

# Franklin Cruise FR 9205

## Data Documentation

### JGOFS Western Equatorial Pacific Process Study

#### [1] General

Parameters Concentrations of total dissolvable cadmium, copper, iron, manganese, nickel and zinc.

**The data are considered unreliable due to contamination from the 1 L sample storage bottles, problems with racking all the bottles from the 24-bottle rosette and from malfunctioning of the clean container on *R/V Franklin*.**

Principal Investigator Denis Mackey

Institute Address CSIRO Marine Research  
PO Box 1538  
Hobart  
Tasmania 7001  
Australia

Email Address [denis.mackey@csiro.au](mailto:denis.mackey@csiro.au)

List of Units nmol kg<sup>-1</sup>

#### [2] Sampling

Gear Samples were collected from a CTD rosette using both Teflon coated General Oceanics Niskin bottles (10 litre) with Teflon (PTFE) taps, Kel-F bleed valves, and silicone O-rings and closures and from Helmond/Byrne (6 litre) polycarbonate bottles made at CMR. The H/B bottles had external silicone rubber and nylon (Kevlar) closures and Teflon (PTFE) taps and the only metal components were external to the bottles and made from titanium. Samples were collected from H/B bottles from 15 depths per cast and replicate samples were collected from GO bottles at 9 depths per cast.

Locations 5°N 155°E, 0° 155°E, 5°S 155°E at 15 depths from the surface to 3000 m (5°N), 2500 m (0°) and 3000 m (5°S).

Sampling Procedure The GO bottles were cleaned with 2.5% Extran, rinsed with Milli Q water and filled with 10% HNO<sub>3</sub> for a week. They were then rinsed with Milli Q water and stored in polyethylene bags. The H/B bottles were cleaned with 0.1% Triton X-100, rinsed with Milli Q water soaked with 5% HCl overnight. They were then rinsed with Milli Q water and stored in polyethylene bags. All Teflon fittings were acid cleaned.

Kartell LDPE sample bottles (1 L) were cleaned in 2.5% Extran for a week, rinsed with Milli Q water, acid-cleaned with boiling quartz-distilled 6 M HCl in an Ausdampf cleaning apparatus and rinsed again with Milli Q water. The bottles were stored in polyethylene bags / tote boxes. Gloves were used for all sampling procedures.

The CTD was equilibrated at depth for about 30 sec then lowered at 10 m min<sup>-1</sup> and fired after 30 sec so that samples were collected approximately 5 m below the initial depth. At 5°S and 0°, replicate bottles were fired immediately except at 2000 m where the rosette was raised and lowered again. The latter procedure was used for all replicates at 5°N. On recovery of the CTD, external silicone rubber bands were fitted to the H/B bottles to prevent leaking. The GO or H/B bottles were removed from the CTD rosette and mounted on the outside of a portable clean laboratory. Teflon (PFA for H/B, and PTFE for GO bottles) lines and taps (PTFE) were connected to the bottles and the lines passed through ports into a

laminar flow clean cabinet inside the clean laboratory where the samples were collected by gravity. Due to the large number of bottles, some bottles had to be stored temporarily on the CTD rosette (covered) or in PVC boxes.

### [3] Analysis

Instrument	Perkin Elmer Zeeman 5000
Method	GFAAS after extraction of DDDC/APDC complexes into Freon TF and back extraction into HNO <sub>3</sub> .
Precision	Estimated to be $\approx 10\%$
Comments	The cleaning of the GO bottles and sample bottles (Ausdampf apparatus) was done in a general laboratory. All other cleaning of reagents and equipment, analyses and sample manipulations were performed in a Class 100 clean laboratory using standard ultra-clean procedures. All sample bottles, reagent bottles, separating funnels etc were made from Teflon or LDPE.

