Results

Deeper casts (>1000m) are known to be affected by pressure-induced hysteresis with this sensor. This is corrected automatically within CapPro using the method discussed in *AN64-3: SBE 43 Dissolved Oxygen (DO) Sensor - Hysteresis Corrections* (Sea-Bird, 2014). There is a small mismatch between downcast and upcast dissolved oxygen due to the response time of the sensor. No correction for the sensor lag effect has been applied.

On the first two casts, there was a significant difference between the primary and secondary dissolved oxygen sensor readings. The secondary dissolved oxygen sensor was replaced after cast 2 to a sensor with a more recent membrane service. This configuration was kept till the end of the voyage, refer to Table 1. For the secondary oxygen, four calibration groups were used with the associated SBE43 upcast data to compute the new Soc and $Voffset$ coefficients and two calibration groups for the primary. Figure 7 plots CTD SBE43 - bottle oxygen differences for both upcast (Hydro bottle) and downcast (CTD SBE43) data. The 'bad' outliers (magenta dots, red dots and red + markers) are excluded from the calibration, the 'suspect' outliers (blue dots) are used in the calibration but are weighted based on their distance from the mean. All green dots are considered 'good' data points and are not weighted based on distance from the mean. The box plot (Figure 8) of calibrated downcast dissolved oxygen readings (primary - secondary) at the bottle sampling depths for all deployments shows that the calibrated primary and secondary dissolved oxygen sensor responses corresponded well to each other. Both primary and secondary oxygen sensor calibrations have been further divided into two sets: 1-52 and 53-103, to account for gradual sensor drift from by a relatively long voyage.



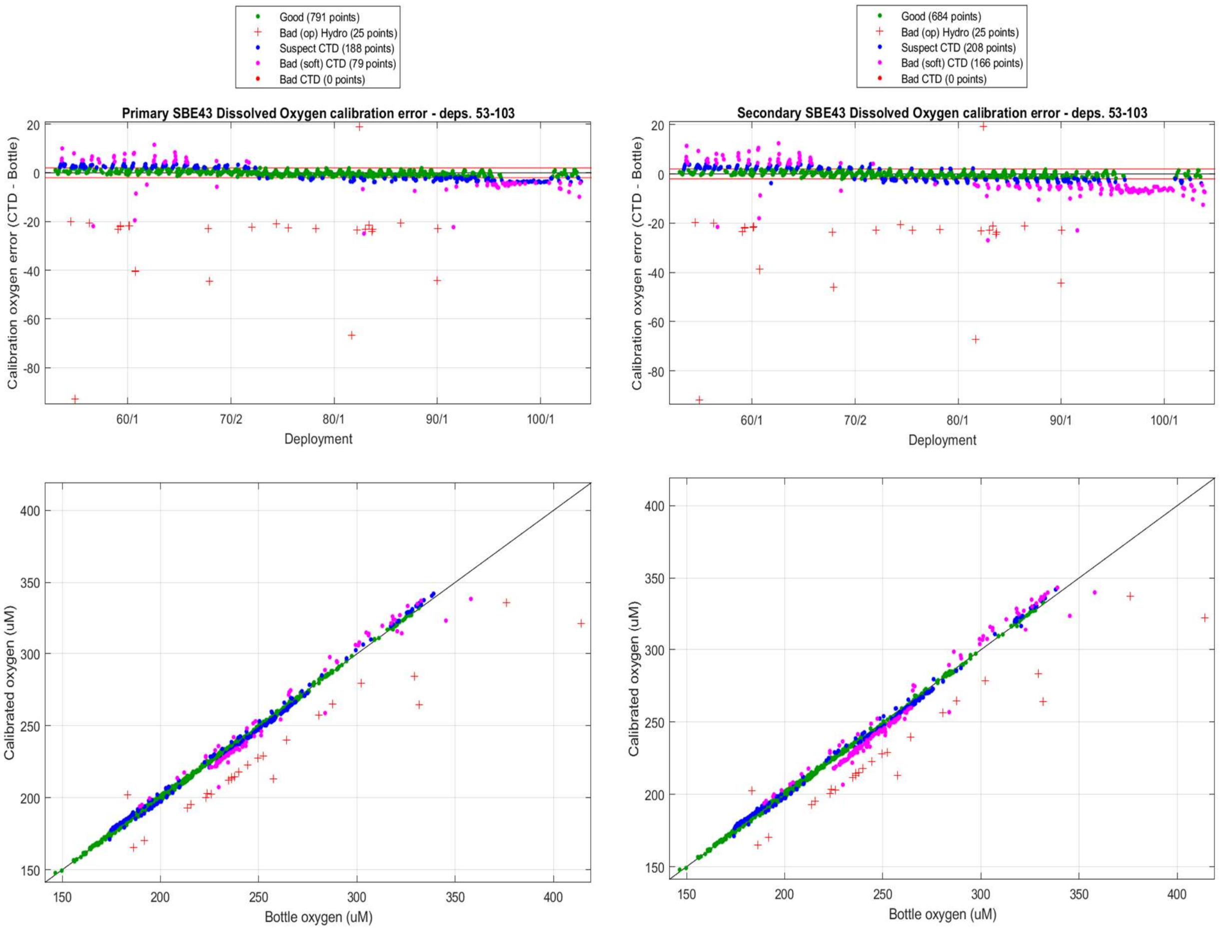


Figure 7: CTD SBE43 - bottle dissolved oxygen difference and calibration error (left: primary, right: secondary)

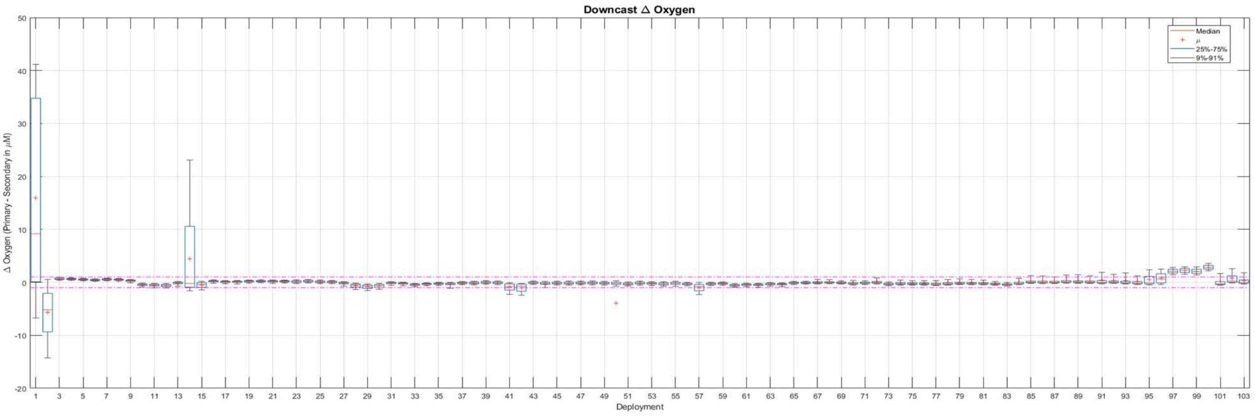


Figure 8: Difference (primary - secondary) between dissolved oxygen sensor values on downcast

The old and new *Soc* and *Voffset* values for DO sensors are listed in Table 4. The *Soc* value is a linear slope scaling coefficient; *Voffset* is the fixed sensor voltage at zero oxygen. As expected, over time, the increasing *Soc* scale factors show the SBE43 sensor is losing sensitivity. Full plots of residuals before and after calibration are available in A.2. The calibrations were applied for each sensor and the averaged files were created using the result from the primary sensor. Note that an anomaly was observed on the primary oxygen sensor at cast #53 at around 2160 dbar (blockage or fault) lasting over several dbars which was not detected by CapPro (see appendix A.3)

Sensor	Calibration Source	Casts:	Calibration Coefficients				Dissolved Oxygen (µM)	
			Voffset	±	*Soc*	±	Residual SD	M.A.D.
Primary	CapPro	1-52	-0.44717	0.0012128	0.49553	0.00055687	0.94146	0.97618
		53-103	-0.48291	0.00085716	0.52217	0.00043486	0.94773	1.0056
	Sea-Bird 3155	1-103	-0.5007		0.50630			
Secondary	CapPro	1	0.40292	3.0362	0.24629	0.36852	0.57144	0.16003
		2	-0.44787	0.0069257	0.44502	0.0025269	1.0061	0.77762
		3-52	-0.42158	0.0013967	0.39158	0.00040188	0.91316	0.7985
		53-103	-0.47502	0.0012259	0.41515	0.00040842	0.98538	1.109
	Sea-Bird 3647	1	-0.5234		0.52803			
	Sea-Bird 3646	2	-0.4616		0.53156			
	Sea-Bird 3198	3-103	-0.4947		0.41235			

Table 4: Dissolved oxygen calibrations

2.5 Other Sensors

2.5.1 WET Labs C-Star Transmissometer

The C-Star transmissometer was used on all deployments. It was calibrated by the manufacturer by measuring the output with the beam blocked, in air with a clear beam path and with clean water in the path. These values are used to determine a scale and offset for use in SBE Data Processing software to convert the raw counts to a beam transmittance output of 0 - 100 percent. The sensor worked as expected during this voyage.

2.5.2 WET Labs ECO CDOM Sensor

The WET Labs ECO CDOM (coloured dissolved organic matter) sensor was used for all deployments. The CDOM has been calibrated with manufacturer supplied coefficients. This sensor worked as expected during this voyage.

2.5.3 WET Labs ECO Fluorometer-Scattering Sensor

The WET Labs ECO Fluorometer-Scattering sensor was used for all deployments. The fluorometer (Chlorophyll-*a*) has been calibrated with manufacturer supplied coefficients to give outputs in mg/m^3 (= µg/L). The scattering (optical backscatter, OBS) has been calibrated with manufacturer supplied coefficients to give volume scattering outputs in $m^{-1}sr^{-1}$.

2.5.4 Chlorophyll-a Chelsea Aquatracka Fluorometer

The instrument operated without fault or issue throughout the voyage.

2.5.5 Sea-Bird Scientific Deep SUNA V2 nitrate sensor

The Sea-Bird Scientific Deep SUNA V2 nitrate sensor was not used on this voyage.

2.5.6 Biospherical PAR Sensor

The Biospherical PAR (photosynthetically active radiation) sensor was used for all deployments. The output is a nominal 0 - 5 volts which is converted to the unit µEinsteins/m2/second using a manufacturer supplied wet calibration factor and the dark voltage determined at calibration. This data channel has been included in the output files for all deployments. Time of day and environmental factors such as sea state and cloud cover impact these readings. If most or all of the values for a deployment are near zero it indicates a night-time cast. In deployments where the PAR profiles have sub-surface maxima the CTD may have been shaded by the ship. This sensor worked as expected during this voyage

2.6 Bad-Data Detection

The value limits for each sensor are configured in CNV_to_Scan conversion software and are written to the NetCDF scan file. Typical limits used for the sensor range and maximum second difference are in **Error! Reference source not found.**. The rejection rate is recorded in the CapPro processing log file.

Sensor	Range minimum	Range maximum	Maximum Second
Pressure	-7	6500	0.5
Temperature	-2	40	0.05
Conductivity	-0.01	7	0.01
Dissolved Oxygen	-1	500	0.5
Fluorometer	0	100	0.5
Altimeter	0	50	0.5
PAR	-5	2000	0.5
Transmissometer	0	100	0.5
CDOM	-5	515	0.5
OBS	0	0.008	0.5
Nitrate	0	100	10

Table 5: Sensor limits for bad-data detection

2.7 Heave Filtering

Sensor data impacted by ship heave impeding the CTD deployment is filtered out in three stages and applied during data binning. The first stage detects negative acceleration of the CTD which can cause trailing mixed water to be pumped through the sensors. The second stage looks at all negative density gradients and flags readings which are above 10 times the standard deviation of all negative gradients, for 2 seconds. The third stage flags any pressure reversals which are greater than the height of the CTD sensor pump inlet above the frame.

2.8 Temperature-Conductivity Lag

To precisely align the temperature and conductivity measurements for a sample of water, a temporal offset can be applied. A manufacturer-recommended nominal offset (Δt_{c_SBE9}) of -0.073 seconds is initially applied at time of acquisition by the SBE9+ deck unit on both primary and secondary conductivity channels. This offset advances the conductivity sensor readings in time to compensate for the amount of time it takes for the measured water sample to move from the temperature sensor through into the conductivity sensor cell.

Post-voyage inspection of the temperature and conductivity data in CapPro can determine fine-tuning adjustments to the conductivity sample time (seconds) offset (Δt_{c_CP}) that will optimally align the data. The final adjustments applied to the conductivity sample time can be found in Table 6 and **Error! Reference source not found.**. Note that although CapPro can set an offset (‘lag’, in number of scans, with a scan frequency of 24 Hz) for both temperature and conductivity samples, DAP only sets a lag for the conductivity sample to maintain consistency with the nominal offset applied by the SBE9+ to the conductivity data. The equation governing this conductivity sample time adjustment is given below, where $t_{c\_aligned}$ is the best-estimate of the conductivity measurement time (seconds) to align it with the temperature measurement from the same sample of water on the downcast, and t_{c_meas} is the original, uncorrected conductivity measurement time (seconds).

$$t_{c\_aligned} = t_{c\_meas} + \Delta t_{c\_SBE9+} + \Delta t_{c\_CP}$$

Cast #	Nominal Offset Time Applied by SBE9+, Δt_{c_SBE9+} (sec)	Offset (‘Cond lag’) Set in CapPro (scans)	Calculated Offset Time from CapPro ‘Cond lag’, Δt_{c_CP} (sec = scans/24 Hz)
1-103	-0.073	-0.55	-0.0229

Table 6: Primary conductivity sensor offset adjustments

Cast #	Nominal Offset Time Applied by SBE9+, Δt_{c_SBE9+} (sec)	Offset (‘Cond lag’) Set in CapPro (scans)	Calculated Offset Time from CapPro ‘Cond lag’, Δt_{c_CP} (sec = scans/24 Hz)
1-103	-0.073	-1.70	-0.0708

Table 7: Secondary conductivity sensor offset adjustments

2.9 Averaging

The calibrated data were ‘filtered’ to remove pressure reversals and binned into the standard product of 1-decibar averaged NetCDF files. The binned values were calculated by applying a linear, least-squares fit as a function of pressure to the sensor data for each bin, using this to interpolate the value for the bin mid-point. This method is used to avoid possible biases which would result from averaging with respect to time.

Each binned parameter is assigned a quality control (QC) flag (also in the NetCDF files). Our QC flagging scheme is described in (Pender & NCMI Information & Data Centre, 2022).

The QC Flag for each bin is estimated from the values for the bin components. The QC Flag for derived quantities, such as salinity and dissolved oxygen, is taken to be the worst of the estimates for the parameters from which they are derived.

3 References

Tim O'Hara. (2022). *The RV Investigator. Voyage Plan* IN2024_V01*.* Retrieved from Marine National Facility: Voyage Plans and summaries: https://mnf.csiro.au/en/Voyages/Voyage-Catalogue

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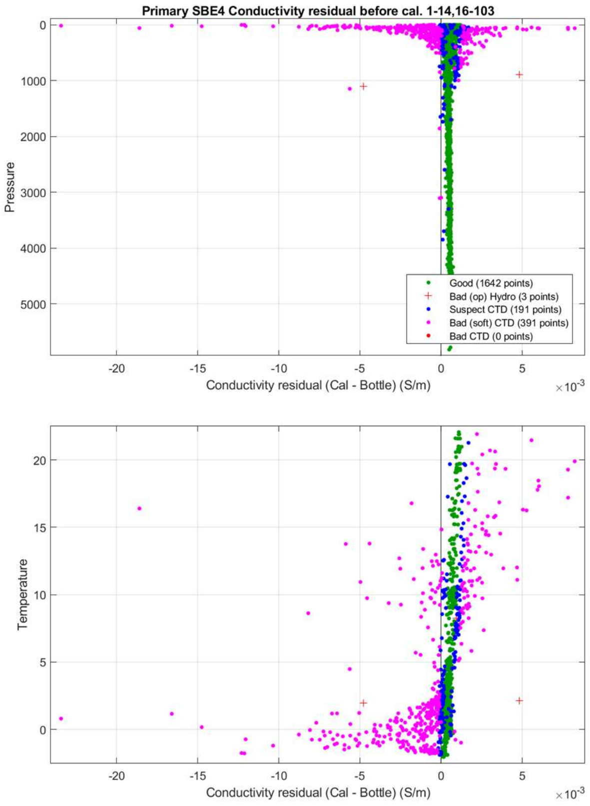
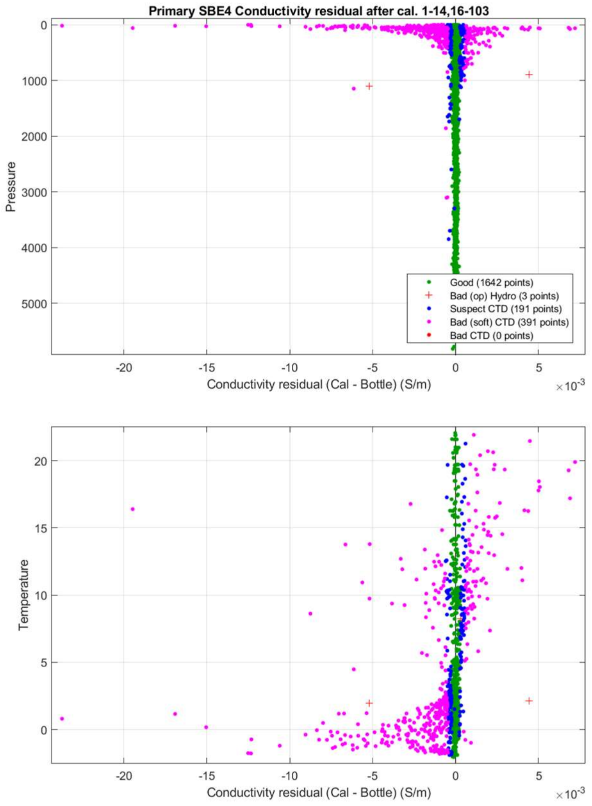
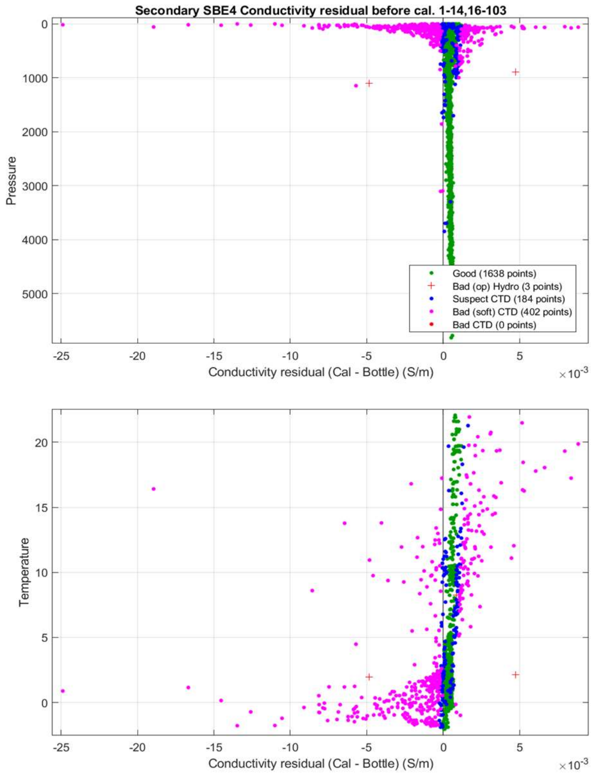
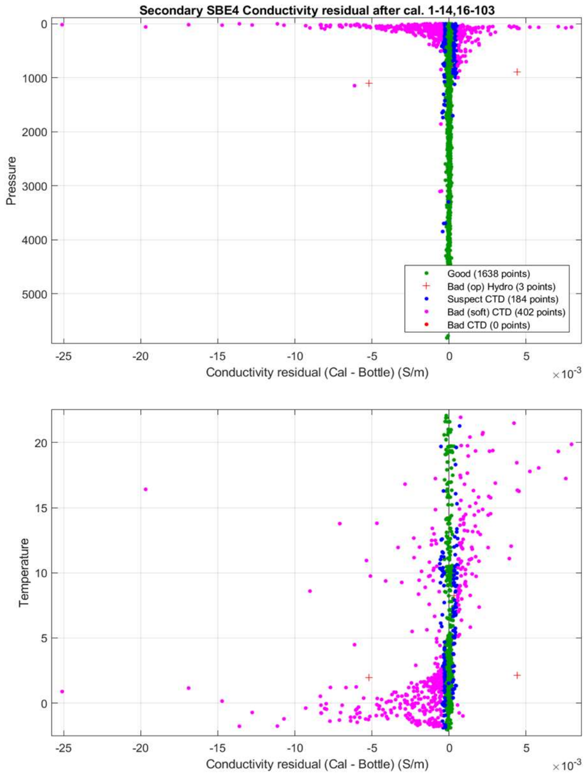
4 Appendices

