# INTEGRATED MARINE OBSERVING SYSTEM

# NATIONAL REFERENCE STATIONS BIOGEOCHEMICAL OPERATIONS

# A PRACTICAL HANDBOOK

CSIRO Marine and Atmospheric Research Laboratories Report for



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# National Reference Stations INTEGRATED MARINE OBSERVING SYSTEM

# IMOS BIOGEOCHEMICAL OPERATIONS MANUAL

#### Introduction:

An often understated part of experimental and observational protocols is that part played by sampling correctly. If proper procedures for sampling are not followed then even the most meticulous of laboratory analysts and finely tuned apparatus are all worthless and have little meaning – it can quite rightfully be said that: "no data is better than bad data".

For this reason, it is recognised that IMOS Biogeochemical samplers' annual training workshops are conducted; with the sampling team members rotating through on a regular basis to ensure consistency in sampling technique is maintained nationwide and regular networking of the participants can occur.

The following procedures and methodologies for biogeochemical sampling, sampling regimes, analyses and data flow conducted to meet the requirements of the Australian IMOS NRS project are laid out purposely in detail. The steps in the body of this document are to be followed to ensure that the best and most consistent quality samplings between sites are acquired, thus leading to quality data being obtained from the ensuing analyses.

This manual has come about from an initial scoping meeting where it was decided that not all parameters that were desired could effectively and logistically be obtained. Those that were considered the most important and achievable are those that are enclosed herein.

A person following the proper and agreed procedures – with a particular emphasis on sampling techniques – as outlined in the body of this handbook will give the laboratory analysts the best opportunity to obtain quality data. In some instances there are **deliberate** repetitions of some directions, which have been included to assist in bringing attention to particular details that should be observed – and why.

The sampling and analytical regime that is described in this document utilises the same "blue water" methods for collection and analysis as on larger vessels such as the" Australian Marine National Facility – Southern Surveyor". However owing to the smaller size of the vessels involved in the Australian IMOS ANMN NRS Biogeochemical sampling, there are limitations as to what can and cannot be achieved – e.g. the use of niskin style sampling bottles on a wire cable, as opposed to the use on larger vessels of a "real time" rosette sampler.

Of the nine NRS, three build on Oceanographic time series data collection sites that go as far back as the early 1940's. The concept of the IMOS NRS Biogeochemical sampling is to enhance the existing and expand the national coverage of time series data.

The manner in which this manual has been laid out enables it to be "broken up" into smaller pieces, for example: "detailed sampling procedures", or "pre-analyses sample treatment", etc. without the necessary need of a large document.

Every endeavour to achieve monthly collection of biogeochemical data from each site, based within the major continental boundary currents, will be made in order to obtain monthly, seasonal, annual and long term variability or shifts in the Australian marine ecosystem – in particular as a response to Climate Change. NRS Sampling Manual In addition to the monthly sampling there will be co-located moorings with instrument arrays at 2 depths – some with a third surface meteorological surface buoy – that are deployed at the National Reference Stations; recording a suite of time series data which will be complementary to the discrete monthly water column samples.

The moored instruments are Sea-Bird<sup>™</sup> sensor packs modified by WetLabs<sup>™</sup>, and as a package they are marketed as Water Quality Meters (WQM's). These packages measure: Conductivity, Temperature, Depth, Time (UTC & Local), Dissolved Oxygen, Fluorescence and Turbidity at two set depths only.

The biogeochemical results will be used to monitor and assess the performance of the moored WQM's as well as creating a large independent suite of other extremely valuable data obtained from a number of depths that cannot be sensor determined.

From the outset, this manual has been written as a hands on guide to the acquisition of quality samples and hence quality data. It is not a "research" publication as such; it is more a collation of the best techniques in practice in today's Biogeochemical and blue-water Oceanographic community for ensuring the output of reliable, quality data to the end-user community.

