Southampton
Oceanography Centre
UNIVERSITY OF SOUTHAMPTON AND
NATURAL ENVIRONMENT RESEARCH COUNCIL

CRUISE REPORT No. 54

RRS *DISCOVERY* CRUISE D279
04 APR – 10 MAY 2004

A Transatlantic hydrography section at 24.5°N

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Cruise Report

DOCUMENT DATA SHEET

AUTHOR	*PUBLICATION DATE*
CUNNINGHAM, S A et al	2005

TITLE

RRS *Discovery* Cruise D279, 04 Apr – 10 May 2004. A Transatlantic hydrographic section at 24.5°N.

REFERENCE

Southampton Oceanography Centre Cruise Report, No. 54, 198pp.

ABSTRACT

The cruise report describes the acquisition and processing of transatlantic hydrographic, velocity, chemistry and other measurements made during three cruises in Spring 2004 at 24.5°N. Measurements were made from shallow water near Africa to shallow water just off Palm Springs beach on the eastern seaboard of the USA. During the principal cruise, RRS *Discovery* Cruise D279 (4 April to 10 May 2004), 125 full depth CTD and lowered acoustic Doppler current profiler (LADP) stations were completed between the USA and Africa and continuous underway observations were made of currents in the upper 1000m using a ship mounted 75kHz ADP and of surface salinity and temperature. At each station up to 24 water samples were captured for the analysis of oxygen, salinity, nitrate, silicate, phosphate, CFC11, 12, 113 and CCl4 (carbon tetrachloride), discrete total inorganic carbon (TCO_2), discrete total alkalinity (TA) and, discrete partial pressure of CO_2 (discrete pCO_2). Direct, near real-time measurements were also made of the air-sea turbulent fluxes of momentum and sensible and latent heat in addition to various mean meteorological parameters including testing of a new Licor sensor to determine its suitability for making direct measurements of the air-sea CO_2 flux. Atmospheric dust samples were gathered on a daily basis. Two prior cruises D277 (26 February to 16 March) and D278 (19 to 30 March) completed 33 full depth CTD/LADP stations in the Florida and Deep Western Boundary Currents, including continuous underway observations of currents in the upper 1000m and of surface salinity and temperature. No LADP or chemistry measurements were made during these cruises. The three cruises provide one CTD and one CTD/LADP transect of the Florida Current, two Florida Current transects at 5knots with the shipboard ADP measuring to the bottom for high accuracy well resolved direct velocity measurements, one section of 16 CTD stations across the Deep Western Boundary Current and a 125 station transatlantic section with a full suite of physical and chemical measurements. The principal scientific objective is to estimate the circulation across 24.5°N, using for the first time, LADP profiles at each station as constraints in an inverse study. Using this circulation and the transatlantic distribution of temperature and other properties we will calculate Atlantic heat and property fluxes. We will also define the size and structure of the Atlantic Meridional Overturning Circulation (MOC) to compare to results from a recently deployed transatlantic mooring array designed to continuously measure the size and structure of the MOC. The 24.5°N section has now been occupied five times since 1957 (including the 2004 section reported here). Therefore, we will analyse temporal trends of temperature to see if the widely reported warming of the thermocline and intermediate waters and cooling of deep water is continuing. Carbon measurements were also obtained in 1992 and 1998 so this section provides a unique decadal view of anthropogenic carbon fluxes.

KEYWORDS

ADCP, Atlantic Ocean, atmospheric chemistry, carbon tetrachloride, carbon, CFC, circulation, cruise D277 2004, cruise D278 2004, cruise D279 2004, CTD, *Discovery*, Lowered ADCP, Meridional Overturning Circulation, meteorology, MOC, nutrients, Ocean Surveyor, oxygen, shipboard ADCP

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27. CARBON

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The CO_2 parameter analytical equipment was set up in the seagoing laboratory container of the Laboratory for Global Marine and Atmospheric Chemistry (LGMAC), University of East Anglia (UEA), Norwich, UK. Four instruments were set up for the analysis of discrete total inorganic carbon (TCO_2), discrete total alkalinity (TA), discrete partial pressure of CO_2 (discrete pCO_2) and, continuous partial pressure of CO_2 (continuous pCO_2) and oxygen. The discrete instrumentation was used to analyse seawater samples collected from the Niskin bottles of the CTD, the continuous pCO_2 was analysing sea surface pCO_2 and oxygen was continuously measured in the non-toxic seawater supply. Due to the length of time needed for the analyses, particularly the TIC (30 min per sample), every second station was sampled for the three discrete analyses, apart from the beginning of the cruise (Florida Straits), where almost every station was sampled. TA could not be analysed at the beginning of the cruise due to the instrument not being operational. It was a new system and delivered one week before transport to the cruise, hence setting up this system took until station 15; samples sampled prior to that had been fixed and stored, and were run later during the cruise.