A.1 Conductivity Calibration Residual Plots

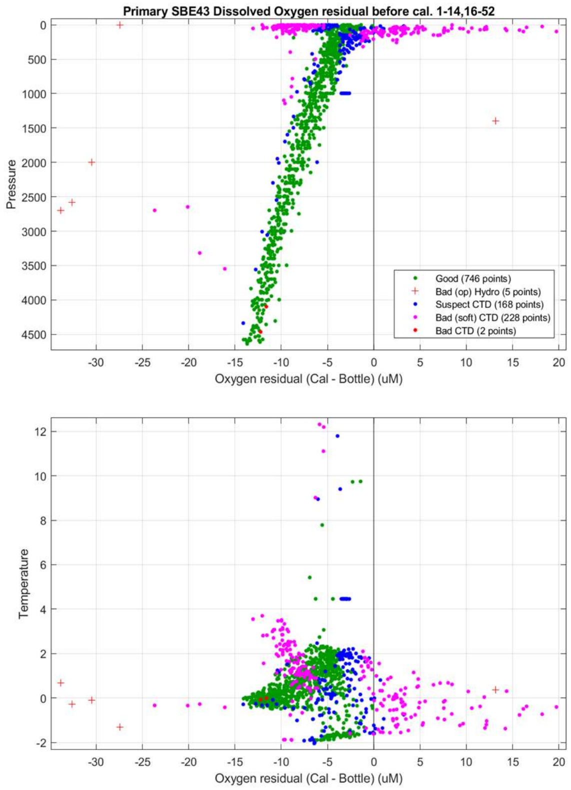


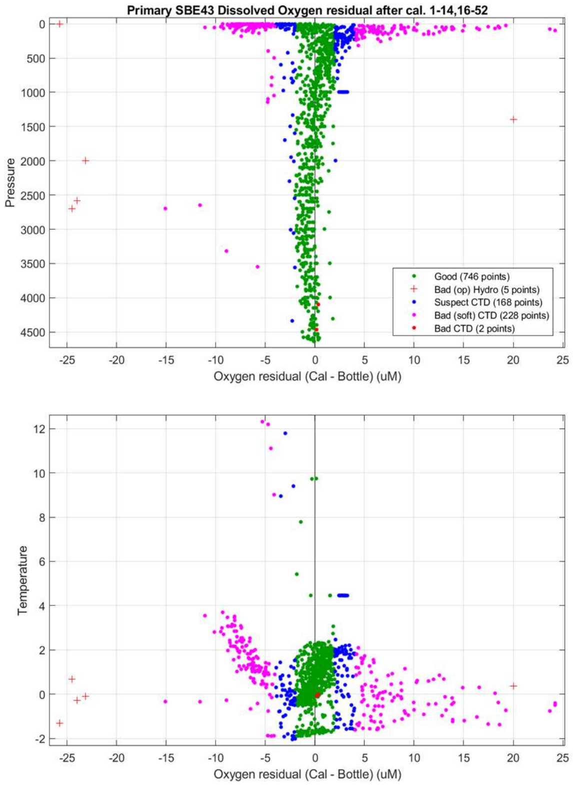


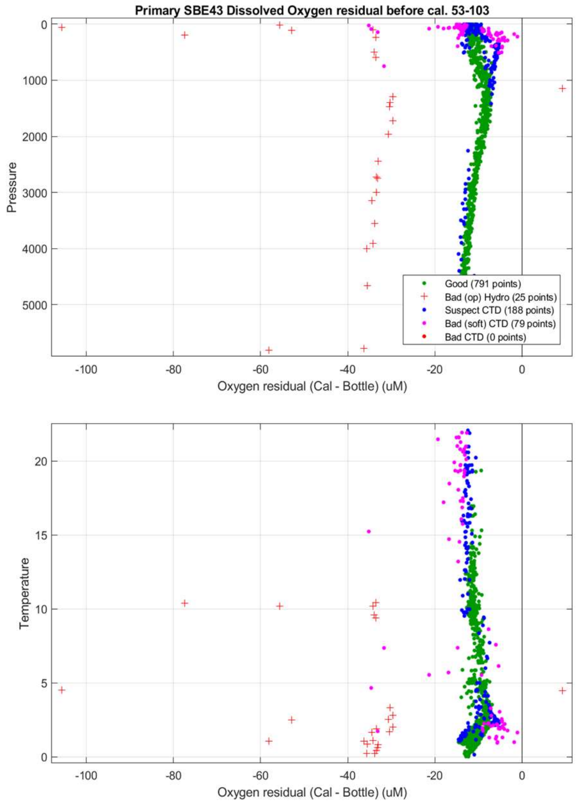


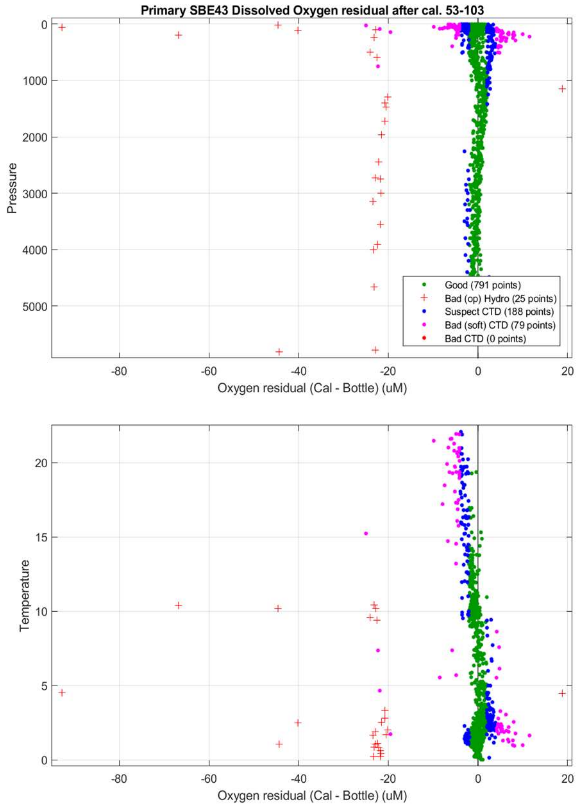


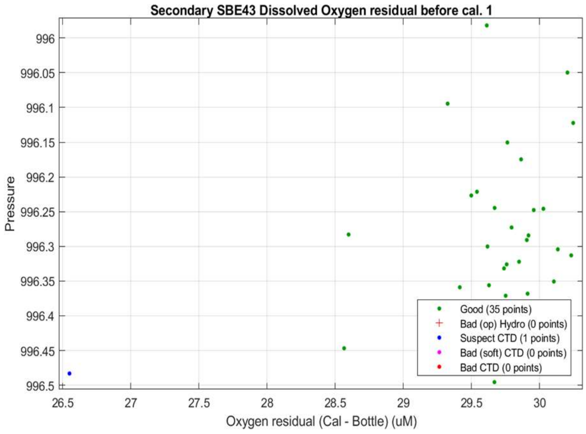
A.2 Dissolved Oxygen Calibration Residual Plots

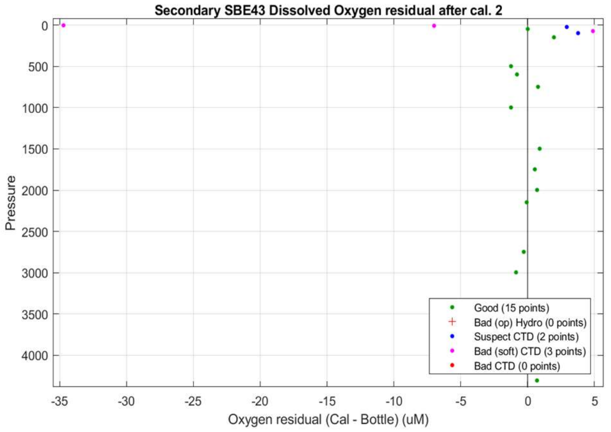









Secondary SBE43 Dissolved Oxygen residual before cal. 1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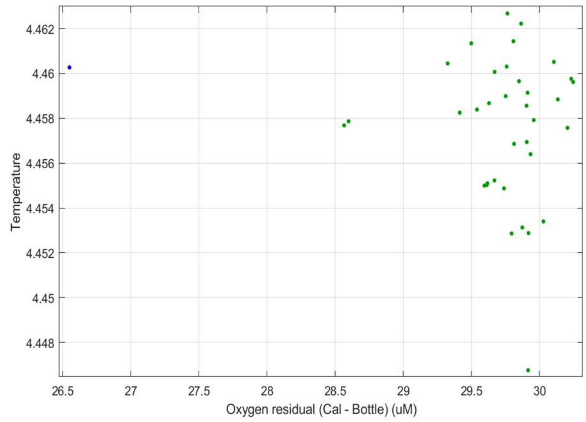
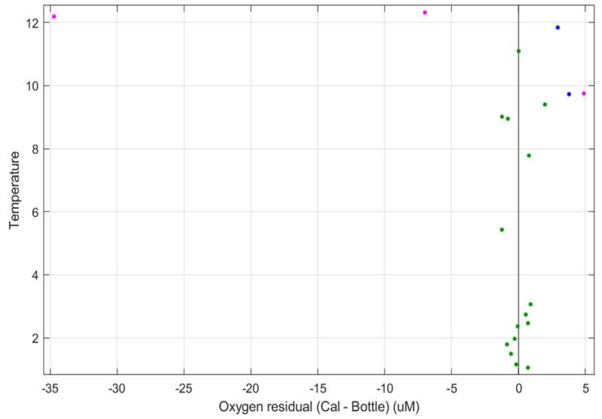
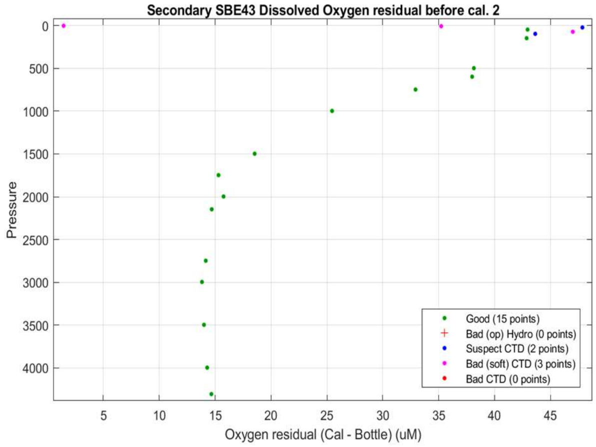
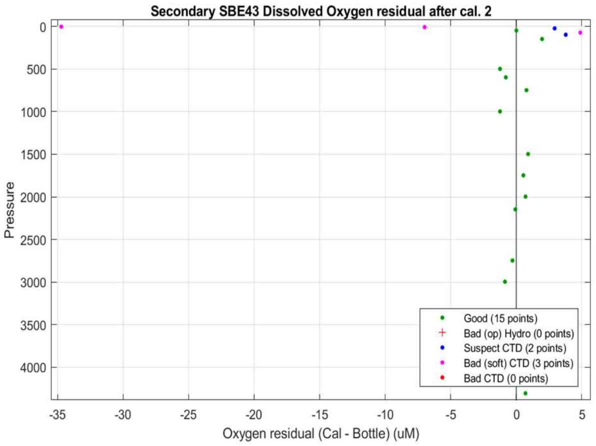
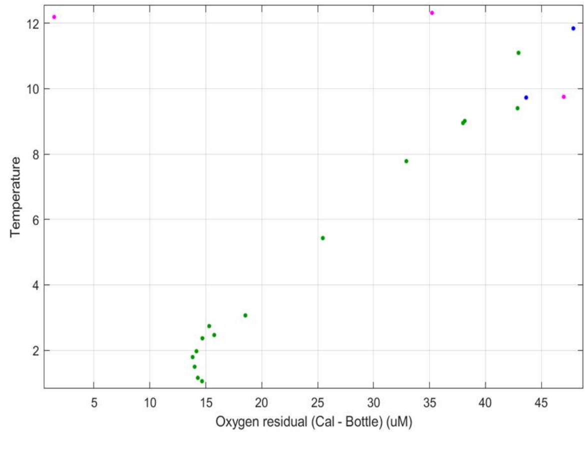
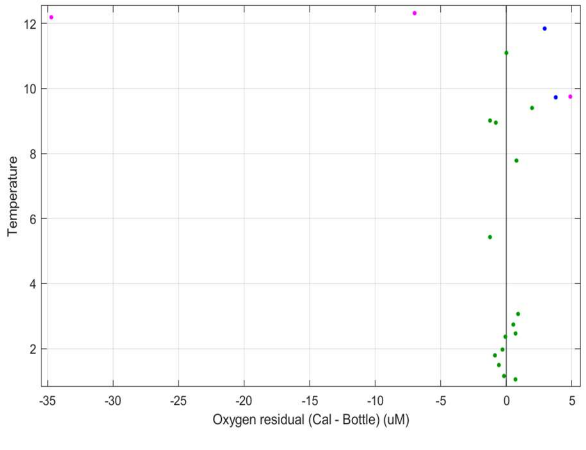