The aim is for the sampling, analytical, and reporting standards to be at least equivalent to: the WOCE (World Ocean Circulation Experiment) and JGOFS (Joint Global Ocean Flux Study) studies.

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www.imos.org.au

The National Reference Station information may be found at the following link:

http://imos.org.au/anmnnrs.htmL

As stated previously, the NRS sites will be sampled monthly – weather and remoteness of locality permitting – for biogeochemical data; with mooring servicing intervals yet to be fully resolved.

It is not within the scope of this manual to cover the use of, acquisition, downloading, storing, calibrating or doing QA/QC on data acquired from the profiling CTD's in use on the NRS vessels or the NRS WQM moorings. Another short companion manual is planned to be produced in the near future, to accompany this one: "Profiling CTD Guidelines for IMOS National Reference Stations"; which will deal with the basic operation of profiling CTD's at the NRS sites and their set up for NRS requirements.

There must be standardised site coding for site identification and field sheets and sampling labels used consistently and correctly.

Sample collection methodologies for the suite of biological and physical parameters; including sample preservation must be followed consistently at all sites. Good collection techniques will ensure good samples for analyses

. Sample storage and transportation to points of analyses also need to be strictly adhered to

Analytical protocols for the above biological and chemical parameters must be consistent and if carried out at more than one laboratory – would require many inter-laboratory comparisons to be run; hence this spread of analytical laboratories has been kept to a minimum and these already participate in international comparison trials.

Standardised units of measurement appropriate to each biological, chemical and physical characteristic have been agreed to and applied. Accepted SI units should be used wherever possible.

It is also necessary to set standardised processing procedures in place for each water and biological parameter which includes quality assurance and quality control.

Each data point/set that has been sampled, analysed, processed and checked for QA/QC at all stages of collection and analysis is required to be entered into a standard national database (eMII), with fully descriptive metadata; which may include a short report if necessary, for each data set which will be openly accessible to all participants and the end users of the collected data – which includes free and open access to any party who may wish to access and utilise the data.

I would like to express my personal thanks to Mr. S. Allen, Technical Director, IMOS, for the faith shown in me for the methods description and successful implementation of a functional Biogeochemical sampling and data gathering project for IMOS

I would like to express my personal thanks to Dr. T. McDougall for his support.

**BIOGEOCHEMICAL OPERATIONS MANUAL** 

Figure 1, below, shows the location, and geographical spread of the 9 NRS Biogeochemical sampling stations, accurately charted using decimal degrees. Refer to Table 1, following Fig.1, for the actual latitudes and longitudes of each site. There is currently consideration being given to introduce another 2 or 3 National Reference Stations, however dependant upon their remoteness, they may not be able to be fully sampled for Biogeochemical data on a monthly basis and the sampling may occur only at changeover times of double depth WQM moorings.



Fig. 1

#### **BIOGEOCHEMICAL OPERATIONS MANUAL**

The biogeochemical sampling stations which are complemented by the NRS moored network are shown below in Table 1.

The table is shown in the operations manual for the interest of all those involved with the sampling and shows the geographic spread of the National Reference Stations. It was intended that the 9 station roll-out be covered over 2 financial years, with 6 being the target for commencement in the first fiscal year 2008/2009. However, with a lot of effort and overcoming the many logistics of sampling and sample movement to overcome, it was possible to exceed this target and fully kit out 8 (in the first fiscal year of the proposed 9 over 2 fiscal years) National Reference Stations for Biogeochemical operations.