Discrete seawater samples were taken according to Standard Operating Procedure (SOP) 1 outlined in DOE (1994). Reagent bottles of 250ml volume were used for TCO_2 and TA samples, and 500ml volumetric flasks were used for discrete pCO_2. They were drawn from the Niskin bottles immediately after the oxygen samples were taken. All seawater samples were taken with Tygon tubing into pre-cleaned bottles and flasks. They were rinsed once, filled from the bottom, and overflown once. Bottles and flasks were stoppered without any gas bubbles entrapped. The samples were fixed by creating a headspace and adding saturated mercuric (II) chloride (HgCl2) solution according to DOE (1994). Samples were fixed and stored at room temperature and run within 16 hours of sampling, except for those TCO_2 samples which were stored at 12°C until post-cruise analysis back at the UEA laboratory.

Replicate samples were taken for all discrete analyses from random Niskin bottles at several stations, and run on board for all TA and discrete pCO_2. TIC replicates of Niskin bottles were analysed on board or stored for analysis back at UEA. Additional replicates were taken from the ship's non-toxic seawater supply and analysed on board.

Table 27.1 lists number of samples taken and analysed on board from either CTD Niskins or the ship's non-toxic seawater supply, including replicates. A total of 4672 samples were taken, 1623 for pCO_2, 1526 for TA and 1523 for TCO_2. A total of 4280 samples were analysed on board, 1563 for

pCO_2, 1501 for TA and 1216 for TCO_2. A total of 297 fixed TCO_2 samples were stored for analysis back at UEA.

27.1 Discrete Total Inorganic Carbon (TCO_2)

Total inorganic carbon was analysed by coulometry. The instrument consisted of a coulometer (model 5100, UIC Inc, USA) and a CO_2 extraction unit based on the Single Operator Multiparameter Metabolic Analyzer (SOMMA), developed by Kenneth Johnson (Johnson et al. 1985, 1987, 1993) and modified at UEA.

In this system, all inorganic carbonate is converted to CO_2 (gas) by addition of excess phosphoric acid (1 M, 8.5%) to a calibrated volume of seawater sample. OfN nitrogen gas passed through soda lime to remove any traces of CO_2 is used to carry the evolving CO_2 to the coulometer cell. In the coulometer cell, all CO_2 is quantitatively absorbed forming an acid, which is coulometrically titrated. The coulometer is set to integrate the titration as counts (CTS) and the titration endpoint are set to within 25 CTS per 60 min.

The accuracy of the analysis on board was determined regularly by measuring certified reference material (CRM), supplied by Dr. A. Dickson of Scripps Institution of Oceanography (SIO), Batch #62 (certified TCO_2 value: 2126.46±0.56μmol/kg). A total of 66 CRMs were run (Figure 27.1). The cruise-length average of CRM analyses was 2126.65±2.3μmol/kg.

Standard deviation of replicate TCO_2 analysis is plotted in Figure 27.2 (station 1 was a test station, and station 11 was repeated as station 12, hence used for replicate analysis). The cruise-length standard deviation of Niskin replicate analyses was ±0.5μmol/kg (n=33) and for replicates of the non-toxic supply was ±1.1μmol/kg (n=23).

Post-cruise work will involve the analysis of the stored samples, which could not be analysed on board. A post-cruise calibration of the temperature sensor and the pipette volume will also be done, and the sample results recalculated if necessary.

27.2 Discrete Total Alkalinity (TA)

Total alkalinity was determined by the titration of a calibrated volume of seawater, equilibrated to 25°C, with a strong acid (HCl). The s-shaped titration curve produced by potential of a proton sensitive electrode shows two inflection points, characterizing the protonation of carbonate and bicarbonate, respectively. The acid consumption up to the second point is equal to the titration alkalinity. From this value, the carbonate alkalinity is calculated by subtracting the contributions of

other ions present in the seawater. These concentrations can be derived from the pH and salinity of the sample.

For this analysis, the VINDTA (Versatile INstrument for the Determination of Titration Alkalinity, Marianda, Kiel, Germany) was used. It is an open cell titration system, with sample delivery via a thermostated calibrated pipette. Sample handling and titration is program controlled. The titration is carried out using a Titrino (Model 719 S, Metrohm, Switzerland). The results are calculated using a non-linear curve fitting approach, comparing a calculated curve to the data points and making use of the best-fit coefficients for alkalinity calculation.

A 0.1M solution of hydrochloric acid was made up for the titrations. This acid was made up on board and a sub-sample taken for post-cruise analysis to determine the exact concentration. The correct concentration will then be used to recalculate the results.