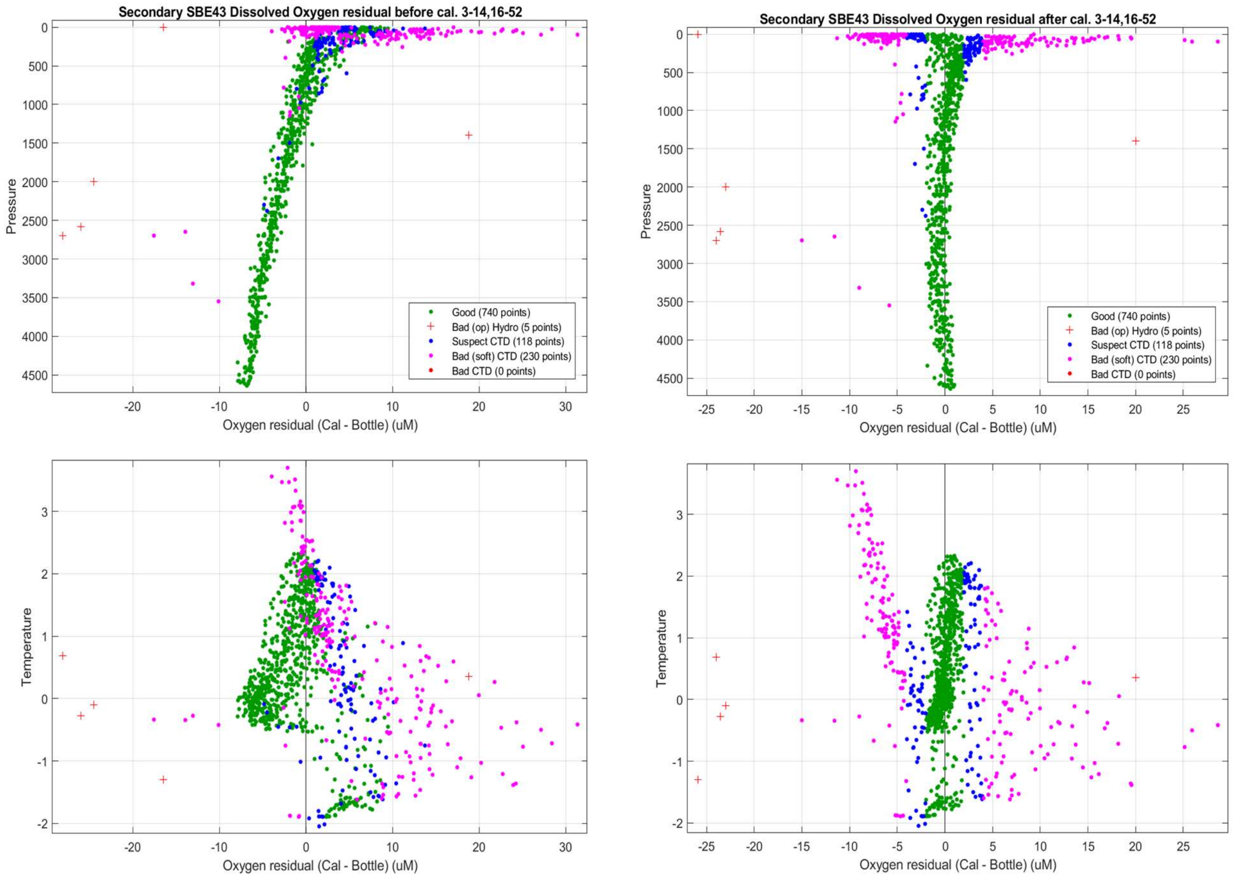


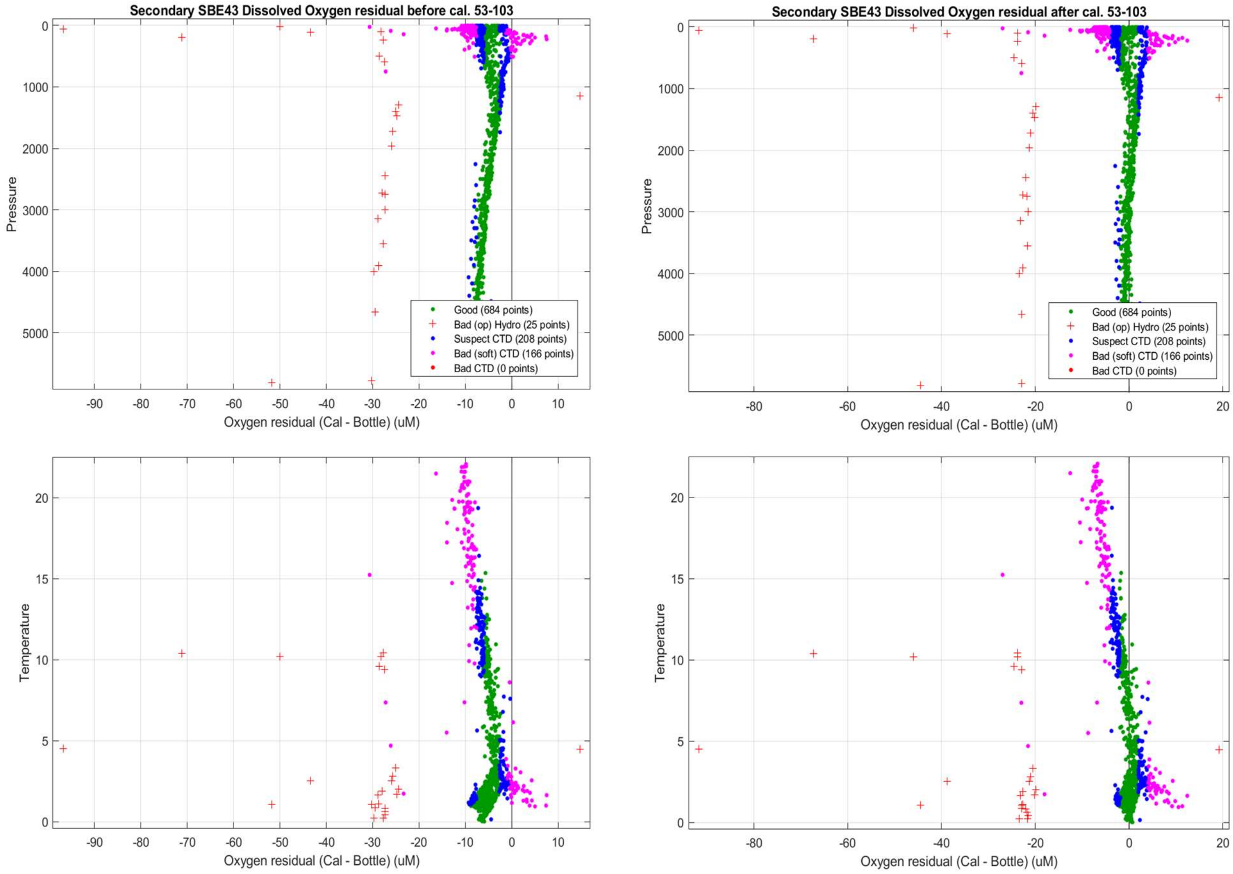

Secondary SBE43 Dissolved Oxygen residual before cal. 2


Secondary SBE43 Dissolved Oxygen residual after cal. 2



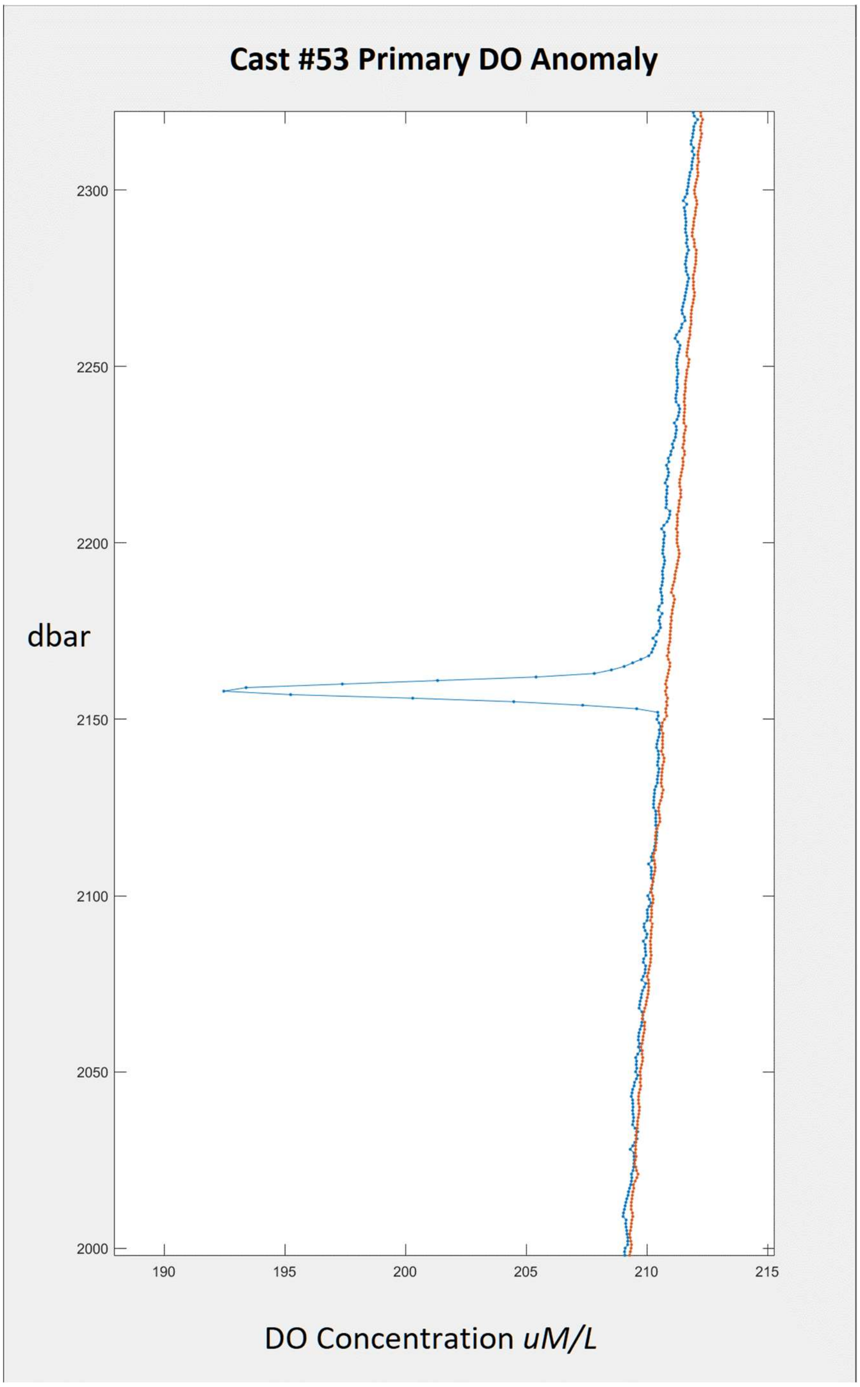



Secondary SBE43 Dissolved Oxygen residual before cal. 3-14,16-52
Secondary SBE43 Dissolved Oxygen residual after cal. 3-14,16-52
Pressure
Temperature
Oxygen residual (Cal - Bottle) (uM)
Good (740 points)
Bad (op) Hydro (5 points)
Suspect CTD (118 points)
Bad (soft) CTD (230 points)
Bad CTD (0 points)


Secondary SBE43 Dissolved Oxygen residual before cal. 53-103
Secondary SBE43 Dissolved Oxygen residual after cal. 53-103
Pressure
Temperature
Oxygen residual (Cal - Bottle) (uM)
Good (684 points)
Bad (op) Hydro (25 points)
Suspect CTD (208 points)
Bad (soft) CTD (166 points)
Bad CTD (0 points)

A.3 Cast #53 Primary Dissolved Oxygen Anomaly

Anomaly observed on the primary oxygen sensor at cast #53 at around 2160 dbar (blockage or fault) not flagged using second differences filtering method by CapPro, this is illustrated below where the blue plot is the primary oxygen and the orange is the secondary oxygen.



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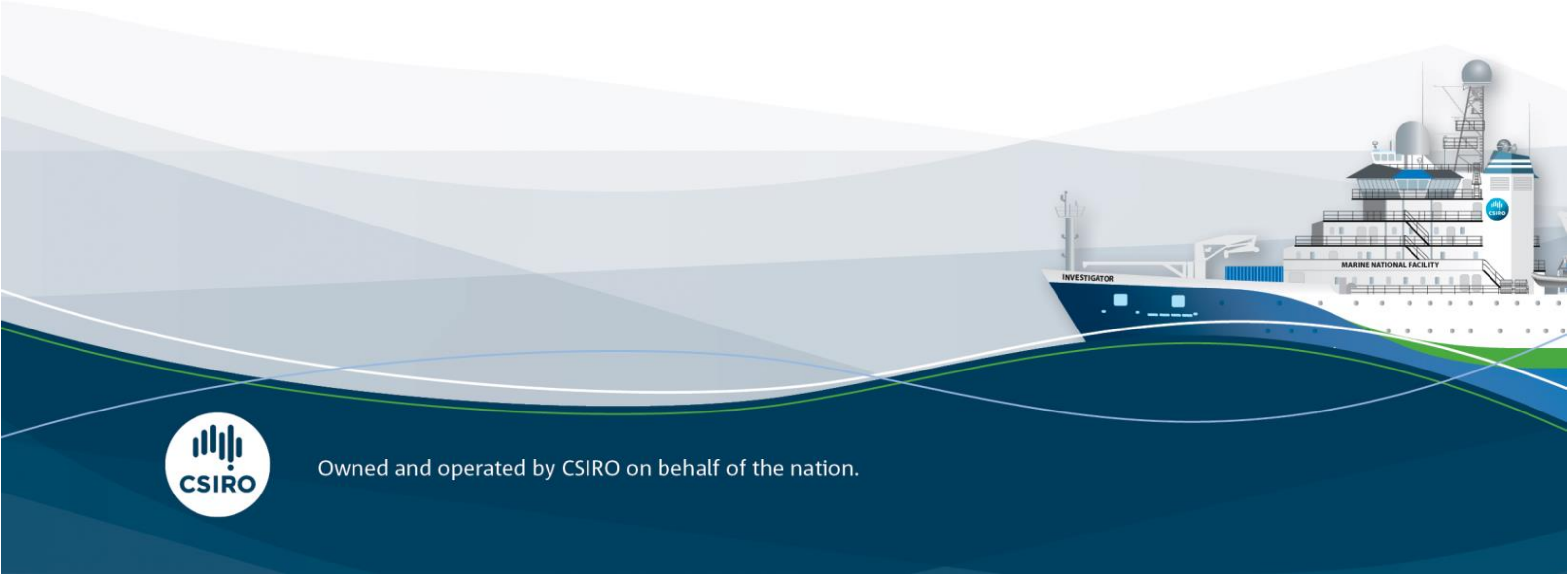
RV *INVESTIGATOR*

HYDROCHEMISTRY DATA PROCESSING REPORT

Voyage:	IN2024_V01
Chief Scientist	Dr Annie Foppert and Dr Steve Rintoul
Voyage title:	Multidisciplinary Investigations of the Southern Ocean (MISO): Linking Physics, Biochemistry, Plankton, Aerosols, Clouds and Climate
Report compiled by:	Merinda McMahon, Pavie Nanthasurasak, Christine Rees and Maddy Lahm



Owned and operated by CSIRO on behalf of the nation.

Contents

1 Executive Summary

1.1 Objectives

The objective of this voyage was to improve the understanding of how the Southern Ocean region influences the Earth system and use this knowledge to improve models. This voyage characterised the properties of aerosols, clouds, radiation, and precipitation over the Southern Ocean south of Australia and investigated how they are shaped by interactions between the ocean, atmosphere, and biosphere. Repeat observations were used to discover how and why the region is changing and the consequences of Southern Ocean change for climate, biogeochemical cycles, biological productivity, and the future of the Antarctic Ice Sheet. The voyage sought new insights into the processes controlling the availability of iron and other trace elements and their role in regulating productivity in the Southern Ocean and the production of marine organic aerosols that can drive cloud nucleation. The observations and insights gained from the voyage will be used to develop, test, and implement new parameterisations for models used for weather forecasts and climate projections.

1.2 General Hydrochemistry Information

Water samples collected during the voyage were analysed in the ship's hydrochemistry laboratory for nutrients, dissolved oxygen, and salinity. Overall data collected was of high quality. No significant sample collection, analysis, or data processing issues were encountered.

Five nutrients were determined: silicate, phosphate, nitrate + nitrite, nitrite and ammonium using AA3HR autoanalyser. Certified reference materials for nutrients in seawater (RMNS) were within 3% of their certified values. Missing and suspect hydrology samples are listed in Appendix section.

Please cite the following manuscript when reporting or publishing data for silicate, phosphate, nitrate+nitrite (NOx) and nitrite:

Rees, C., L. Pender, K. Sherrin, C. Schwanger, P. Hughes, S. Tibben, A. Marouchos, and M. Rayner. (2018) "*Methods for reproducible shipboard SFA nutrient measurement using RMNS and automated data processing*."

Limnol. Oceanogr: Methods, 17(1): pp. 25-41.

doi:10.1002/lom3.10294

If publishing ammonium data, please cite the following:

Rees, C., Janssens, J., Sherrin, K., Hughes, P., Tibben, S., McMahon, M., McDonald, J., Camac, A., Schwanger, C. and Marouchos, A., (2021*) "Method for Reproducible Shipboard Segmented Flow Analysis Ammonium Measurement Using an In-House Reference Material for Quality Control."*

Frontiers in Marine Science, 8.

doi:10.3389/fmars.2021.581901

Final hydrology data, analytical methods, related log sheets and processing notes can be obtained from the CSIRO data centre.

For Data, contact: NCMI_DataLibrarians@csiro.au

2 Itinerary

Departed: Hobart at 1300, 02 January 2024
Arrived: Fremantle at 1000, 05 March 2024

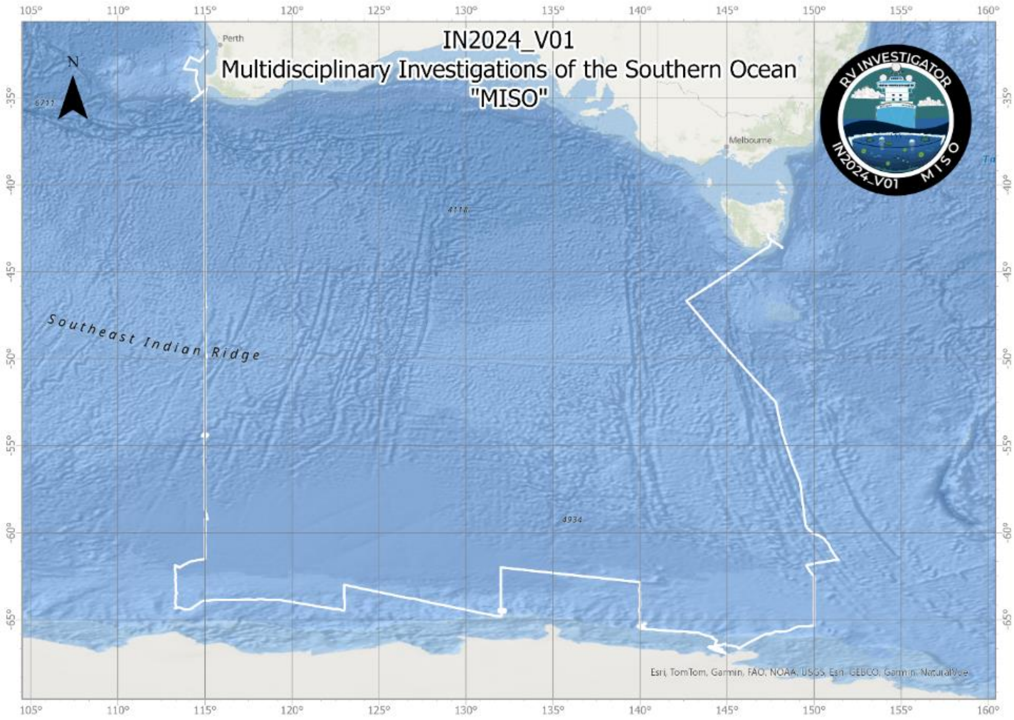


Figure 1. Voyage track.

3 Key personnel list

Table 1: Key Personnel list

Name	Role	Organisation
Dr Annie Foppert	Co-Chief Scientist	UTAS
Dr Steve Rintoul	Co-Chief Scientist	CSIRO
Margot Hind	Voyage Manager	CSIRO
Merinda McMahon	Hydrochemist	CSIRO
Christine Rees	Hydrochemist	CSIRO
Pavie Nanthasurasak	Hydrochemist	CSIRO
Maddy Lahm	Hydrochemist	CSIRO

4 Summary

4.1 Sample Type and Number Assayed

Table 2: Sample Type and Number Assayed

Analysis	Samples Assayed	Type
Salinity	2233	CTD
	60	TSG
	25	UWY
Dissolved Oxygen	2258	CTD
	25	UWY
Nutrients	2260	CTD
	25	UWY
	491	EXP
	45	TMR

4.1.1 CTD samples (Conductivity, Temperature, Density)

- Taken from the 12 L Ocean Test Equipment bottles on the CTD rosette that is deployed at depth for water collection.
- A total of 103 CTD deployments were sampled by:
    - Science party: Annie Foppert, Kathy Gunn, Paul Spence, Kaihe Yamazaki, Julia Neme, John Akl, Wayne Dillon, and Sophie Bestley.

4.1.2 Thermosalinograph (TSG) samples

- Taken from the underway instrument clean seawater line supplying the pCO2 instrument in the underway laboratory.
- TSG samples collected by hydrochemistry. Results emailed to Vito Dirita (CSIRO) at the completion of the voyage.
- TSG sampling team: Pavie Nanthasurasak, Merinda McMahon, Maddy Lahm and Christine Rees
- Refer to voyage EVERlog for TSG sample information.

4.2 Data Processing Overview

4.2.1 Conventional hydrology data

The sample meta-data, measured bottle salinity results, dissolved oxygen assay results and the nutrient assay raw data are processed by the CSIRO program HyPro. The final output is the hydrology data set. An overview of this process is illustrated below (Fig.2).

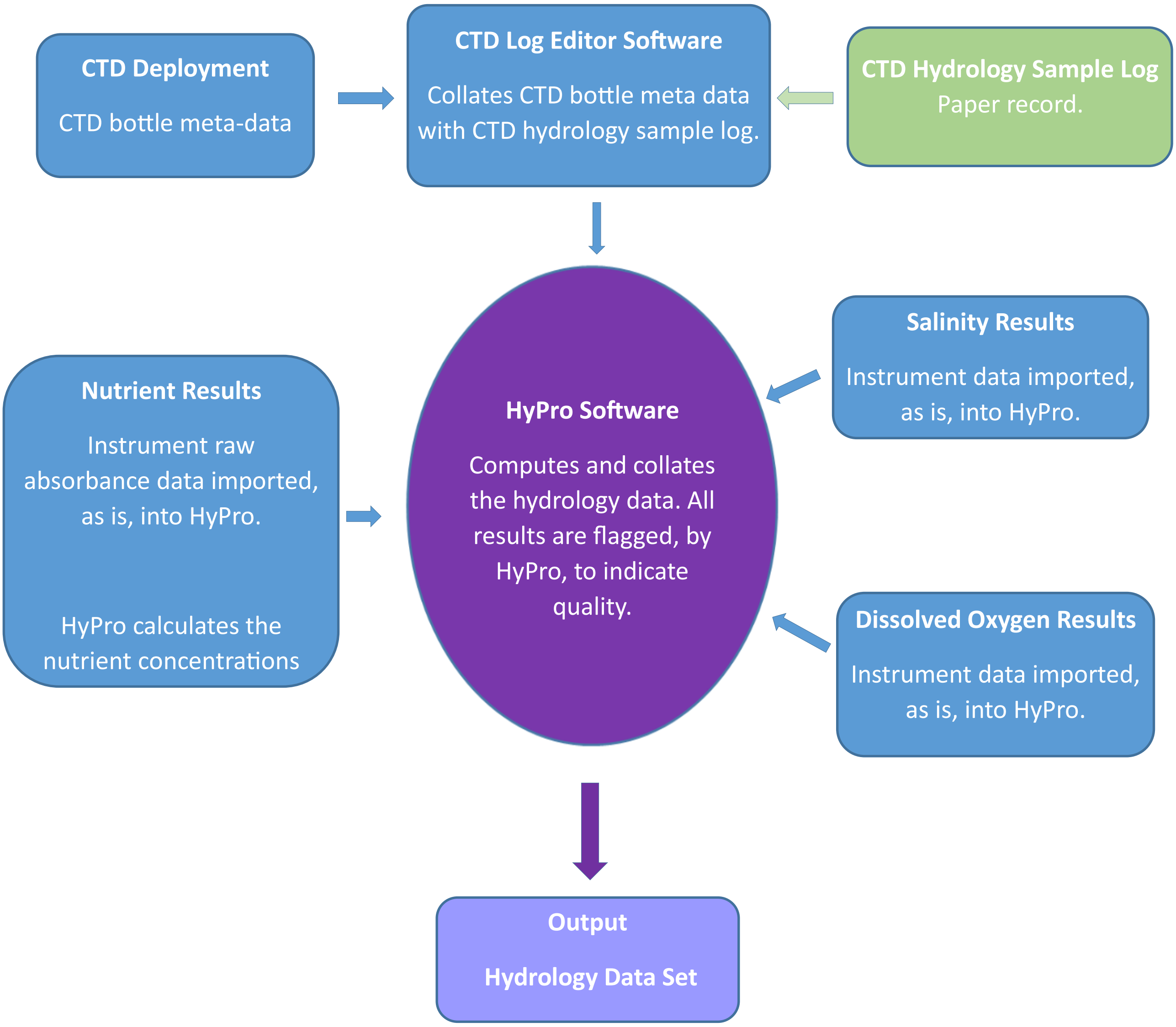


Figure 2. Hydrology Data Processing Flow Diagram.

5 Salinity

5.1 Salinity Measurement Parameters

Table 3: Salinity Measurement Parameters

Details	
HyPro Version	5.7
Instruments	Guildline Autosal Laboratory Salinometer 8400(B) – SN 72088. Bath temperature 24.0°C
Software	Ocean Scientific International Ltd (OSIL) Data Logger version 1.2
Hydrochemistry Methods	Sampling: WI_Sal_002 Analysis: SOP 006
Accuracy	± 0.001 practical salinity units
Reference Material	OSIL IAPSO – Batch P167, use by 21/02/2026, K_{15} = 0.99988
Sample Container	200 ml volume OSIL bottles made of type II glass (clear) with disposable plastic insert and plastic screw cap.
Sample Storage	Stored in salinometer lab for minimum of 8 hrs before the measurement.
Lab Temperature	Mean 21.8°C SD 0.6°C (Ruuvi sensor)
Analysts	Pavie Nanthasurasak
Comments	See DAP report for CTD calibration details.

5.2 Salinity Method

Salinity samples were measured on a Guildline Autosal 8400B instrument operated in accordance with its technical manual. The measured value is recorded with an OSIL data logger.

Practical salinity (S) is defined in terms of the ratio (K_{15}) of the electrical conductivity measured at 15°C 1 atm of seawater to that of a potassium chloride (KCl) solution of mass fraction 32.4356 x 10^{-3}.