### [4] Results

Quality of data	Blanks were measured at all stages of the procedure and the detection limits ( $3 \times$ standard deviation of blanks) were Cd ( $0.008 \text{ nmol kg}^{-1}$ ), Cu ( $0.19 \text{ nmol kg}^{-1}$ ), Fe ( $0.34 \text{ nmol kg}^{-1}$ ), Mn ( $0.15 \text{ nmol kg}^{-1}$ ), Ni ( $0.49 \text{ nmol kg}^{-1}$ ) and Zn ( $0.56 \text{ nmol kg}^{-1}$ ). Replicate analyses were performed for all 'anomalous' results and the data were verified by regular analyses of NASS certified reference materials. There was considerable scatter in the analyses of all TM which was attributed to contamination from the Kartell bottles. In addition there were problems with the clean container on <i>R V Franklin</i> during the cruise and the data, although showing generally the same features as found on FR 9008 and FR 9308 is considered unreliable.
-----------------	--

### [5] Brief description of analytical method

On returning to Hobart, the samples were acidified with 1 ml of Seastar HCl and stored for at least 3 months before being analysed. A subsample (50 ml) was adjusted to pH 4-5 by the addition of NH<sub>4</sub>OH followed by an ammonium citrate buffer. Trace metals in the subsample were then complexed by adding 0.3 ml of a solution containing 1% (w/v) each of diethylammonium diethyldithiocarbamate (DDDC) and ammonium pyrrolidinedithiocarbamate (APDC), extracted into 10 ml of quartz-distilled Freon TF (1,1,2 trichloro- 1,2,2 trifluoroethane) and back extracted with 25  $\mu$ l of concentrated Seastar HNO<sub>3</sub> followed by 1 ml of Milli Q water. The dilute HNO<sub>3</sub> extract was then analysed for Cd, Cu, Fe, Ni and Zn by GFAAS. For Mn, a separate subsample of seawater was adjusted to pH 7.5-8.5 with NH<sub>4</sub>OH before adding 3.0 ml of DDDC/APDC reagent and extracting into Freon. The Freon was then back extracted twice with Seastar HNO<sub>3</sub> and Milli Q water. The NH<sub>4</sub>OH ( $\approx 6 \text{ M}$ ) was prepared by diffusion of NH<sub>3</sub> from concentrated NH<sub>4</sub>OH into Milli Q water in a closed container. The mixed dithiocarbamate reagent was cleaned by repeated extraction with Freon. The citrate buffer was cleaned by adding a small amount of the DDDC/APDC reagent and extracting repeatedly with Freon. All reagents were cleaned until trace metal concentrations in the (DDDC/APDC)/Freon/HNO<sub>3</sub> extracts were negligible.

### References

- Mackey, D.J., 1983. The strong complexing capacity of seawater - an investigation of south-eastern Australian coastal waters. *Marine Chemistry* 14, 73-87.
- Sedwick, P., DiTullio, G., and Mackey, D., 1995. Dissolved iron and manganese in surface waters of the Ross Sea during the spring bloom 1994. *Antarctic Journal of the United States*, 30, 199-201.
- Mackey, D.J., O'Sullivan, J.E., Watson, R., 2002. Iron in the western Pacific: a riverine or hydrothermal source for iron in the Equatorial Undercurrent. *Deep-Sea Research I*, 49, 877-893.
- Mackey, D.J., O'Sullivan, J.E., Watson, R., XXXX. Trace metals in the western Pacific: temporal and spatial variability in the concentrations of Cd, Cu, Mn and Ni. *Deep-Sea Research I*, – submitted

### [6] Comments

**Contamination of the samples with Fe and Zn was severe. The profiles of Cd, Cu, Mn and Ni are generally similar to those obtained on FR 9008 and FR 9308 although**

**there is considerably more scatter in the data.** The trace metal data from this cruise are considered unreliable due to contamination from the 1 L sample storage bottles, problems with racking all the bottles from the 24-bottle rosette and from malfunctioning of the clean container on R V Franklin. Contamination of the samples with Fe and Zn was severe. The data is not considered of publishable quality and must not be used without acknowledgement of the problems that are outlined in the metadata document.

The trace metal data in the FR 9205 Trace Metal Data are password protected and may be released only by request to the CMR Data Centre. Please contact [data-requests@marine.csiro.au](mailto:data-requests@marine.csiro.au) to have the data forwarded to you. The data are contained in the file FR9205\_trace\_metal\_data.csv, about 5kb in size.