The accuracy of the analysis was determined twice daily by measuring Certified Reference Materials (CRM), supplied by Dr. A. Dickson of Scripps Institution of Oceanography (SIO), Batch #62 (certified TA value: 2338.2±0.46μmol/kg). A total of 43 CRMs were run (Figure 27.3). The cruise-length average of CRM analyses was 2337.8±1.8μmol/kg.

Alkalinity data was calibrated with CRMs. However, the calculation method is dependent on a realistically estimated ratio of acid factor and pipette calibration, and since the same calibration factor can also be obtained with various combinations of these two parameters, the quality of the curve fit will be different. Therefore a re-calibration of the pipette and exact calculation of the acid factor will be processed post cruise. Changes that would exceed the mean standard deviation of the method are not likely. A number of early stations were analysed using an inaccurate acid factor. These stations have an incorrect concentration at the end of the cruise. Recalculation is required post cruise to enter the correct acid factor and thus obtain a corrected result. The nutrient and salinity data will also be included in the post cruise processing, together with back calculation of rejected samples.

Analysis of replicates taken from Niskin bottles or the ship's non-toxic supply have a standard deviation of ±1.1μmol/kg and ±1.5μmol/kg respectively (Figure 27.4).

For the calculation of carbon alkalinity from total alkalinity, the phosphate and silicate alkalinity has to be known. This can be done using the separately determined nutrient concentrations. However, the contribution is low for phosphate about equal to the phosphate concentration (i.e. 0-3μmol/kg for open ocean waters), and a factor of 10 lower for silicate. Nutrient data was not available immediately during this cruise and therefore not included in the calculations. This will be part of the post-cruise recalculation.

A problem of system blockages was encountered during the mid phase of the cruise. This resulted in pipette emptying problems and incorrect sample volumes. Tubing was renewed to overcome the problem, but a number of stations were affected and the samples were rejected. Stations rejected were 73, 75, 77, 79, 81, 83, 85, and 87. Although these samples have been rejected, back calculation is possible from the values of pCO_2 and TCO_2. This will be carried out in post-cruise reprocessing.

27.3 Discrete Partial Pressure of CO_2 (Discrete pCO_2)

The partial pressure of CO_2 in seawater was determined by infrared absorption of CO_2 in a gas stream that was equilibrated with CO_2 in a seawater sample at 15°C. The system was built new at UEA prior to this cruise, its design based on the one described by Waninkhof & Thoning (1993).

A headspace was created in the 500ml volumetric flasks by replacing a volume of seawater with a gas of a CO_2 concentration close to that of the seawater. Six gas standards (10 litre, BOC, UK) were available with different CO_2 concentrations: 267.43ppm, 357.35ppm, 479.27ppm, 696.49ppm, 890.54ppm and 1150.11ppm, which had been calibrated against primary NOAA gas standards prior to the cruise. Headspace volumes created in sample flasks ranged from 62 to 84ml, and were measured for each sample. The headspace gas was circulated through the seawater sample and the IR detector (LiCor model 6262, LiCor, Inc., USA) until equilibrium was reached, generally after 20 min, whilst maintaining close to atmospheric pressure within the loop.

The system had two loops, which were used alternatively, saving analysis time by equilibrating one sample, whilst preparing the next. On 02 May 2004, loop 2 failed, and remaining samples were analysed only on loop 1.

All gas standards were run after each 12 to 15 samples, in order to calibrate the LiCor detector. The precision of the analysis was determined by running replicate samples, taken either from Niskin bottles or the ship's non-toxic seawater supply.

27.4 Continuous Partial Pressure of CO_2 (Continuous pCO_2)

The partial pressure of CO_2 in surface seawater was determined by infrared absorption of CO_2 in a gas stream being continuously equilibrated with the CO_2 of surface seawater. The system used was built new at UEA prior to this cruise, its design based on the one described by Cooper et al (1998).

Seawater from the continuous non-toxic supply of RRS *Discovery* was tee-ed off from a high flow (>50 litres/min) bypass, passed through a strainer and housing containing an oxygen/temperature sensor (Aanderaa model 3930, Aanderaa Instruments AS, Norway), and into a perculator type equilibrator at 5 litres/min. A coulterflow of air was continuously circulated through the equilibrator

and the detector (LiCor model 6262, LiCor, Inc., USA). At least once per hour, the system analysed CO_2 in air, pumped in from the foremast. Gas standards of 267.43ppm, 357.35ppm, and 479.27ppm CO_2 in air were measured throughout the cruise, in order to calibrate the LiCor detector.

Under controlled conditions in the laboratory, and during a pool side international intercomparison in Japan in 2003, the type of instrument used for this cruise gave a precision of ± 0.7ppm CO_2.