Before each lot of sample measurements, the Autosal is calibrated with standard seawater (OSIL, IAPSO) of known K_{15} ratio. A new bottle of OSIL standard is used for each calibration. The frequency of calibration is at least one per run.

Method: The salinity sample is collected in a 200 ml OSIL bottle. The bottle is rinsed then filled from the bottom, via a polytetrafluoroethylene (PTFE) straw, till overflowing. The bottle is removed from the straw and the sample is decanted to allow a headspace of approximately 25 cm^3. A dry plastic insert is fitted, the bottle inverted and rinsed with water then capped and stored cap-down until measured. To measure, the Autosal cell is flushed three times with the sample and then measured after the fourth and fifth flush. The OSIL data logger software captures the conductivity ratio and calculates the practical salinity. The output from the data logger is imported into HyPro and collated with the CTD deployment meta-data.

5.3 CTD Salinity vs Bottle Salinity Plot

For this voyage, the difference between the unprocessed (uncorrected) CTD value and the measured bottle value is generally less than 0.02 PSU. The larger differences are for shallow samples across the sudden changes in the thermohaline profile.

The unprocessed CTD values are adjusted (corrected) by DAP using the bottle results. The corrected values are not reported in the hydrology set. Please contact the NCMI_DataLibrarians@csiro.au for corrected CTD data.

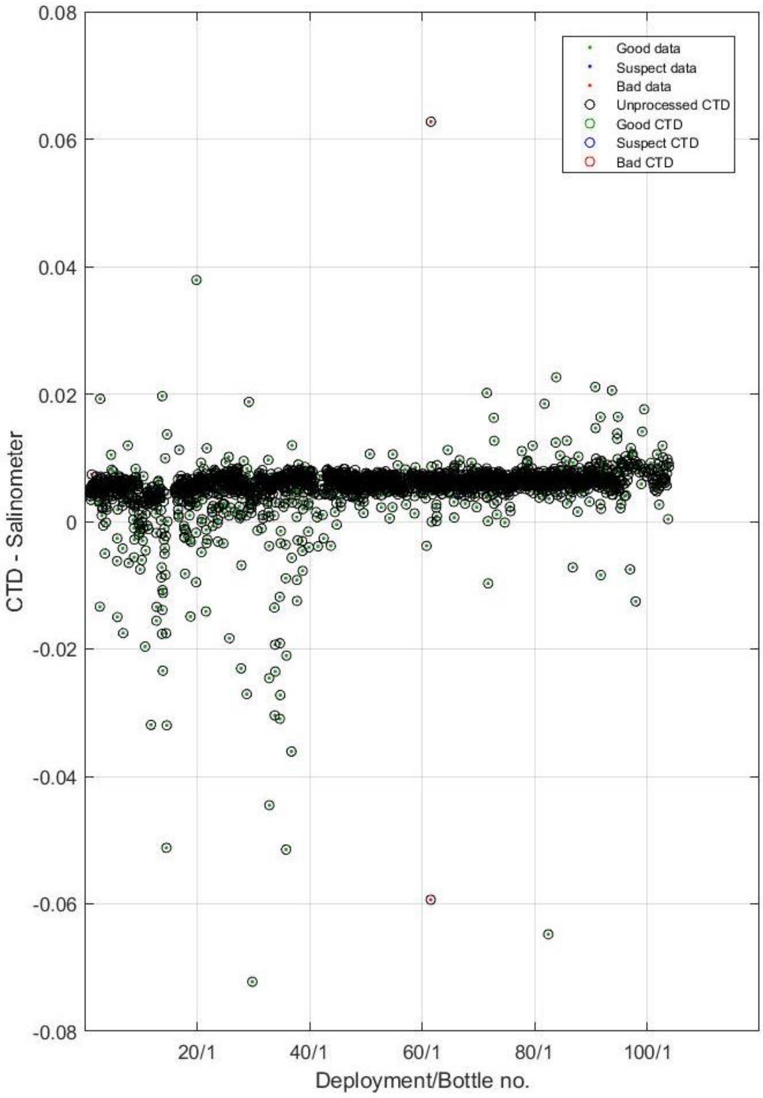


Figure 3. CTD Salinity - Bottle Salinity vs CTD deployment plot. The data quality is coded by colour and delineated by a dot for the bottle salinity and a circle for the CTD salinity. Green = GOOD. Red = BAD, Black = UNPROCESSED. Units: PSU (dimensionless). **Note: Bad salinity bottle data is listed in appendix 8.4.*

5.4 OSIL Salinity Standard Plot

The instrument is calibrated with OSIL standard seawater lot P167 (PSU = 34.995). The plot below shows the OSIL lot P167 measured results for each run on this voyage. The blue line represents the mean of all standards measured for standardisation.

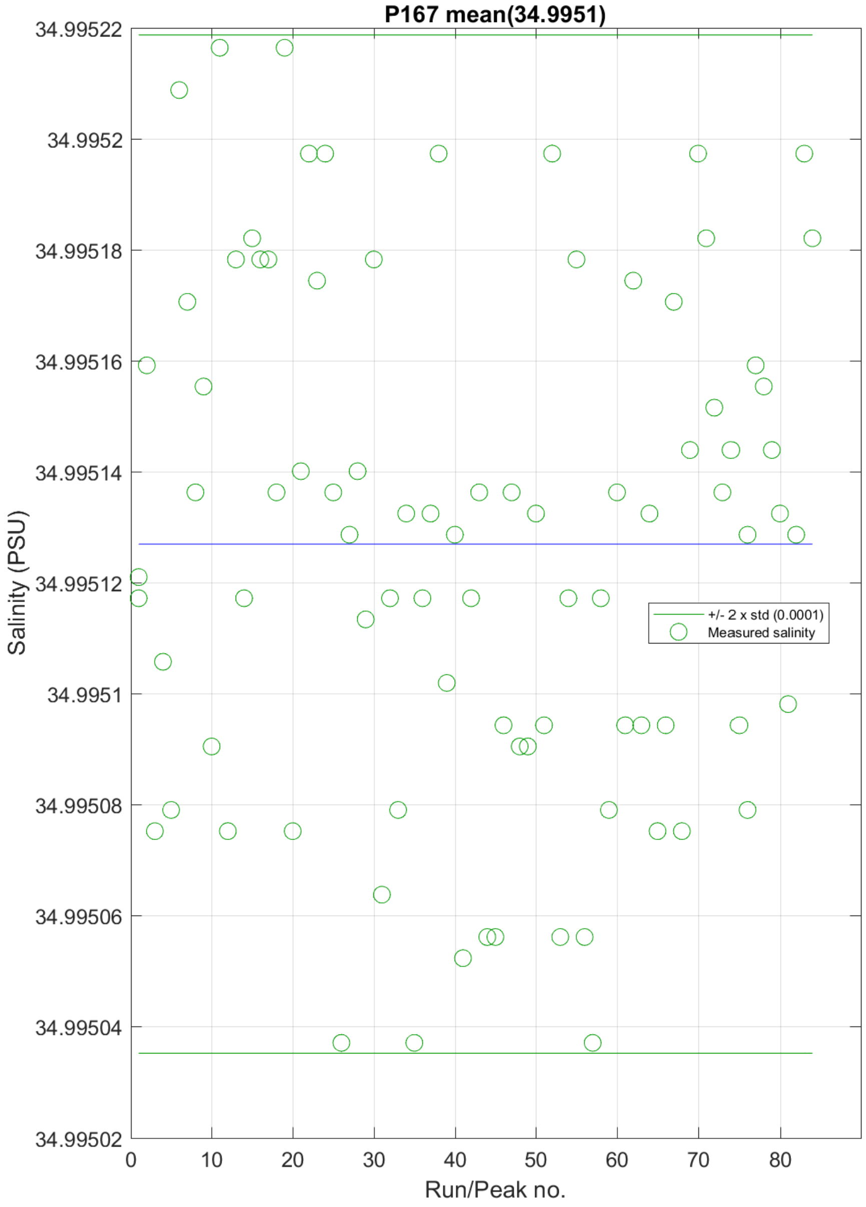


Figure 4. Measured OSIL standard for each salinity run and average value (P167 mean) across IN2024_V01.

6 Dissolved Oxygen

6.1 Dissolved Oxygen Measurement Parameters

Table 4: Dissolved oxygen measurement parameters.

Details	
HyPro Version	5.7
Instrument	Automated Photometric Oxygen System
Software	Scripps Institution of Oceanography (SIO)
Hydrochemistry Methods	Sampling: WI_DO_001 Analysis: SOP 005
Accuracy	± 0.5 µmol L^{-1}
Lab Temperature	Mean 20.7°C SD 0.3°C (Ruuvi sensor)
Sample Container type	140 ml glass iodine determination flasks with glass stopper.
Sample Storage	Samples stored in the hydrochemistry lab until analysis.
Analysts	Maddy Lahm
Comments	See DAP report for CTD calibration details.

6.2 Dissolved Oxygen Method

Scripps Institution of Oceanography method used. The method is based on the whole bottle modified Winkler titration of Carpenter (1965) plus modifications by Culberson *et al* (1991).

Method: The sample is collected in an iodine determination flask of known volume. 1 ml of manganese (II) chloride solution followed by 1 ml of alkaline iodide solution is added to the sample, the flask stoppered and inverted a minimum of 30 times. The dissolved oxygen oxidizes an equivalent amount of Mn (II) to Mn (IV) which precipitates. Just before titration, the sample is acidified, Mn (IV) is reduced to the divalent state liberating iodine. The iodine is titrated with a standardised thiosulphate solution using a Metrohm 876 Dosimat fitted with a 1 ml burette. The endpoint is determined by measuring the decrease in the UV absorption 365 nm.

The thiosulphate solution is standardised by titrating it against a 10 ml aliquot of potassium iodate primary standard. A blank correction is also determined from the difference between two titres of consecutive additions of 1 ml aliquots of potassium iodate to the same blank sample. The standardisation is done at least once per 12-hour shift, when samples are being assayed.

The output from the SIO instrument software is imported into HyPro and collated with the CTD deployment meta-data.

6.3 CTD Dissolved Oxygen vs Bottle Dissolved Oxygen Plot

For this voyage, the difference between the unprocessed CTD value and the measured bottle value is generally less than 20 µmol L^{-1}. The larger differences are for shallow samples across the sudden changes in the dissolved oxygen profile.

The unprocessed CTD values are adjusted (corrected) by DAP using the bottle results. The corrected values are not reported in the hydrology set. Please contact the NCMI_DataLibrarians@csiro.au for corrected CTD data.

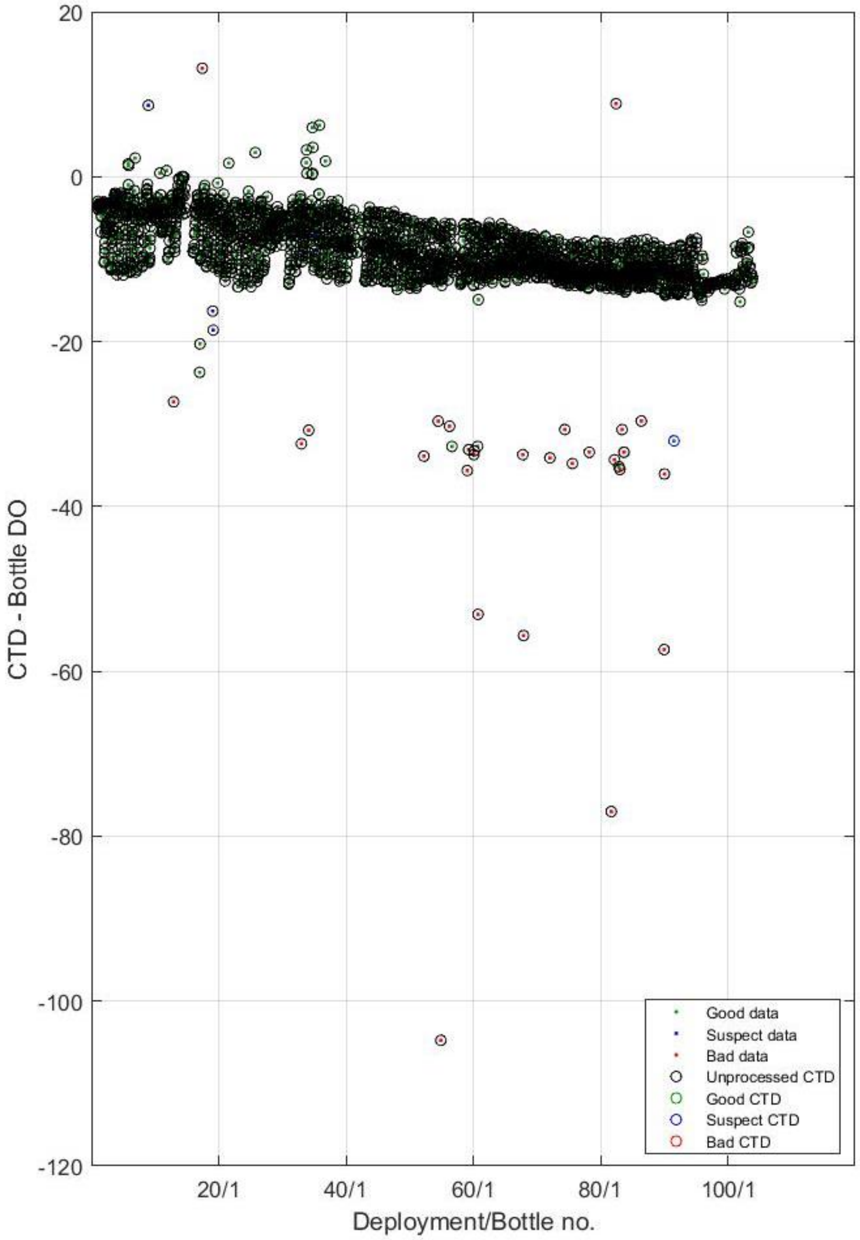


Figure 5. CTD Dissolved Oxygen - Bottle Dissolved Oxygen vs Deployment Plot**.** The data quality is coded by colour and delineated by a dot for the bottle DO and a circle for the CTD DO. Green = GOOD. Blue = SUSPECT. Red = BAD. Black = UNPROCESSED. Units: µmol L^{-1}. **Note: Bad oxygen bottle data is listed in appendix 8.5.*

6.4 Dissolved Oxygen Instrument titrant: thiosulphate normality and blank correction

The variation in thiosulphate concentration is within our QC parameter of less than 0.0005 N between standardisations. Three batches of thiosulphate reagent were used during the voyage. The mean normality is as follows:

CTD Deployment 1 to 103:	Mean: 0.24229 N SD: 0.00031 (n=50)

The blank correction is used in the calculation of the thiosulphate normality and is due to oxidisable species in the MQ water that is added to the KIO_3 aliquot before the titration.

The red lines in figure 5 indicate ± 0.0005 N either side of the mean titrant (thiosulfate) concentration and the blank concentration. The Thiosulphate normality should not vary more than 0.0005 N between analyses.

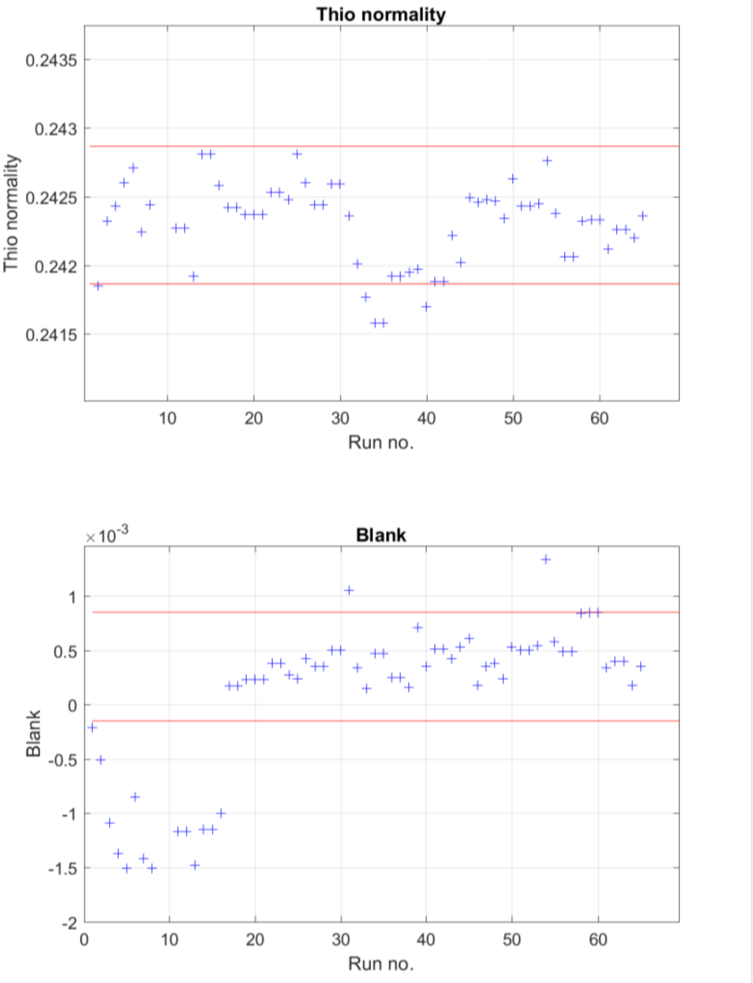


Figure 6. Thiosulphate standardisation (top) and blank correction plots (bottom). Thiosulfate standardization values seen outside of the lines comply with the QC parameter, that is the Thiosulphate normality should not vary more than 0.0005 N between analyses. Blanks from earlier runs were ran with an alkaline iodide solution known to produce negative blank values. High blanks seen twice reflected the low standard volume and high volatility of the solution noted.

7 Nutrients

7.1 Nutrient Measurement Parameters

Table 5: Nutrient measurement parameters analysed with Seal AA3HR segmented flow analyser. All instrument parameters, reagent batches and instrument events are logged for each analysis run. This information is available on request.

Details					
Instrument	Seal AA3HR segmented flow analyser				
HyPro version	5.7				
Operating Software	AACE 7.10				
Hydrochemistry Sampling Method	WI_Nut_001				
Hydrochemistry analysis method	SOP001	SOP002	SOP003	SOP003	SOP004
Nutrients Analysed	Silicate SiO_4^{4-} as Si	Phosphate PO_4^{3-} as P	Nitrate + Nitrite $NO_3^- + NO_2^-$ as N	Nitrite NO_2^- as N	Ammonium NH_4^+ as N
Top concentration (µmol L^{-1})	140.0	3.0	42.0	1.4	2.0
Method detection limit (µmol L^{-1})	0.2	0.02	0.02	0.02	0.02
Reference Material	KANSO RMNS lot CM				
Sample Container	CTD: 50 ml HDPE with screw cap lids. Reused after acid wash with 10% HCl solution.				
Sample Storage	< 4 hours at room temperature after collection or < 12 hours at 4°C after collection				
Sample preparation	Assayed as neat. No filtration.				
Lab Temperature (°C)	Mean 20.7°C SD 0.3°C (Ruuvi sensor)				
Analysts	Merinda McMahon and Christine Rees				
Comments	N/A				

7.2 Nutrient Methods

Nutrient samples are assayed on a Seal AA3HR segmented flow auto-analyser fitted with 1 cm flow-cells for colorimetric measurements and a JASCO FP2020 fluorescence instrument as the ammonium detector.

Silicate (SOP001): colourimetric, molybdenum blue method. Based on Armstrong et al. (1967). Silicate in seawater is reacted with acidified ammonium molybdate to produce silicomolybdic acid. Tartaric acid is added to remove the phosphate molybdic acid interference. Tin (II) chloride is then added to reduce the silicomolybdic acid to silicomolybdous acid and its absorbance is measured at 660 nm.

Phosphate (SOP002): colourimetric, molybdenum blue method. Based on Murphy and Riley (1962) with modifications from the NIOZ-SGNOS[1] Practical Workshop 2012 optimizing the antimony catalyst/phosphate ratio and the reduction of silicate interferences by pH. Phosphate in seawater forms a phosphomolybdenum complex with acidified ammonium molybdate. It is then reduced by ascorbic acid and its absorbance is measured at 880 nm.

Nitrate (SOP003): colourimetric, Cu-Cd reduction – naphthylenediamine method. Based on Wood et.al (1967). Nitrate is reduced to nitrite by first adding an ammonium chloride buffer then sending it through a copper – cadmium column. Sulphanilamide is added under acidic conditions to form a diazo compound. This compound is coupled with 1-N-naphthly-ethylenediamine di-hydrochloride to produce a reddish purple azo complex and its absorbance is measured at 540 nm.