Site	Node	Station code	State	Start-up Date	Nominal Sonic Depth	Nominal Longitude	Nominal Latitude
With WQMs							
Maria Island*	CMAR	MAI	TAS	Oct 1944	90m	148.233333	-42.596667
Kangaroo Island	SARDI	KAI	SA	New	100m	136.448	-35.836
Esperance	CMAR	ESP	WA	New	50m	121.85	-33.933333
Rottnest Island*	CMAR	ROT	WA	Apr 1951	50m	115.416667	-32
Ningaloo	CMAR	NIN	WA	New	50m	113.94665	-21.871733
Darwin	AIMS	DAR	NT	New	20m	130.7827	-12.417467
Yongala	AIMS	YON	QLD	New	28.9	147.26	-19.306
North Stradbroke Island	CMAR	NSI	QLD	New	60m	153.580217	-27.388917
Port Hacking 100*	DECC	PHB	NSW	May 1953	100m	151.25	-34.083333

**Table 1**. The National Reference Stations codes, depths, locations (Decimal Degrees)

\*Denotes long term stations already sampled and analysed historically by CMAR – some dating back to the 1940's.

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Standard Sampling Depths for water chemistries, other discrete depth sampling and phytoplankton (except Carbon – see table 3)

The following table (Table 2.) shows the sampling depths for the water chemistry and phytoplankton sampling, with the excess (residual) left in each of the niskins (sampled to 50m), measured, recorded and placed into a 20l carboy – based on the **surface** niskin residual volume – to give an "integrated water column" sample. This is often the only cast for a station, unless they are in deeper locations. These previously determined depths, laid out in Table 2 are carried out to give coverage of the photic zone – of course some of the stations are sampled deeper than shown here (see table 4).

Because the only Carbon sampling depth common to all sites is the surface niskin sampling (See Table 3); It is necessary to record the residual volume to be transferred to the composite sample carboy from each subsequent niskin, based on the residual left after sampling from the surface bottle.

By basing the collection of the residual volumes for the other niskins upon the surface bottle, it avoids biasing the "integrated/composite" carboy sample - as there will be greater residuals in niskins not sampled for Carbon. Table 3 lists all the Carbon sampling depths – which do put constraints on the total water budgets for the 5l niskins. Any water left in a niskin after the niskin sample volume is measured as equivalent to the surface residual and added to the carboy, can then be discarded.

Site	Station code	Sonic Depth	Officer Responsible	Biogeochemistry sampling depths (excluding carbon) – First Cast
With WQMs				
Maria Island*	MAI	90m	Tim Lynch	Surface, 10, 20 , 30, 40, 50
Kangaroo Island	KAI	110m	Charles James	Surface, 10, 20 , 30, 40, 50
Esperance	ESP	50m	Tim Lynch	Surface, 10, 20, 30, 40, 50
Rottnest Island*	ROT	50m	Tim Lynch	Surface, 10, 20, 30, 40, 50
Ningaloo	NIN	50m	Tim Lynch	Surface, 10, 20, 30, 40, 50
Darwin	DAR	25m	Craig Steinberg	Surface, 10, 20 , bottom + 2.5 (2) *
Yongala	YON	28.9	Craig Steinberg	Surface, 10,20 , bottom + 2.5 (2) *
North Stradbroke Island	NSI	60m	Anthony Richardson	Surface, 10, 20, 30, 40, 50, <b>60</b> *** (Single bottles – now WQM's yet)
Port Hacking 100*	PHB	100m	Tim Pritchard	Surface, 10, 20 , <b>25</b> , 30, 40, 50 **

#### Table 2

#### Notes regarding Table 2, above

\* NOTE: DAR & YON are shallow sites which will have to do a (measured) double collection to ensure there is enough sample water in the "water column" carboy for later sample preparation for later analyses.

\*\* NOTE: PHB, 25meter sample water is **not** to be measured nor added to the water column carboy, but still sampled for other parameters for historical reasons

\*\*\* NOTE: NSI – does **not** include 60m water in the water column carboy

• **Note:** Due to the historical nature of some of these stations they cannot be sampled with niskins at 15m and 20m depths for example. If an historical station has been consistently sampled at 20m, or in the case of PHB (25m) the historical depth must still be sampled at that depth for retention of data continuity.

At the next cast, collect the other water chemistry samples deeper than 50m where they are required or possible – for a particular site.