Table 27.1: Number of samples taken and analysed during the cruise for the three discrete carbon parameters pCO_2, TA, and TIC, from either CTD Niskins or the RRS *Discovery*'s non-toxic seawater supply. Numbers sampled include replicates. TIC samples not analysed were stored to be analysed back at UEA.

Station	Samples taken from		pCO_2		TA		TIC	
	CTD Niskins	non-tox. supply	Sampled	Analysed on board	Sampled	Analysed on board	Sampled	Analysed on board
1	24		20	8			20	13
2	3		3	3	3	2	3	0
3	4		4	4	4	2	4	4
4	5		5	5	5	5	5	5
5	6		6	6	6	5	6	6
6	6		6	6	6	6	6	5
7	7		8	8	7	7	8	8
8	7		7	7	7	7	7	7
9	6		6	6	6	6	6	6
10	5		5	5	5	5	5	5
11	12		12	12			12	10
12	5		5	5	5	5	5	5
13	14		14	14	14	14	14	14
14	16		16	16	16	16	16	16
15	20		20	19	20	0	20	20
16	22		22	22	22	22	22	22
17	23		23	22			23	0
18	24		24	23	24	24	24	24
19	24		24	0			24	0
20	24		24	24	24	24	24	24
22	24		24	24	24	24	24	24
24	24		24	24	24	24	24	24
26	22		22	22	22	22	22	0
29		X	6	6				
29	24		24	24	24	24	24	24
31	23		23	23	23	23	23	23

Station	Samples taken from		pCO_2		TA		TIC	
	CTD Niskins	non-tox. supply	Sampled	Analysed on board	Sampled	Analysed on board	Sampled	Analysed on board
33		X	6	6				
33	24		24	24	24	24	24	0
35	23		23	22	25	25	23	23
37		X	6	6				
37	24		24	24	24	24	24	24
39		X	6	6				
39	24		24	24	24	24	24	24
41	24		24	24	24	24	24	24
43		X	6	6				
43	24		24	23	24	24	24	24
45		X	12	10	10	9		
45	24		24	24	24	24	24	24
47		X	6	6	5	5		
47	24		24	24	24	24	24	24
49		X	6	6				
49	24		24	24	24	24	24	24
51		X	6	6	10	10		
51	24		24	24	24	24	24	24
53		X	6	6	8	8		
53	24		24	24	24	24	24	24
54		X			15	15		
55		X	6	6				
55	24		24	24	24	24	24	24
57		X			15	15		
57	24		24	23	24	24	24	24
58		X	6	6				
58	1		1	1				
59	23		23	22	23	23	23	23
60		X	6	6				
60	1		1	1				

Station	Samples taken from		pCO_2		TA		TIC	
	CTD Niskins	non-tox. supply	Sampled	Analysed on board	Sampled	Analysed on board	Sampled	Analysed on board
61		X					4	4
61	24		24	24	28	28	28	26
62		X	6	6				
63	24		24	24	24	24	24	24
65		X	6	6	6	6		
65	24		24	24	24	24	24	24
66		X	6	6				
66	1		1	1				
67	24		24	23	24	24	24	24
69	24		24	23	24	24	24	24
71	24		24	23	24	24	24	24
72		X					10	10
73	24		24	23	24	24	24	24
75	24		24	24	24	24	24	24
77	24		24	24	24	24	24	0
79	24		29	29	29	29	24	24
81	24		24	23	24	24	24	0
83	24		24	24	24	24	24	24
85	24		24	24	24	24	24	0
87	24		24	24	24	24	24	24
89		X	2	2	2	2	2	2
89	24		26	26	26	26	26	26
90		X	5	4	4	4	4	4
91	24		24	24	24	24	24	24
93		X	5	3	5	5		
93	24		26	26	26	26	26	26
95		X			5	5	5	3
95	24		26	26	26	26	26	0
97	24		26	26	26	26	26	24
99	24		26	25	26	26	26	26

Station	Samples taken from		pCO_2		TA		TIC	
	CTD Niskins	non-tox. supply	Sampled	Analysed on board	Sampled	Analysed on board	Sampled	Analysed on board
101		X	10	9	10	10		
101	24		26	25	26	26	26	26
103	24		26	26	26	26	26	25
105		X			10	10	10	10
105	24		26	26	26	26	27	26
107	24		26	25	26	26	26	25
109	24		26	26	26	26	26	2
111	24		26	26	26	26	26	26
113		X	10	10	10	10		
113	24		26	26	27	27	26	0
115	20		22	20	22	22	22	20
117	21		23	23	21	21	23	22
119	19		21	21	21	21	22	20
121	15		17	16	17	17	17	0
123	12		13	13	13	13	14	0
125	7		8	8	8	8	8	0
Total			1623	1563	1526	1501	1523	1216