Nitrite (SOP003): colourimetric, naphthylenediamine method. As per nitrate method without the copper cadmium reduction column and buffer. Absorbance measured at 520 nm.

Ammonium (SOP004): fluorescence, ortho-phtaldiadehyde method. Based on Kérouel and Aminot (1997). Ammonium reacted with ortho-phtaldialdehyde and sulphite at a pH of 9.0-9.5 to produce an intensely fluorescent product. Its emission is measured at 460 nm after excitation at 370 nm.

SOP methods can be obtained from the CSIRO Oceans and Atmosphere Hydrochemistry Group.

[1] Royal Netherlands Institute for Sea Research – Study Group on Nutrient Standards.

7.3 HyPro Processing Summary for Nutrients

After a run, the raw absorbance/ fluorescence data is exported from the instrument and processed by HyPro. For each analyte, HyPro re-creates the peak traces, defines the region on the peak's plateau (peak window) used to determine the peak heights, constructs the calibration curve, applies corrections for carry-over, baseline and sensitive drifts then, derives the nutrient concentrations for each sample. The corrections are quantified using dedicated solutions included in every run.

HyPro uses criteria to identify suspect calibration points, noisy peaks, method detection limits that are above the nominal limit and duplicate sample results that do not match.

Suspect calibration points are weighted less when fitting the calibration curve. The cut-off limits for good calibration data are:

- ±0.5% of the concentration of the top standard for silicate and nitrate+nitrite (as per WOCE[1]).
- 0.02 umol L^{-1} for phosphate, nitrite and ammonium.

HyPro classifies the quality of data as good, suspect, or bad and flags accordingly. The Flag key is in Appendix 8.7. Missing or suspect nutrient data is tabulated in Appendix 8.6.

[1] World Ocean Circulation Experiment

Table 6: HyPro 5.7 Processing Parameters. All instrument parameters, reagent batches, and operation events are logged for each analysis run. This information is available on request.

Result Details	**Silicate**	**Phosphate**	**Nitrate + Nitrite (NOx)**	**Nitrite**	**Ammonium**
Data Reported as	µmol L^{-1}	µmol L^{-1}	µmol L^{-1}	µmol L^{-1}	µmol L^{-1}
Calibration Curve degree	Linear	Linear	Linear	Quadratic	Quadratic
# of points in Calibration	7	6	7	6	6
Forced through zero	N	N	N	N	N
Matrix correction	N	N	N	N	N
Blank correction	N	N	N	N	N
Peak window defined by	HyPro	HyPro	HyPro	HyPro	HyPro
Carryover correction (HyPro)	Y	Y	Y	Y	Y
Baseline drift correction (HyPro)	Y	Y	Y	Y	Y
Sensitivity drift correction (HyPro)	Y	Y	Y	Y	Y
Data Adj for RMNS variance.	N	N	N	N	N
Medium of Standards	Low nutrient seawater (LNSW, bulk on PW1 wharf, CSIRO Hobart) collected in June 2021. Sub-lot passed through a 5-micron filter (filtered in December 2023) and stored in 20 L carboys in the clean dry laboratory at 22°C.				
Medium of Baseline	18.2 Ω water. Dispensed from the Milli Q IQ 7010 system.				
Duplicate samples.	CTD: Niskins fired at the greatest depth were analysed in duplicate. Single samples were analysed for remaining depths.				
Comments	The reported data is not corrected to the RMNS. Per deployment RMNS data tabulated in appendix 8.3.				

7.4 Accuracy - Reference Material for Nutrient in Seawater (RMNS)

Descriptive statistics are used to ascertain the accuracy and precision of the analysis from the repetitive measurement of the RMNS for silicate, phosphate, NOx, and nitrite in seawater.

For IN2024_V01, Japanese KANSO certified RMNS lot CM was assayed in triplicate in each run to monitor accuracy. The certified values are listed in Table 7. RMNS lot CO and CP were analysed in 6 runs spread across the voyage as additional accuracy monitoring. An internal bulk quality control (BQC) was also analysed in each run for analysis on AA3HR segmented flow analyser.

For RMNS lot CM, CO and CP NOx, phosphate, and silicate were within 2% and nitrite within 0.04 µmol L^{-1} of their certified mean concentration.

The GO-SHIP criteria (Hyde et al., 2010), appendix 8.8, specifies using 1-3 % of full scale (depending on the nutrient) as acceptable limits of accuracy.

KANSO publishes the RMNS nutrient values in µmol kg^{-1}. These are converted to µmol L^{-1} at 21°C. The RMNS is not certified for ammonium. NO_x is derived by summing the NO_3 and NO_2 values. The assayed RMNS values per CTD deployments are listed in the appendix 8.3.

Table 7: RMNS certified concentrations ± expanded uncertainty (U) at 21°C. Units: µmol L^{-1}

RMNS	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite
Lot CM	102.917 ± 0.512	2.437 ± 0.031	34.017 ± 0.313	0.018 ± 0.006
Lot CO	35.552 ± 0.164	1.205 ± 0.014	16.281 ± 0.195	0.041 ± 0.041
Lot CP	62.569 ± 0.307	1.795 ± 0.018	25.714 ± 0.379	0.318 ± 0.072

Table 8: RMNS CM statistics for of this voyage. Units: µmol L^{-1}

RMNS CM	Silicate	Phosphate	Nitrate + Nitrite (NO_x)	Nitrite
Minimum	101.600	2.420	33.630	0.018
Maximum	103.200	2.480	34.530	0.052
Median	102.400	2.450	33.920	0.039
Mean	102.448	2.452	33.924	0.039
Repeatability	0.327	0.011	0.117	0.005

7.5 Nutrient plots of RMNS

The green, pink and red contours are at 1%, 2% and 3% from the RMNS certified mean value. Exception: nitrite, the contours are at 0.02 µmol L^{-1} increments from the certified value. The blue line is the certified value's expanded uncertainty. Plots are RMNS value versus instrument run number.

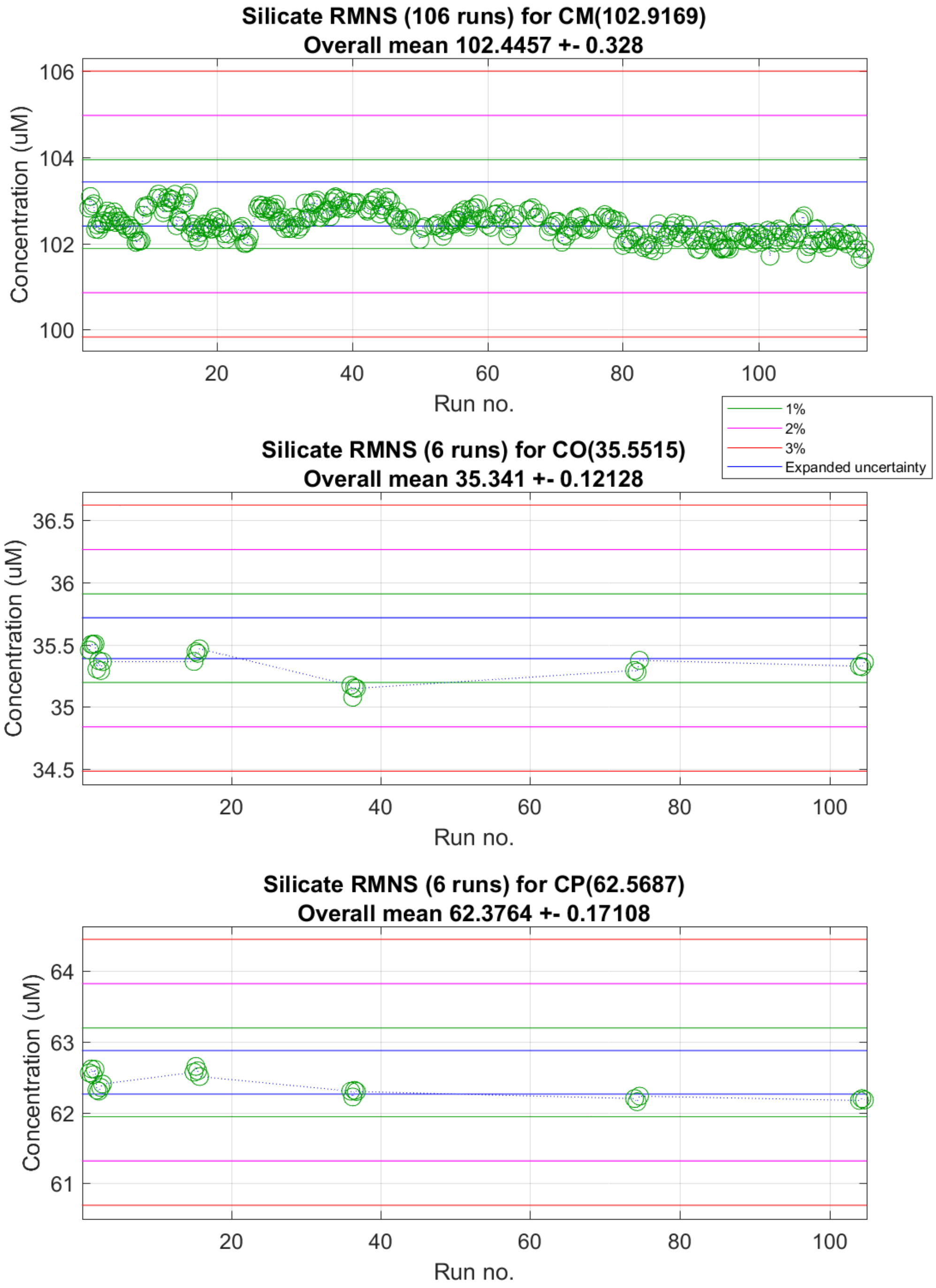


Figure 7. Silicate RMNS plot (µmol L^{-1})

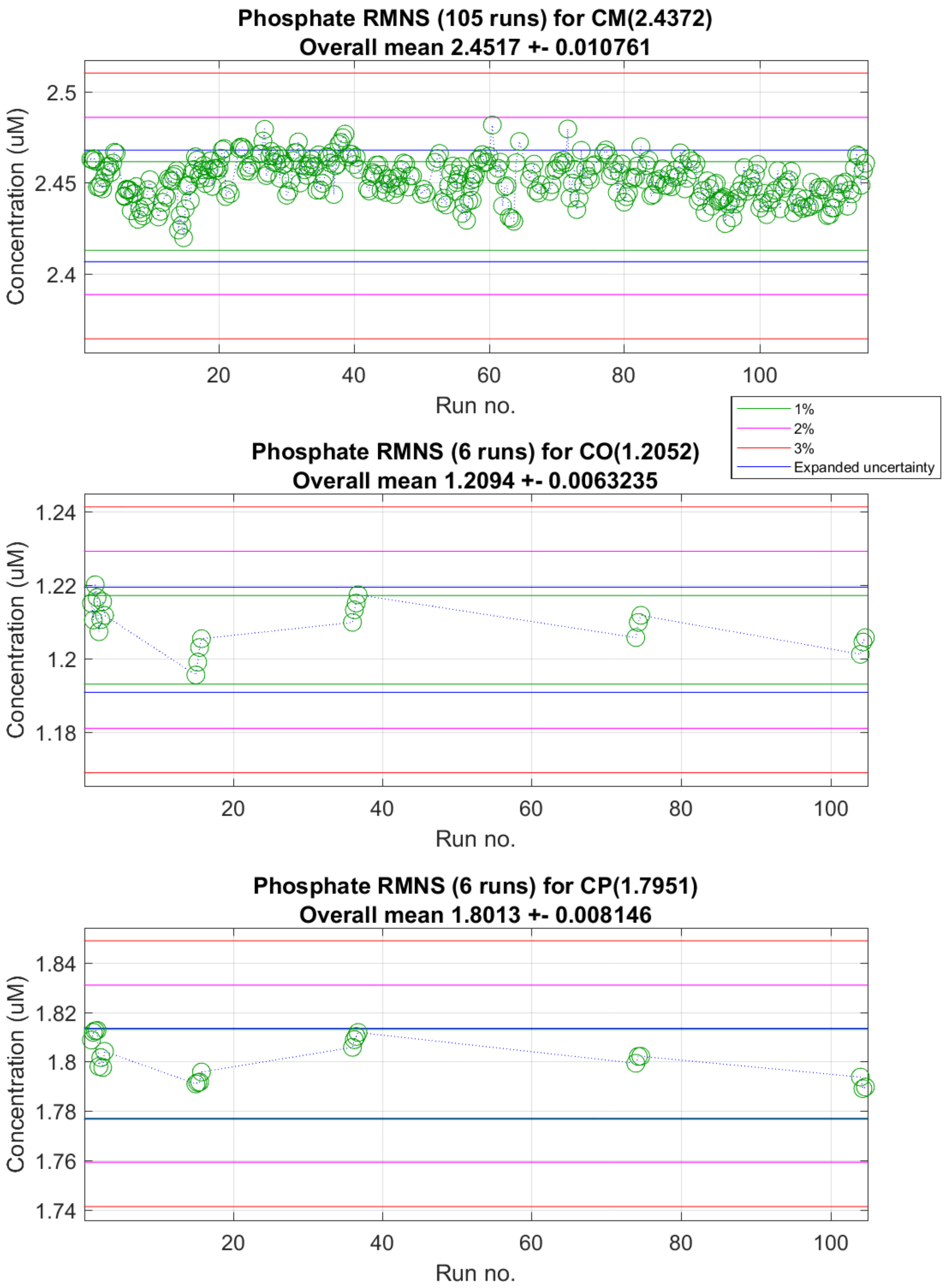


Figure 8. Phosphate RMNS plot (µmol L^{-1})

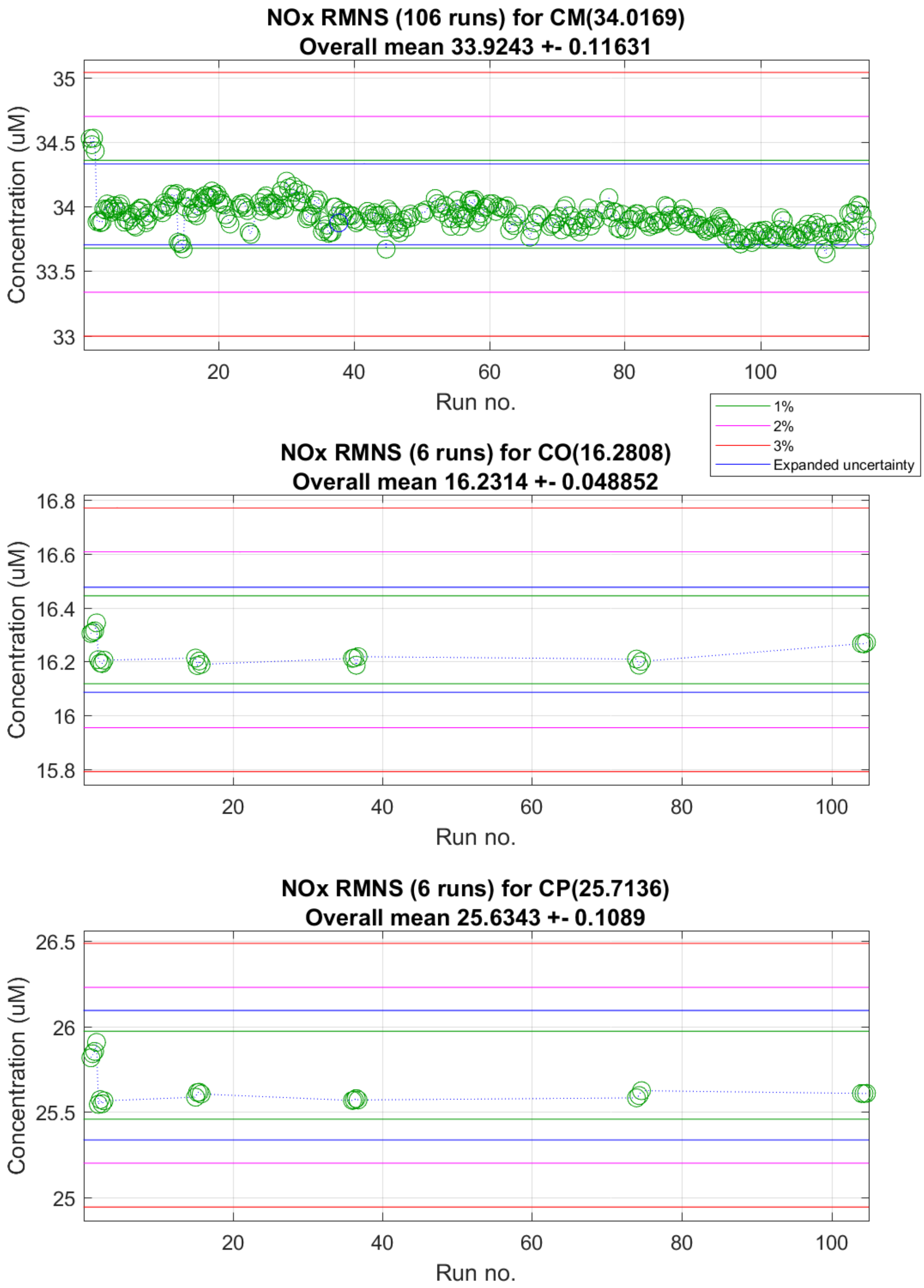


Figure 9. Nitrate + Nitrite (NOx) RMNS plot (µmol L^{-1})

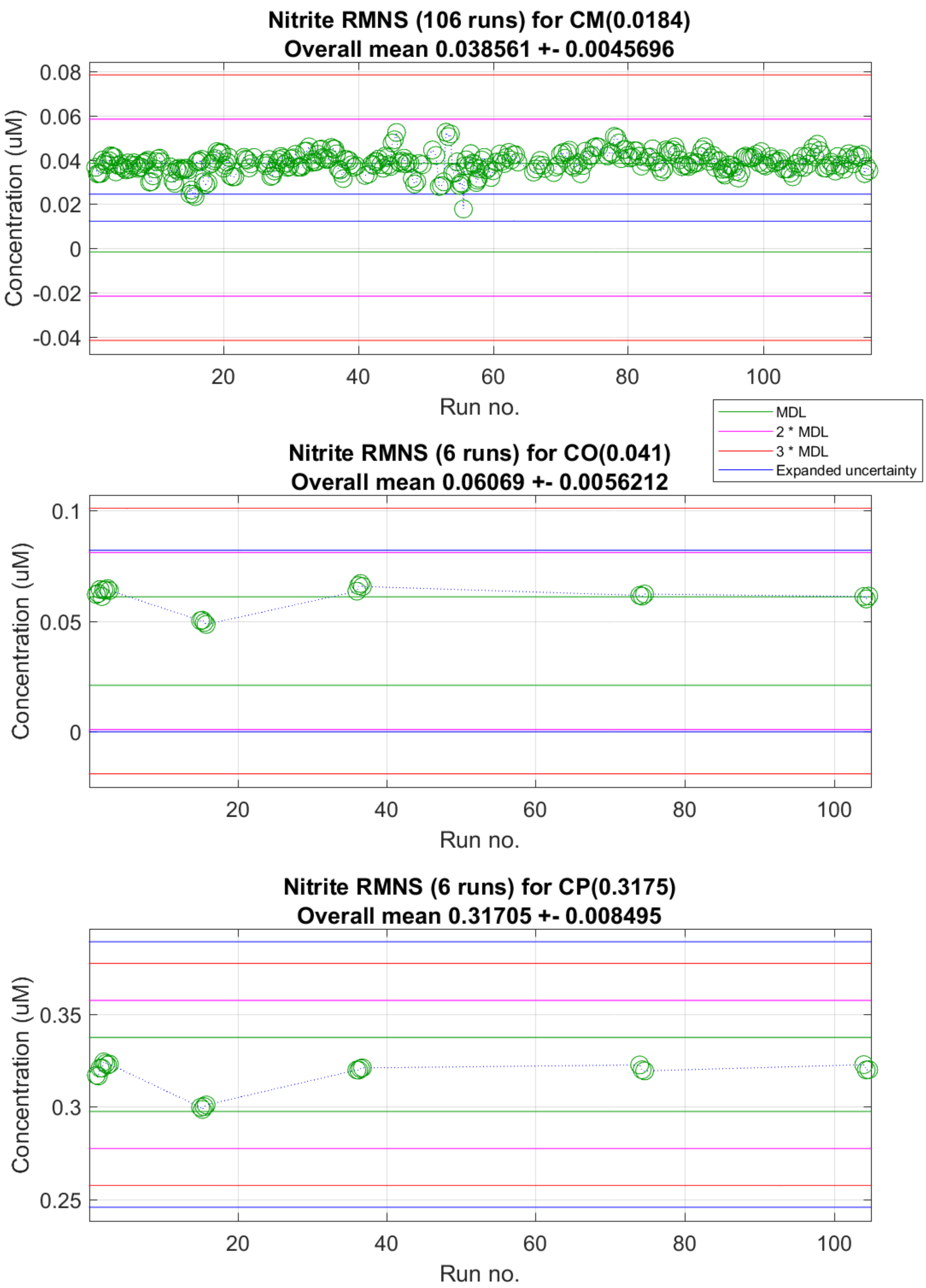


Figure 10. Nitrite RMNS plot (µmol L^{-1})

7.6 Measurement Uncertainty

The CSIRO hydrochemistry method measurement uncertainty (MU) has been calculated for each nutrient based on the variation in the calibration curve, calibration standards, pipette and glassware calibration, and precision of the RMNS over time (Armishaw, 2003).