For each site the sampling vessel's capability will determine whether it is possible to gather all the depths for the biogeochemical suite, to the bottom in one cast, and then conduct a further cast for the two WQM (5I) samples. It may turn out that a third cast is necessary for deeper stations if the vessel is of limited capability for the particular NRS it will be used for.

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Table 3 – Sampling Depths for **CARBON SAMPLES** which are taken, in addition to the standard chemical parameters (Table2) from the niskin bottles

**Note**: Samples are collected from the near-bottom Niskin bottle and the Niskin bottle above it, in order to determine if there are intrusions of  $CO_2$  rich water onto the shelf. If sampling depths are shallower, according to the sonic depth, than as shown in the table, please ensure the two deepest samples are collected

#### Table 3

Site	Station code	Sonic Depth	Officer Responsible	Biogeochemistry sampling depths ( <u>excluding carbon) – First</u> Cast	Number/total Carbon sampling depths per site
With WQMs					
Maria Island*	MAI	90m	Tim Lynch	Surface, 10, , 30, , 50, 75, bottom + 2.5	6
Kangaroo Island	KAI	110m	Charles James	Surface, 10, , 30, , 50, 75, 90, bottom + 2.5	7
Esperance	ESP	50m	Tim Lynch	Surface, , 20, , 40, bottom + 2.5	4
Rottnest Island*	ROT	50m	Tim Lynch	Surface, 10, , 30, , 50, bottom + 2.5	5
Ningaloo	NIN	50m	Tim Lynch	Surface, 10, , 30, , 50, bottom + 2.5	5
Darwin	DAR	25m	Craig Steinberg	Surface, 10, 20, bottom + 2.5	4
Yongala	YON	28.9	Craig Steinberg	Surface, 10, 20 , bottom + 2.5	4
North Stradbroke Island	NSI	60m	Anthony Richardson	Surface, 10, , 30, , 50, bottom + 2.5	5
Port Hacking 100*	PHB	100m	Tim Pritchard	Surface, , 20 , , 40, , 60, 80, 100, bottom + 2.5	7

Due to variation of depths at different sites requested by the Carbon sampling group, as shown in the above Table 3, there will be unique station field logs and labels created that are tailored for use at each unique site. They will clearly identify which sample depth is sampled for each parameter type and cover all necessary unique information for any particular sampling at any particular site.

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Table 4 – indicates the sampling depths for water chemistry and Carbon samples (See Table 3) from **deeper** than ~ 50m, which may not be obtained concurrently from the first niskin cast to capture the < 50m "integrated water column" carboy water. As mentioned earlier, dependant upon the sampling vessel capabilities, these may be conducted on separate casts. It is also **not** necessary to keep any of the residual niskin waters after sampling these depths (> 50m.)

**Note:** Samples are collected from the near-bottom Niskin bottle and the Niskin bottle above it to determine if there are intrusions of  $CO_2$  rich water onto the shelf. Again, if the sonic depths are shallower than indicated in the table, please ensure the two deepest samples are collected

Site	Station	Sonic	Officer	Casts for chemistries >50m	
code Depth Responsible		Sampling depths per site (metres)			
With WQMs					
Maria Island*	MAI	90m	Tim Lynch	75, 100, bottom + 2.5	
Kangaroo Island	KAI	110m	Charles James	75, 90, bottom + 2.5	
Esperance	ESP	50m	Tim Lynch	N/A	
Rottnest Island*	ROT	50m	Tim Lynch	N/A	
Ningaloo	NIN	50m	Tim Lynch	N/A	
Darwin	DAR	25m	Craig Steinberg	N/A	
Yongala	YON	28.9	Craig Steinberg	N/A	
North Stradbroke Island	NSI	60m	Anthony Richardson	(60m already sampled as in Table 2)	
Port Hacking 100*	PHB	100m	Tim Pritchard	60, 80, 100, bottom + 2.5	

#### Table 4