Table 9: CSIRO Hydrochemistry nutrient analysis uncertainty values. Units: µmol L^{-1}

Calculated Measurement Uncertainty @ 1 µmol L^{-1}				
Silicate	Phosphate	Nitrite	Nitrate + Nitrite (NOx)	Ammonium
±0.017	±0.024	±0.14	±0.019	±0.30$^{¥}$

The reported uncertainty is an expanded uncertainty using a coverage factor of 2 giving a 95% level of confidence.

$^{¥}$The ammonium MU precision does not include data for the RMNS.

7.7 Method Detection Limit for Nutrients

The method detection limit (MDL) is set to three times the standard deviation (SD) of the LNSW results (National Association of Testing Authorities 2013). The resultant MDL was used to assess the analysis precision at low concentrations.

Table 10: AA3HR auto analyser MDL statistics for this voyage. The minimum, maximum, mean, median, and reproducibility (standard deviation) are calculated from every analytical run performed over the voyage. Units: µmol L^{-1}

Silicate **Phosphate**

MDL			**Nitrate + Nitrite (NOx)**	**Nitrite**	**Ammonium**
Nominal MDL	**0.200**	**0.020**	**0.020**	**0.020**	**0.020**
SD Min	0.000	0.000	0.000	0.000	0.000
SD Max	0.115	0.015	0.006	0.008	0.006
SD Median	0.000	0.006	0.000	0.001	0.000
SD Mean	0.018	0.004	0.002	0.001	0.001
Precision of MDL (SD)	0.018	0.004	0.002	0.001	0.001

7.8 Sampling Precision

Initial sampling precision is determined with the CTD test deployment (CTD 1) where multiple bottles are fired the same depth, each of which is then sampled for hydrochemistry (Table 11).

Table 11: CTD deployment 1. 36 bottles at 1000 dbar. Units: µmol L^{-1}.

	Silicate	Phosphate	Nitrate + Nitrite (NO_X)	Nitrite	Ammonium
Minimum	52.000	2.250	32.830	0.006	-0.010
Maximum	52.600	2.270	33.020	0.014	0.000
Mean	52.222	2.259	32.911	0.01	-0.009
SD	0.124	0.004	0.055	0.002	0.002

Duplicate nutrient samples were collected from the greatest depth of subsequent CTD deployments. For nutrients, the sampling precision is good if the difference from the mean of duplicate measurements is less than the nominal method detection limit. The exception: NOx which uses the limit 0.06 µmol L^{-1}

Duplicate samples that exceed this limit are flagged 69 (suspect). These are tabulated in appendix 8.6.

7.9 Redfield Ratio Plot (14.0) for CTD Deployments.

The Redfield ratio for this voyage: **14.45**

The Redfield Ratio is a check for the accuracy of phosphate and NOx analysis. The ratio is the required amount of P to N for marine phytoplankton growth.

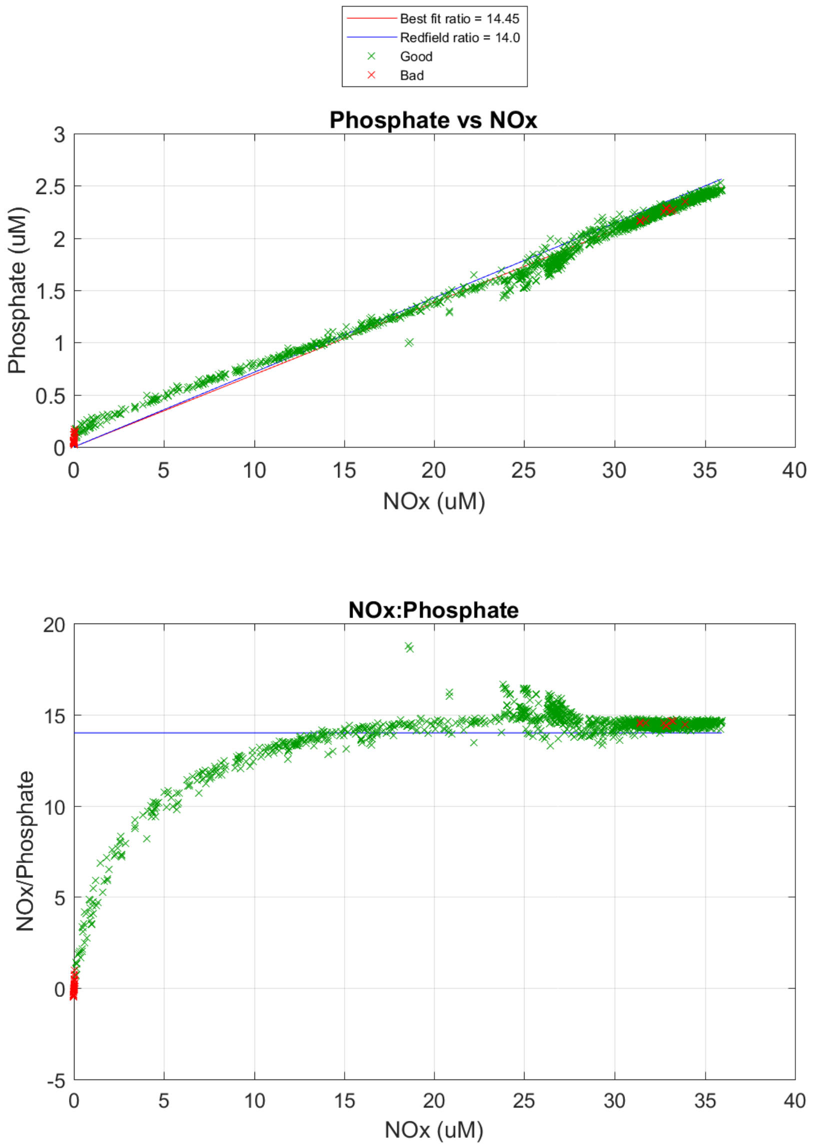


Figure 11. Redfield ratio plots. Note: please refer to appendix 8.6 for explanation of the outlier point in this plot.

7.10 Temperature and Humidity Change over Nutrient Analyses

The ambient conditions in the hydrochemistry laboratory and within the AA3HR instrument were measured and logged in the following locations:

1) Above the AA3 auto sampler
2) On each deck of the AA3 chemistry modules, post heater
3) Inside each detector of the AA3

Data was measured using Ruuvi temperature logger and humidity sensor and logged and monitored in Grafana. Measurements were recorded every 1 second for the duration of the voyage. If required, this data will be provided on request.

8 Appendix

8.1 Salinity: Reference material used

OSIL IAPSO Standard Seawater	
Batch	P167
Use by date	21/02/2026
K_{15}	0.99988
PSU	34.995

8.2 Nutrients: RMNS results for each CTD Deployment

8.2.1 Lot CM (µmol L^{-1})

Run #	CTD #	Other Samples	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite
1	1	N/A	102.927	2.463	34.491	0.034
2	2	N/A	102.391	2.448	33.883	0.039
3	3	N/A	102.603	2.457	33.989	0.041
4	4	N/A	102.602	2.462	33.982	0.037
5	5	N/A	102.538	2.445	33.986	0.037
6	6 (5 PO4 repeat)	N/A	102.403	2.443	33.889	0.037
7	7	N/A	102.345	2.433	33.888	0.037
8	8	N/A	102.052	2.444	33.977	0.039
9	9	N/A	102.810	2.463	33.910	0.032
10	10	N/A	N/A	N/A	N/A	0.040
11	10	N/A	102.880	2.435	33.967	N/A
12	11	N/A	102.880	2.447	34.010	0.033
13	12	N/A	103.033	2.454	34.090	0.036
14	13 + 14	N/A	102.516	2.426	33.705	0.036
15	15	Uwy 001-004 TMR NPP1 (1-12)	103.035	2.443	34.047	0.025
16	16	N/A	102.348	2.460	33.953	0.039
17	17	N/A	102.206	2.456	34.032	0.030
18	18	N/A	102.412	2.455	34.075	0.039
19	19	N/A	102.455	2.455	34.097	0.043

20	20	N/A	102.449	2.465	34.028	0.039
21	21	N/A	102.182	2.444	33.902	0.032
23	22	N/A	102.332	2.469	34.011	0.039
24	N/A	Exp20240123 SIMBA mid, PSI light mid and PSI dark mid	102.047	2.458	33.887	0.040
26	23	N/A	102.852	2.471	34.015	0.039
27	24	Exp20240125 SIMBA final	102.803	2.460	34.032	0.034
28	25	N/A	102.817	2.463	34.001	0.040
29	26	N/A	102.542	2.459	34.049	0.038
30	27	N/A	102.383	2.447	34.134	0.041
31	N/A	Exp20240126 PSI light final, PSI dark final uwy005-uwy009	102.495	2.467	34.108	0.037
32	28	N/A	102.422	2.456	34.057	0.045
33	N/A	Exp20240127 SOAPIE Exp20240127ME2_T0	102.703	2.459	33.925	0.039
34	29	tmr20240128_R1-R12 Exp20240128ME2_T1	102.951	2.457	34.035	0.043
35	30		102.634	2.450	33.841	0.040
36	N/A	Exp20240129Blob mid Exp20240129ME2_T2	102.727	2.464	33.813	0.045
37	31	Exp20240130ME2_T3	103.037	2.459	33.948	0.034
38	32	N/A	102.898	2.475	33.951	0.040
39		Exp20240131ME2_T4	102.860	2.465	33.930	0.037
40	33	Exp2024201ME2_T5	102.933	2.460	33.887	N/A
41	33	N/A	N/A	N/A	N/A	0.033
42	34	Exp carboy2 Lavy Exp carboy3 Lavy Exp carboy5 Lavy	102.807	2.450	33.923	0.038
43	35	Exp2024202ME2_T6 Exp20240202SIMBA mid	103.021	2.458	33.938	0.038
44	36	Exp20240202Blob final	102.804	2.449	33.827	0.039
45	37	Exp2024203ME2_T7	103.018	2.451	33.959	0.050
46	38	N/A	102.639	2.448	33.830	0.039
47	39	N/A	102.514	2.459	33.870	0.039

48	40 + 41 (NO NO2 for 41 and exp)	Exp2024204ME2_T8 Exp20240204ME2 NO3 and Mn mid	102.557	2.452	33.922	0.03
49	41	Exp2024204ME2_T8 Exp20240204ME2 NO3 and Mn mid	N/A	N/A	N/A	0.038
50	N/A	Exp20240205PS2 SIMBA final Tmr20240205_R1-R12 Exp20240205ME2_T9 Uwy 010 – 011	102.280	2.445	33.958	N/A
51	N/A	Exp20240205PS2 SIMBA final Tmr20240205_R1-R12 Exp20240205ME2_T9 Uwy 010 – 011	N/A	N/A	N/A	0.043
52	42 + 43	Exp20240205SOAPIE2	102.430	2.464	34.023	0.029
53	44	Exp20240206ME2_T10	102.274	2.439	33.989	0.052
54	45 +4413	Exp20240206PS2 final	102.473	2.454	33.886	0.036
55	46	N/A	102.536	2.452	33.949	0.028
56	47	Exp20240206ME2_T11	102.724	2.434	33.918	0.040
57	48	Exp20240207ME2 NO3 and Mn Final	102.556	2.448	34.039	0.034
58	49	N/A	102.860	2.46	33.905	0.039
59	50	N/A	102.573	2.463	33.970	0.035
60	N/A	Exp20240208ME2_T12	102.404	2.473	34.021	0.037
61	51	N/A	102.731	2.458	33.984	0.040
62	52	N/A	102.656	2.444	33.990	0.041
63	53	N/A	102.306	2.430	33.846	0.041
64	N/A	Exp20240212SIT HL, LL and HLL Exp20240212SOAPIE3	102.623	2.467	33.932	N/A
65	N/A	Exp20240212SIT HL, LL and HLL Exp20240212SOAPIE3 NO2 only	N/A	N/A	N/A	0.041
66	54	N/A	102.798	2.456	33.817	0.036
67	55	N/A	102.640	2.446	33.928	0.038

69	56	Uwy 012 – 022 Exp20240214ME4_T0 filtered and unfiltered	102.362	2.450	33.859	0.036
70	57	Exp2024015ME4_T1 filtered and unfiltered Uwy 023 – 025 Tmr20240215_R1-R12	102.498	2.460	33.882	0.042
71	58	N/A	102.133	2.468	33.945	0.042
72	59	N/A	102.349	2.450	33.884	0.038
73	60	Exp2024016ME4_T12 filtered and unfiltered	102.599	2.448	33.834	0.038
74	61	N/A	102.370	2.453	33.932	0.041
75	62	N/A	102.416	2.457	33.883	0.046
77	63	Exp2024017ME4_T3	102.631	2.466	34.005	0.043
78	64	N/A	102.561	2.457	33.943	0.049
79	65	Exp2024018ME4_T4	102.431	2.454	33.866	0.043
80	66	N/A	102.033	2.442	33.851	0.041
81	67	Exp2024019ME4_T5	102.117	2.453	33.924	0.043
82	N/A	Exp20240219 SIMBA4 mid, PS4 mid	102.167	2.464	33.923	0.038
83	68	N/A	101.956	2.458	33.867	0.042
84	69	Exp20240220ME4_T6	101.887	2.446	33.892	0.038
85	70	N/A	102.334	2.453	33.881	0.038
86	71	N/A	102.112	2.450	33.978	0.044
87	72	Exp20240221ME4_T7	102.399	2.452	33.875	0.043
88	73	Exp20240222 SOAPIE5_T0	102.203	2.460	33.948	0.037
89	74	Exp20240222ME4_T8	102.406	2.454	33.906	0.038
90	75	Exp20240222_SOAPIE4	102.099	2.460	33.883	0.040
91	76	N/A	101.898	2.443	33.844	0.045
92	77	Exp20240223ME4_T9	102.158	2.444	33.824	0.041
93	N/A	Exp20240223 SIMBA4 final, PS4 final	102.222	2.445	33.845	0.039
94	78	N/A	101.952	2.441	33.890	0.035
95	79	Exp20240224ME4_T10	101.890	2.435	33.810	0.037
96	80	N/A	102.207	2.437	33.759	0.034
97	81	N/A	102.191	2.451	33.735	0.041
98	82	N/A	102.126	2.448	33.743	0.041

99	83	N/A	102.132	2.454	33.795	0.042
100	84	N/A	102.128	2.440	33.806	0.038
101	85	N/A	102.040	2.437	33.757	0.040
102	86	N/A	102.148	2.449	33.795	0.040
103	87	N/A	102.281	2.444	33.873	0.036
104	N/A	Exp20240227 SOAPIE5	102.076	2.453	33.770	0.035
105	88	N/A	102.199	2.438	33.752	0.039
106	89	ExpBrandon’s samples	102.583	2.438	33.799	0.039
107	90	N/A	101.890	2.441	33.826	0.043
108	91	N/A	102.247	2.442	33.855	0.045
109	92	N/A	102.048	2.447	33.695	0.037
110	93 + 94	N/A	102.013	2.433	33.819	0.037
111	95	N/A	102.183	2.442	33.778	0.039
112	96 + 97 + 98	N/A	102.075	2.448	33.802	0.040
113	99 + 100	N/A	102.151	2.442	33.926	0.040
114	101	N/A	102.003	2.463	33.995	0.042
115	102 + 103	N/A	101.734	2.455	33.849	0.035

8.2.2 Lot CO (µmol L^{-1})

Run #	**CTD #**	**Other Samples**	**Silicate**	**Phosphate**	**Nitrate + Nitrite (NOx)**	**Nitrite**
1	1	N/A	35.491	1.216	16.318	0.062
2	2	N/A	35.332	1.211	16.200	0.064
15	15	Uwy 001-004 TMR NPP1 (1-12)	35.426	1.201	16.197	0.050
36	N/A	Exp20240129Blob mid Exp20240129ME2_T2	35.138	1.214	16.208	0.066
74	61	N/A	35.316	1.209	16.199	0.062
104	N/A	Exp20240227 SOAPIE5	35.336	1.204	16.268	0.061

8.2.3 Lot CP (µmol L^{-1})

Run #	CTD #	Other Samples	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite
1	1	N/A	62.580	1.811	25.854	0.319
2	2	N/A	62.344	1.800	25.556	0.323
15	15	Uwy 001-004 TMR NPP1 (1-12)	62.58	1.792	25.604	0.300
36	N/A	Exp20240129Blob mid Exp20240129ME2_T2	62.283	1.809	25.570	0.320
74	61	N/A	62.194	1.801	25.600	0.321
104	N/A	Exp20240227 SOAPIE5	62.182	1.791	25.607	0.321

The submitted nutrient results do NOT have RMNS corrections applied.

How to use the RMNS for Correction

Ratio = Certified RMNS Concentration/Measured RMNS Concentration in each run

Corrected Concentration = Ratio x Measured Nutrient Concentration

Or for smoothing data

Ratio = Average RMNS Concentration across voyage/Measured RMNS Conc. in each run

Corrected Concentration = Ratio x Measured Nutrient Concentration

8.3 Missing or Suspect Salinity Data

Data is flagged based on CTD sampling log notes, observations during analysis, and examination of depth profile plots (Flag key: appendix 8.7)

CTD	RP	Flag	Reason for Flag
1	11	133	Data is bad, marked by operator. Bottle insert was not properly pushed in.
38	14	141	No data. The collection of this sample was missed.
38	17	141	No data. The collection of this sample was missed.
38	20	141	No data. The collection of this sample was missed.
55	12	141	No data. The collection of this sample was missed.

61	21	133	Data is bad, marked by operator as it is an obvious outlier on the profile plot. The sample had unstable readings at the beginning and became stable later. Cause is unknown, there were no obvious sampling/collection error observed from analyst.
61	22	133	Data is bad, marked by operator as it is an obvious outlier on the profile plot. Cause is uncertain but analyst suspected that it could be possible of sampling from wrong Niskin bottle.
65	10	141	No data. The collection of this sample was missed.
75	13	141	No data. The collection of this sample was missed.
75	21	133	Data is bad, marked by operator. Salinity lid was not screwed tightly, and insert was not properly pushed in.
82	17	133	Data is bad, marked by operator as it is an obvious outlier on the profile plot. Cause is uncertain but analyst suspected that it could be possible of sampling from wrong Niskin bottle.
94	32	141	No data. The collection of this sample was missed.

8.4 Missing or Suspect Dissolved Oxygen Data

Data is flagged based on CTD sampling log notes, observations during analysis, and examination of the depth profile (Flag key: appendix 8.7).

CTD	RP	Flag	Reason for Flag
8	35	69	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
12	34	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
14	1	133	Bad sample – bubbles in sample.
17	16	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
19	3	69	Suspect, outlier in vertical profile as well as error plot.
19	6	69	Suspect, outlier in vertical profile as well as error plot.
23	20	133	No endpoint found, indiscriminate amount NaOH/NaI added to sample due to issues with dispensette.
26	21	141	No volume for flask ID, lid insert broke, unable to back calculate volume.
27	8	141	Titration error.
33	1	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
34	6	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.

35	8	133	Incorrect lid was placed in sample bottle resulting in incorrect sample volume.
35	10	133	Incorrect lid was placed in sample bottle resulting in incorrect sample volume.
52	10	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
54	34	133	Unable to get good measurement reading, outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
54	34	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
56	11	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
59	3	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
59	11	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
59	12	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
60	5	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
60	7	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
60	26	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
60	28	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset
67	30	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
67	34	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset
72	3	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset. Sample was over titrated twice before acceptable curve found.
74	15	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset. Sample was over titrated twice before acceptable curve found.
75	22	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset. Sample was over titrated twice before acceptable curve found.
78	10	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.

81	26	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
82	8	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
82	17	133	Seems to match previous bottle reading exactly, sensor does not. Sample likely collected from previous Niskin 16.
83	3	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
83	15	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
83	25	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
83	27	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
86	16	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
90	1	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
90	3	133	Outlier in the vertical profile, error to the CTD sensor greater than the acceptable offset.
91	21	69	Had to over titrate. Outlier in vertical profile.

8.5 Missing or Suspect Nutrient Data.

Data is flagged based on CTD sampling log notes, observations during analysis, and examination of the depth profile (Flag key: appendix 8.7). Note: within the csv file many ammonium samples are flagged 63 – below nominal detection limit. Ammonium only occurs in the upper few hundred metres of the ocean and within the Chlorophyl maximum, effectively its concentration is zero at all other depths. Due to the difficulty in analysing ammonium in seawater often the zero concentrations will be reported as a negative value, this is due to the baseline Milli-Q water becoming slightly contaminated due to the air quality within the laboratory, meaning the baseline is slightly greater than zero concentration.

CTD	**RP**	**Analyte**	**Flag**	**Reason for Flag**
4	3	PO4	69	Data point is an outlier on the depth profile plot, however analytically everything looks good.
14	28	All	141	No data. The collection of this sample was missed.
22	1	NO2	133	One duplicate bottle point bad due to baseline step up during analysis. Missing data.

38	16	All	141	No data. The collection of this sample was missed.
39	08	PO4	69	Data point is an outlier on the depth profile plot, however analytically everything looks good.
42	19	All	133	Did not include sample data as it was upside down in rack and was not run until over 12 hrs later after sitting on the bench. Missing data.
45	07	PO4	69	Data point is an outlier on the depth profile plot, however analytically everything looks good. Slow drip from Niskin bottle.
46	07	PO4	69	Data point is an outlier on the depth profile plot, however analytically everything looks good.
47	07	PO4	69	Data point is an outlier on the depth profile plot, however analytically everything looks good.
55	11	All	141	No data. The collection of this sample was missed.
56	19	All	141	No data. The collection of this sample was missed.
58	34	All	141	No data. The collection of this sample was missed.
60	32	All	141	No data. The collection of this sample was missed.
64	14	All	141	No data. The collection of this sample was missed.
82	17	All	133	Data matches previous bottle, same for D.O. and salt. Particularly noticeable in SiO4. Sample likely collected from the previous Niskin 16.
100	25	All	141	No data. The collection of this sample was missed.
TMR240215	12	All	133	Sample in wrong position and air went through system, missing data.
EXP240215ME4 MC1 a T1 F	N/A	NO2	134	Software identified bad peak shape, filtered mesocosm sample became contaminated during filtration process. Missing data.

EXP240223PS4C1	N/A	NH4	129	Data is bad. Data was over range, even with a 1 in 10 dilution. Missing data.
EXP240215ME4MC1aT1F EXP240215ME4MC1bT1F EXP240215ME4MC1cT1F	N/A	NO2	133	Filtered mesocosm samples became contaminated during filtration process, do not use filtered results.
EXP240216ME4MC1aT2F EXP240216ME4MC1bT2F EXP240216ME4MC1cT2F EXP240216ME4MC2aT2F EXP240216ME4MC2bT2F EXP240216ME4MC2cT2F	N/A	NH4	133	Filtered mesocosm samples became contaminated during filtration process, do not use filtered results.

8.6 Data Quality Flag Key

Flag	Description	
0	Data is GOOD	
63	Nutrients only.	Data below nominal detection limit.
65	Data is SUSPECT.	Nutrients only: Absorbance peak shape, measured by the instrument, is marginally outside set limits.
69	Data is SUSPECT.	Duplicate data is outside of set limits (software). Data point is an outlier on the depth profile plot (operator). Tagged by software or operator
79	Data is SUSPECT.	Nutrients only. Measured Method Detection Limit (MDL) for the analysis run is greater than the nominal MDL. All samples in that run tagged.
129	Data is BAD.	Nutrients Only. Absorbance peak exceeds the maximum value that can be measured by the instrument.
133	Data is BAD.	Set by operator.
134	Data is BAD.	Nutrients Only. Absorbance peak shape of calibrants, measured by the instrument, is outside of set limits (software).
141	NO Data.	Used in netcdf results file. Not used in csv results file.

8.7 GO-SHIP Specifications

8.7.1 Salinity

Accuracy of 0.001 is possible with Autosal™ salinometers and concomitant attention to methodology. Accuracy with respect to one particular batch of Standard Sea Water can be achieved at better than 0.001 PSS-78. Autosal precision is better than 0.001 PSS-78. A precision of approximately 0.0002 PSS-78 is possible following the methods of Kawano with great care and experience. Air temperature stability of ± 1°C is very important and should be recorded[2].

8.7.2 Dissolved Oxygen

Target accuracy is that 2 sigma should be less than 0.5% of the highest concentration found in the ocean. Precision or reproducibility (2 sigma) is 0.08% of the highest concentration found in the ocean.

8.7.3 $Si(OH)_4$

Approximately 1-3% accuracy[1], 0.2% precision[3], full scale.

8.7.4 PO_4

Approximately 1-2% accuracy[1], 0.4% precision[3], full scale.

8.7.5 NO_3

Approximately 1% accuracy[1], 0.2% precision[3], full scale.

8.7.6 Notes

[1] If no absolute standards are available then accuracy should be taken to mean the reproducibility presently obtainable in the better laboratories.

[2] Keeping constant temperature in the room where salinities are determined greatly increases their quality. Also, room temperature during the salinity measurement should be noted for later interpretation if queries occur. Additionally, monitoring and recording the bath temperature is also recommended. The frequent use of IAPSO Standard Seawater is endorsed. To avoid the changes that occur in Standard Seawater, the use of the most recent batch is recommended. The bottles should also be used in an interleaving fashion as a consistency check within a batch and between batches.

[3] Developments of reference materials for nutrients are underway that will enable improvements in the relative accuracy of measurements and clearer definition of the performance of laboratories when used appropriately and the results are reported with the appropriate meta-data.

9 References

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IN2024_V01 Carbon Chemistry Report

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Field Personnel

Name	**Role**	**Watch (hrs)**	**Organisation**
Abe Passmore	carbon chemistry	1400 - 0200	CSIRO
Lavenia Ratnarajah	carbon chemistry	1400 - 0200	UTAS
Kathy Gunn	sampling	1400 - 0200	CSIRO
Helen Fry	sampling	1400 - 0200	Ship Doctor
John Akl	carbon chemistry	0200 - 1400	CSIRO
Wayne Dillon	carbon chemistry	0200 - 1400	CSIRO
Kaihe Yamazaki	sampling	0200 - 1400	UTAS

Water sample collection

Seawater samples for analysis of total dissolved inorganic carbon (DIC) and total alkalinity (TA) were collected from CTD station casts immediately after oxygen sampling. For a 36 Niskin bottle CTD cast, about 24 sample depths along with three duplicate samples from the near surface, mid depth and near bottom were collected at every other CTD. A reduced number of samples with near surface and near-bottom duplicates were usually taken from other CTD casts and in waters shallower than about 2000m.

Samples were drawn from 10 litre Niskin bottles into 250ml glass bottles using silicone rubber tubing and taking care to avoid introducing bubbles into the bottle. Each sample was overflowed by about two bottle volumes before collecting the final sample. TA samples were collected in Schott AG® type-33 borosilicate glass bottles and DIC samples were collected in milk dilution bottles with phenolic resin caps containing conical seals. The samples had 0.1ml of a saturated mercuric chloride ($HgCl_2$) solution added to halt biological activity and the bottles were sealed with a 5ml headspace using screwcaps to provide an airtight seal. The samples were stored in the dark at room temperature and analyses were usually carried out onboard within two days of collection.

Data quality control

Data were checked during the cruise as outlined below and went through a final quality check post-cruise with standard GLODAP quality flags (Jiang et al., 2021) assigned.

Table 1: GLODAP quality flag assignments (Jiang et al., 2021).

FLAG	DESCRIPTION
0	Interpolated data (GLODAP uses 0 to indicate calculated data)
1	Not evaluated/quantity unknown
2	Acceptable
3	Questionable
4	Known Bad
6	Average of replicates
9	Missing data

DIC analyses

Seawater measurements of DIC were made using a SOMMA system (Johnson et al., 1993 and Dickson et al., 2007). The SOMMA uses high-purity nitrogen carrier gas (99.999%) to transfer a known volume of sample into a stripping chamber, acidify the sample and extract CO_2 from the sample by bubbling with the carrier gas and transferring the CO_2 into a coulometer cell for quantification.

A coulometer cell was typically used for about 30 water samples plus duplicates and CRMs before the cell and associated anode and cathode solutions were replaced. Casts with 24 depth samples and three duplicates were measured on a single coulometer cell and casts with fewer samples were combined, where possible. Samples from each CTD station were measured in a random order apart from duplicate samples used quantify the measurement precision.

All samples were placed in a 22°C water bath prior to analysis. The samples were loaded into a calibrated pipet (20.290 ± 0.001 ml) and the sample temperature measured using a Fluke 1523 thermometer with a Fluke 5616 RTD mounted in the water line flowing into the pipet (accuracy of

± 0.02°C). The sample was then transferred using a carrier gas to a stripping chamber and a 1ml solution of phosphoric acid (10%(v/v)) added to convert the DIC to CO_2(g). The carrier gas was then bubbled through the sample to extract the CO_2 and the gas transferred into a coulometer cell where the CO_2 reacts with ethanolamine and forms hydroxyethylcarbamic acid. A coulometric titration was used to neutralise the acid with the end point detected photometrically.

A startup procedure was followed for each new cell. A series of measurements were first made by bubbling the CO_2-free carrier gas through the coulometer cell solution followed by analysing test seawater samples. Cells that did not provide a stable blank were replaced, and the startup procedure was repeated. When a consistent blank was achieved the efficiency of the measurement for quantifying CO_2 was checked with multiple injections of pure CO_2 (99.995%) using a VICI® VALCO valve with two gas loops of known volume to calculate a calibration factor for the cell. The calibration factor was typically about 1.005 (99.95% efficiency). The gas calibrations were followed by measurement of Certified Reference Material (CRM) from the Scripps Institution of Oceanography before commencing sample analyses. At the end of a cell, another CRM is analysed, which is used with duplicate sample measurements to assess drift in the measurement over the duration of the sample run.

The final sample concentrations were calculated as described in Johnson et al. (1998). For conversion from µmol/l to µmol/kg the seawater density was initially calculated using the sample temperature from the SOMMA pipet and the salinity determined with the Seabird SBE4 conductivity cell of the SOMMA. The final data was recalculated with the pipet temperature and salinity reported for each corresponding Niskin bottle (Rintoul et al., 2024). There were 9 samples out of a total of 2116 DIC samples with missing Niskin bottle salinities and CTD measured salinities were used. All final reported values of DIC were corrected for the addition of 100 microlitres of a saturated $HgCl_2$ solution to a 250ml sample by multiplying the concentration by 1.0004.

DIC Quality Control

Checks of the variability in gas calibration factors, duplicate and CRM measurements, measurement blanks at the end of each analysis, and tracking different coulometer cells and solutions were used to assess the data quality.

The cell blanks made on measurements of CO_2 free carrier gas were 5 counts/minute (about 0.001 µmolC/minute), with a sample measurement usually taking 8-10 minutes. Two coulometer cells used on 13 and 14 Jan 2024 had higher blank values of 0.002 and 0.004 µmolC /minute, respectively. These two coulometer cells gave gas calibration factors and measurements of CRM values within acceptable ranges (see below) and were used for sample measurements for CTD stations 9 and 10.

Over the duration of the cruise the coulometer cell calibration factors (Figure 1) were 1.0055 ± 0.0008 (1sd, n=68). Values within the range shown in Figure 1 and the blank values described above were used to determine whether to proceed to measurements of CRMs and samples or replace the coulometer cell.

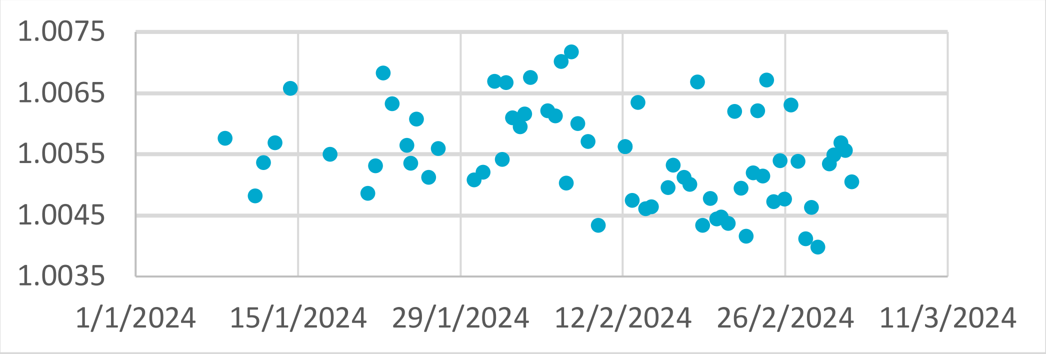

Figure 1. Coulometer cell calibration factors for IN2024_V1.

CRM measurements (Table 2) were made at the start of sample analyses and end of each coulometer cell run. The average DIC values for batch 184, used for CTD stations 1-5, were +1.95 µmol/kg compared to the certified values with a small sample size. Batch 209 measurements for CTD stations 6-100 were on average +0.79 µmol/kg compared to the assigned CRM concentration.

Table 2. Certified and measured DIC for CRMs.

CRM Batch	Certified DIC µmol/kg	CTD Station	Measured DIC µmol/kg
184	2052.75	1-5	2054.70 ± 0.94 (n=6)
209	2060.05	6-100	2060.84 ± 1.14 (n=133)

CRM measurements outside the target range of ± 2 µmol/kg from the certified CRM value were examined at the beginning of a sample run to determine if there was an issue with coulometer setup before proceeding to measure samples. All out of range results were above the certified CRM value and some variability in the CRM values appeared to be related to the glass coulometer cells. Replacement of the cell usually resolved the issues with unusual drift or CRM measurements.

For the voyage, cell 9A generally provided CRM results closest to the certified value and typically less than a 2 µmol/kg change in DIC for CRMs measured at the start and end of the analysis run. Other cells used occasionally drifted higher by less than 3 µmol/kg over the duration of the analysis run. The average of the CRM values for each cell was calculated and the offset from the assigned CRM value was used to calculate an offset correction to DIC measurements for samples (Figure 2). Most corrections were less than 2 µmol/kg and all were less than 3 µmol/kg.

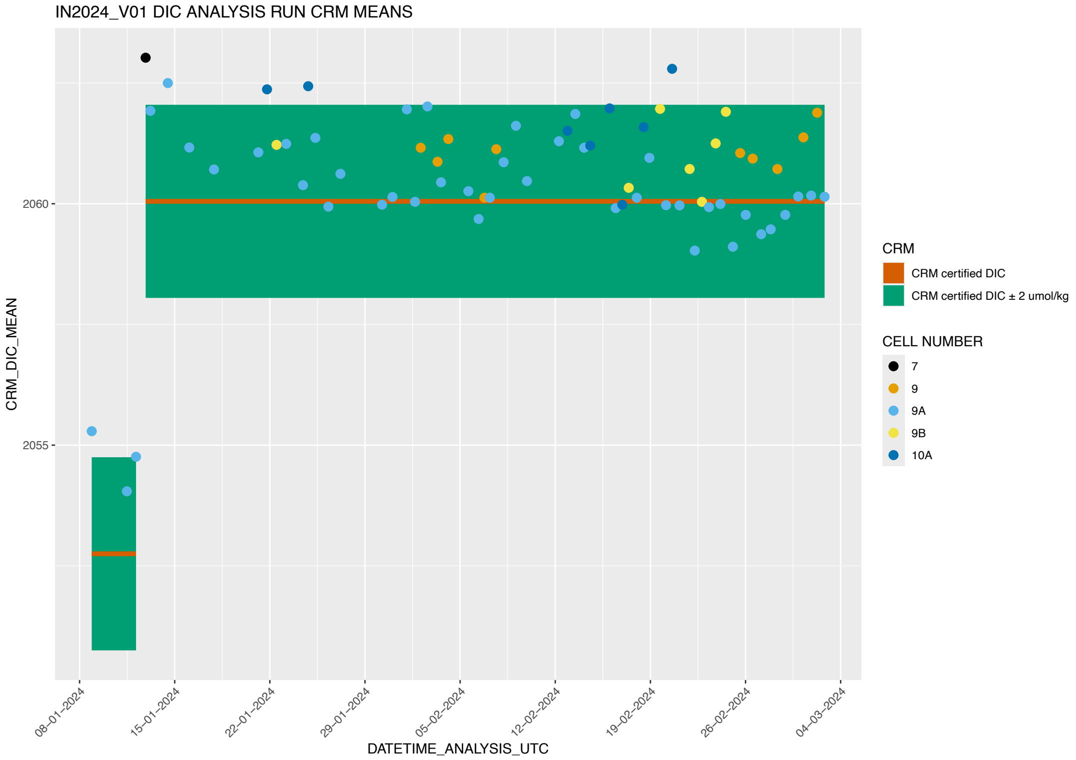

Figure 2. Average of DIC measurements (µmol/kg) of CRM values for IN2024_V1. The coloured dots show different coulometer cells used over the duration of the cruise. CTD stations 1-5 used CRM Batch 184 until 12/01/2024, and subsequent stations used CRM Batch 209.

DIC measurement precision

The precision of the DIC analyses were assessed using duplicate samples. The mean absolute difference across all duplicate pairs was 0.75 ± 0.68 µmol/kg for 219 pairs (Figure 3). The duplicate data for each of the 219 duplicate pairs assigned a quality flag = 2 were averaged and a quality flag of 6 assigned to the reported values.

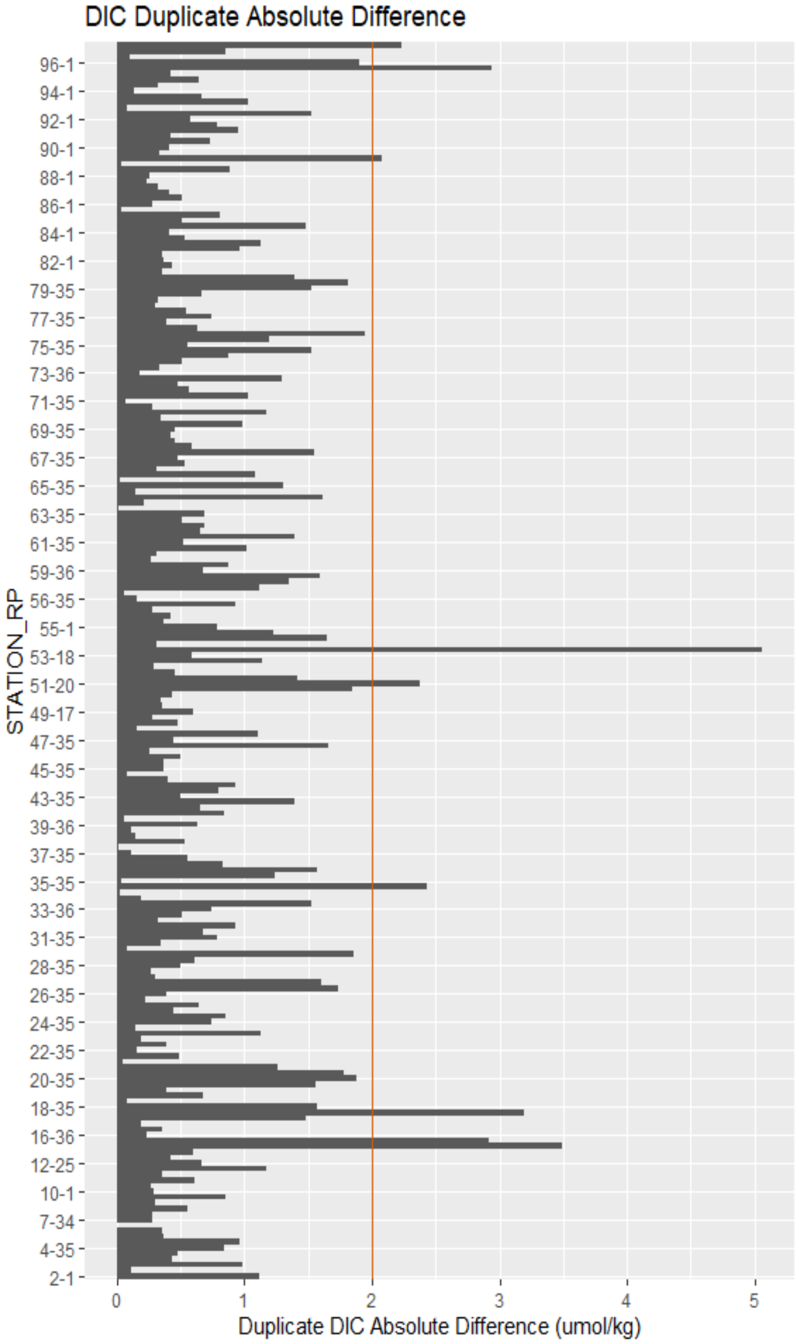

Figure 3. Absolute difference of duplicate measurements (µmol/kg) of samples by CTD station number and CTD rosette position (e.g. “51-20” is CTD station 51 and rosette position 20) for IN2024_V1. All data used to calculate the absolute difference had a quality flag = 2.

TA analyses

TA measurements using an open cell followed the procedure of Dickson et al. (2007). Two Metrohm Titrando 904 systems, named Quoll and Wakmatha, were used with Tiamo software to automate the measurements. Metrohm 801 stirrers mixed the sample in the titration cells, and Metrohm 843 pump units were used to empty cells after a titration and to flush and empty the cell with milliQ water prior to loading new samples. For the titrations, Aquatrode double-junction pH electrodes and PT-1000 sensors were used to track emf change and sample temperature, respectively.

Samples were kept in a water bath at 22°C prior to measurement. For each TA measurement, 100ml of sample was dispensed by 50ml burettes (Metrohm Dosino 800) into a water-jacketed titration cell held at a constant temperature of 22°C using a refrigerated water bath. Water-jacketed burettes at 22°C (Metrohm Exchange Unit – 5ml) were used to dispense 0.1N HCl titrant with 0.7 ionic strength made by adding AR grade NaCl to the titrant. The sample and titrant burette dispensing volumes were calibrated gravimetrically before each voyage. The acid titrant was prepared in batches and stored in one litre Schott borosilicate glass bottles and sealed with screw caps. The concentration of each batch was determined coulometrically (Taylor and Smith, 1959). The density of the acid titrant used to calculate the mass of titrant added was measured using an Anton-Parr DMA 5000M density meter and fitted to a temperature dependent curve.

For each CTD station, duplicate samples were spread through the analyses to assess the precision of the measurements. After a sample was added to a cell, the electrode emf was monitored until drift was less 0.6mV/min, which was the threshold used for all steps in the titration. A volume of titrant was then added to the sample to bring the pH to about 3.5 and convert DIC to CO_2(aq), followed by stirring for 10 minutes to remove CO_2 from the sample. When the electrode drift was below the threshold, titrant was added in about 20 steps to provide approximately equally spaced changes in emf down to a pH of 3. The total alkalinity was calculated using a non-linear regression (Johannsen and Wedborg, 1979; Dickson et al., 2007). Sample water density was initially calculated with CTD salinity data and later recalculated using measured Niskin bottle salinities (Rintoul et al., 2024) or CTD salinities if direct measurements were not available. The final data were corrected for the addition of 0.1ml of a saturated $HgCl_2$ solution to each 300ml sample by multiplying by 1.00033.

TA quality control

Measurements of CRMs and duplicate samples were used to assess data quality. Both titration system showed offsets that between certified and measured TA values for CRMs, which may have resulted from a number of issues including sampling errors, pipet delivery volume errors, and the pH electrodes not following a Nernstian response. Changes in the acid titrant was another possible reason for offsets. Each titration removes about 2.5ml of titrant from the 1000ml titrant reservoir bottle which is vented through a 0.2-micron Pall Acrodisc filter. As the reservoir headspace volume increases with more titrations, evaporation or condensation can cause changes in the titrant concentration from the value measured before the voyage. Titrant reservoir bottles were mixed frequently and were topped up with titrant to minimise this source of error.

The Quoll and Wakmatha titrators were used for different CTD stations and comparisons of measured and certified CRM TA values were used to determine offsets to apply to finalise the data. The offsets were applied in blocks of time that were determined by periods of consistent values of CRM measurements and changes in the operation of the system like topping up or mixing the titrant reservoir, changing the titrant, or periods of inactivity.

Quoll titrator

Quoll provided the best agreement with certified CRM TA values. Measurements on CRMs tended to increase slightly over the first half of the voyage, which may have been due to the titrant evaporating in the headspace of the titrant bottle as the humidity of laboratory air changed. Maintaining a stable laboratory temperature was also difficult on the voyage, which may have caused some drift by altering the evaporation and condensation of droplets in the top of the titrant bottle. Up to CTD station 6, the CRM measurements were on average 7.60 µmol/kg less than the certified TA for CRM 184 of 2226.44 µmol/kg up to CTD 6 (n=5). The analysis method was modified during the voyage to increase the frequency at which the condensate was mixed down into solution from once every 10 samples to once every sample. CRM 209 was used for all subsequent CTDs and was on average 0.83 µmol/kg below the certified value of 2210.40 µmol/kg (n=101). For the duration of the voyage, the CRM measurements and final values after applying an offset values based of measured minus certified CRM TA are shown in Figure 4 by the black and orange dots, respectively. The offsets applied to CTD station data are shown in Figure 5.

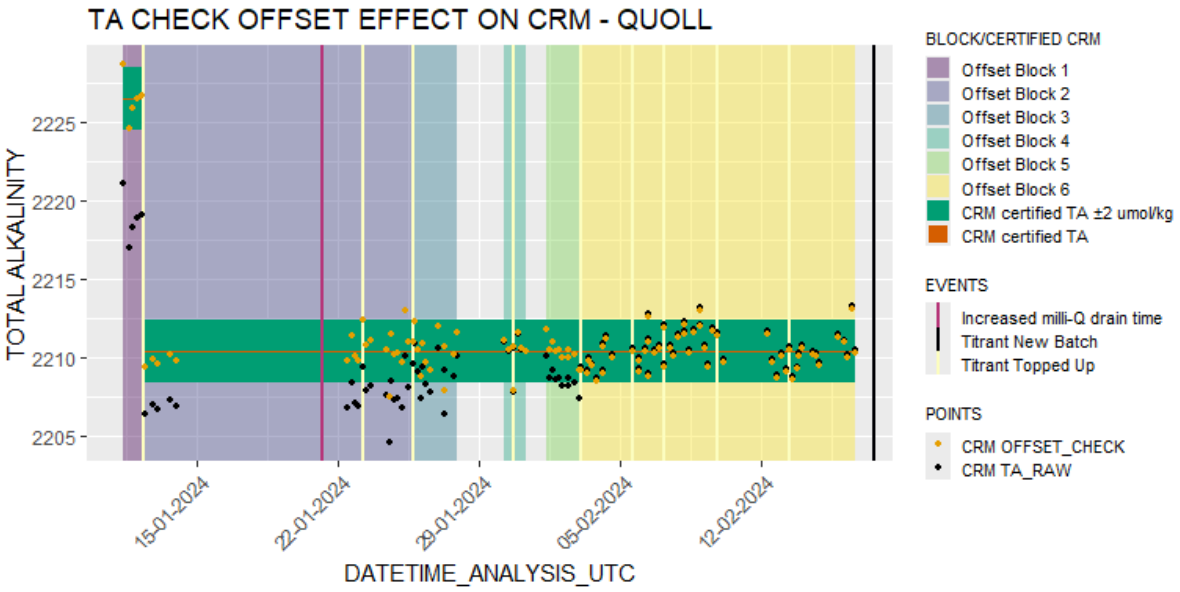

Figure 4. TA measured (µmol/kg) on CRMs 184 and 209 during IN2024_V1 using the Quoll titrator (black dots) and final corrected data (orange dots) based on offsets in measured versus certified CRM values.

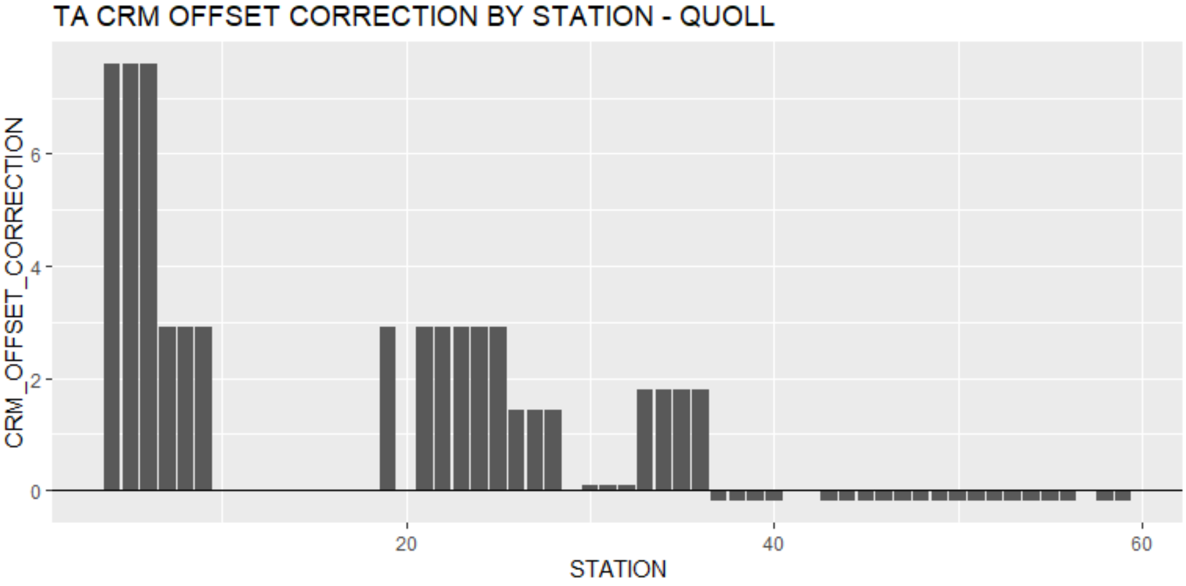

Figure 5. Quoll titrator data offsets (µmol/kg) applied to measured TA values for different CTD stations on IN2024_V1.

Wakmatha titrator

Measurements using the Wakmatha titrator were offset from certified CRM 184 values on average 2231.43 ± 0.95 µmol/kg (n=5), or 4.99 µmol/kg greater than the certified TA value of 2226.44 µmol/kg. The titrator measurements of CRM 209 were on 2217.66 ± 1.60 µmol/kg, or 7.26 µmol/kg greater than the certified CRM value of 2210.40 µmol/kg.

The cause of the persistent offset was not resolved and may have been due to an error in the calibration of the volume delivered by the Titrando 801 burette, or an error in the titrant burette calibration. A new batch of titrant was used from 16/01/2024 and an offset remained. The time taken for a titration gradually increased until 24/01/2024 when the Aquatrode pH electrode was replaced. This titrator was not used again until 16/02/2024 and while the measured CRM values were consistently above the certified CRM value the measurements were usually within ± 2 µmol/kg of each other (Figure 6, black dots). The average measured versus calculated for the data blocks were adjusted to account for the offset (Figure 6, orange dots) and are shown in Figure 7 by CTD station number.

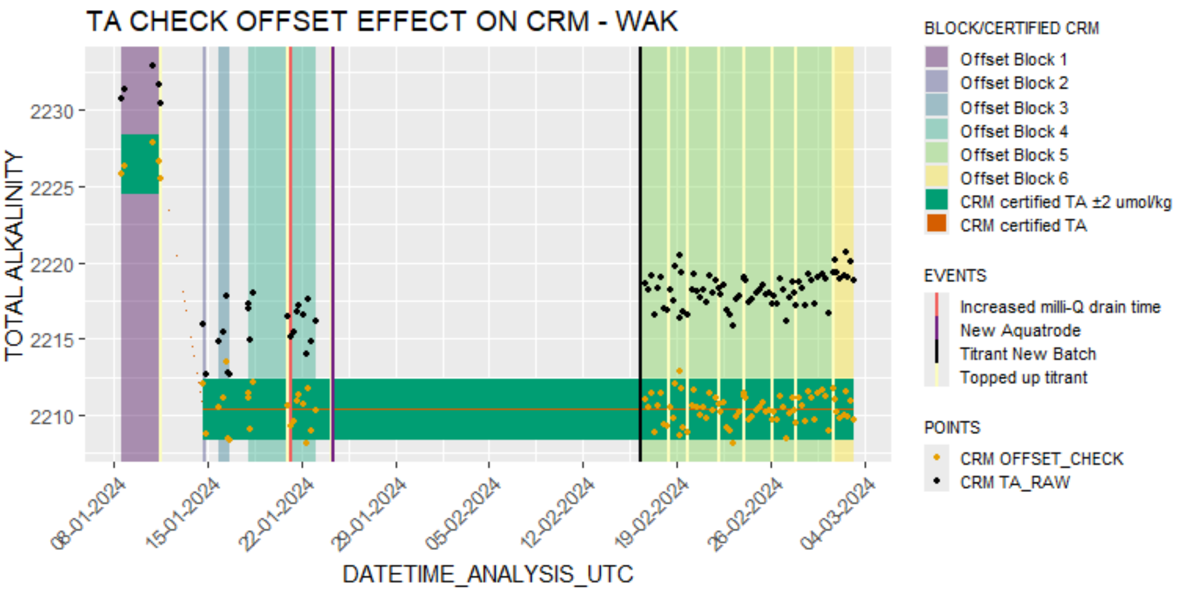

Figure 6. TA (µmol/kg) measured on CRM 184 and CRM 209 during IN2024_V1 using the Wakmatha titrator (black dots) and final data (orange dots) after applying corrections based on offsets in measured versus certified CRM values.

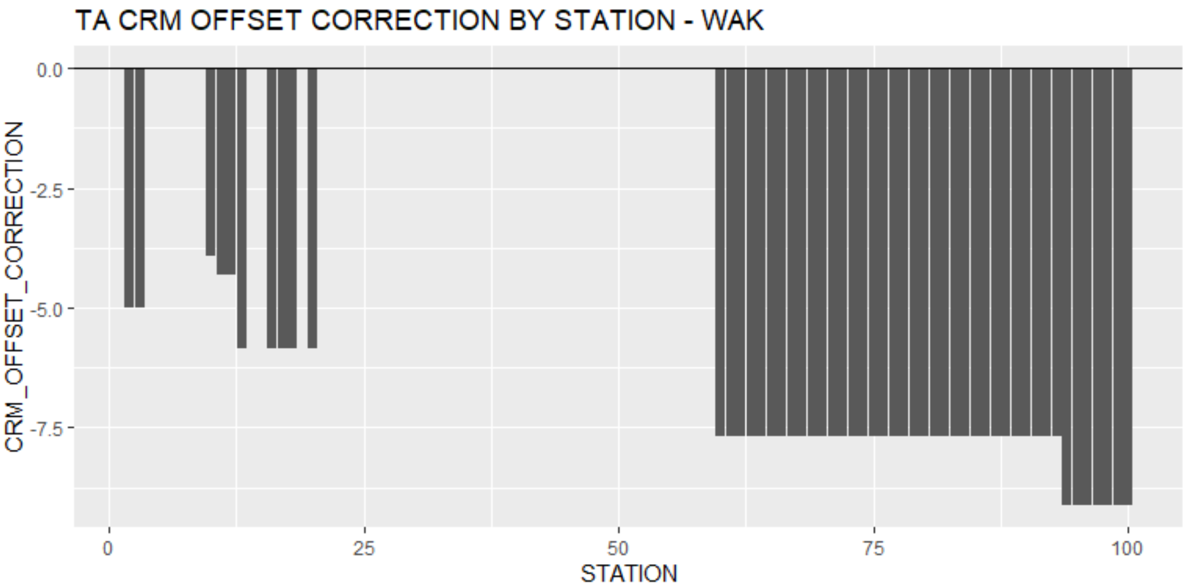

Figure 7. Wakmatha titrator data offsets (µmol/kg) applied to measured TA values for different CTD stations on IN2024_V1.

TA measurement precision

The precision of the TA measurements was calculated as the mean absolute difference of 1.08 ± 0.93 µmol/kg (n=222) using pooled data from the Quoll and Wakmatha titrators (Figure 8). The mean was calculated using duplicates assessed as good quality data and was assigned a quality flag = 6.

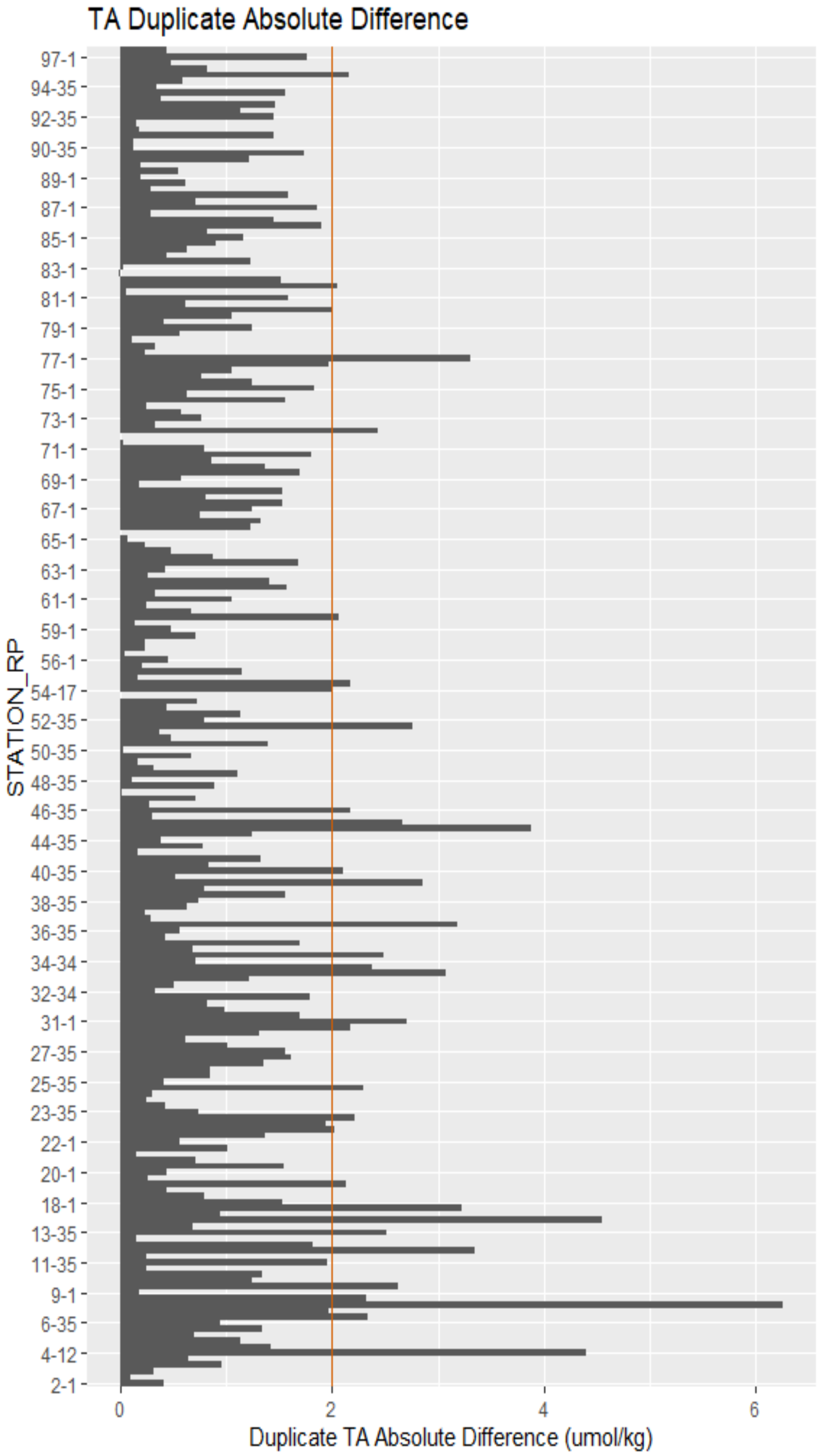

Figure 8. Absolute difference of duplicate measurements (µmol/kg) of samples by CTD station number and CTD rosette position (e.g. "51-20" is CTD station 51 and rosette position 20) for IN2024_V1. All data used to calculate the absolute difference had a quality flag = 2.

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